Karst-Associated Bauxite Deposits of Parnassos-Ghiona, Central Greece: Ore Genesis and Structural Evolution

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Karst-associated bauxite deposits of Parnassos-Ghiona, Central Greece: Ore genesis and structural evolution

The karst-associated bauxites of the Parnassos-Ghiona zone in Central Greece are part of the large Mesozoic age Mediterranean Karst Bauxite belt. Greece is responsible for around 50% of European bauxite production, and has an estimated 600 million tonnes of bauxite reserves. This investigation focuses on the bauxites of Mount Iti and Mount Ghiona, two mountains in the west of the Parnassos-Ghiona zone that are currently being explored and mined by Greek bauxite producer, Elmin S.A. The aim was to develop a better geological understanding of the ore genetic history and regional structural evolution to aid ore deposit science and bauxite exploration. Within the Parnassos-Ghiona zone the bauxites were deposited as three separate ore horizons intercalated with thick limestone layers during the early Jurassic, late Jurassic and late Cretaceous. Only the upper two bauxite horizons are economic and therefore formed the focus of this investigation.

Studies of the texture, mineralogy and lithogeochemistry provide information on the origin and evolution of the ore bodies over time and the temporal and spatial variations between ore bodies. It is proposed that many of the observed textures and geochemical variations are representative of a complex, dynamic and continuously evolving, self-organising system. Models are presented here to show how complex textures of bauxite can be formed through long periods of episodic transport, involving alternating periods of concretion texture development followed by mobilisation and partial destruction of the developed textures. Mineralogical analysis of the bauxites has identified a wide range of Al and Fe phases within the second and third horizons which can be linked primarily to variability in redox conditions.

Particular attention was given to the sulphide mineral-bearing bauxites of Mount Iti, as these sulphides (predominantly pyrite) cause problems during ore processing. Three generations of pyrite were identified, each with distinctive textural characteristics, trace element concentrations and sulphur isotope concentrations. Sulphide formation utilised predominantly bacterially reduced sulphate in a closing system. Epigenetic meteoric fluid flow caused oxidation of pyrite in the third horizon bauxite generating acidic fluids that mobilized iron and several trace and rare earth elements creating zones of bleached bauxite. This investigation has shown that this mobilized iron was re-deposited at the base of the ore bodies and within fractures. A portion of this mobilized iron penetrated deeper into the underlying limestones, significantly enriching them in Fe, Ni, Si and Mn, and creating a distinctive red/yellow colour. This limestone alteration is detectable for up to 50 metres from the ore bodies and could be used as an exploration tool.

The structural evolution of the Parnassos-Ghiona geotectonic zone has a strong control on the orientation, inclination and dislocation of ore bodies. Lineament analysis of remotely sensed LANDSAT 7-TM data helped to identify major structural trends and aided structural interpretations. Compressional deformation during the Eocene created southwest-verging folds in the Parnassos-Ghiona carbonates along the northern edge of Mount Iti, resulting in inclined, vertical and even overturned ore lenses. In the northern Mount Ghiona area, west dipping thrust faulting inclined and imbricated the ore horizons. Later extensional deformation fragmented and offset ore bodies, and provided conduits for alteration fluids. This investigation concludes by presenting an updated ore genetic model for the formation history of the bauxite deposits of the Parnassos-Ghiona zone, drawing together the results of this study and previous data and models for the region.
The author is indebted to Elmin S.A. for their financial, practical and logistical support throughout this project, with particular thanks to Mr. Lyberis Polychronopoulos and Mr. Vasilis Yfantis for their support and positive cooperation. I am also grateful to the invaluable co-ordination and guidance received from Professor Stavros Kalogeropoulos throughout the design and operation of this research programme. At the University of Brighton, I am grateful to my UK supervisory team of Professor Andy Cundy, Dr. Norman Moles and Dr. Martin Smith for help, advice and support throughout the 3.5 years of this research project.

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The organisation, structure and views expressed in this thesis are those of the author, and do not necessarily reflect the views or policy of the supporting organisations and individuals.

Declaration

I declare that the research contained in this thesis, unless otherwise formally indicated within the text, is the original work of the author. The thesis has not been previously submitted to this or any other university for a degree, and does not incorporate any material already submitted for a degree.

Signed

Dated
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Chapter 1: Thesis Introduction

1.1 Thesis outline

This thesis is the result of a three year geological study of the karst-associated bauxite ore deposits that are found within the Parnassos–Ghiona geotectonic zone of the Hellenide mountain range, central Greece. The study was generously funded by, and worked closely with, the Greek bauxite production company Elmin S.A. in order to advance geological knowledge of the bauxite deposits and improve exploration practice.

1.2 Bauxite

Bauxite is an aluminium rich soil or rock formation, which forms as a residual deposit concentrated on the land surface as a result of intense tropical weathering of a suitable parent rock. As such it is found mainly in tropical and sub-tropical regions such as the Caribbean, Africa, South America, Australia and the Mediterranean region, where high annual rainfall and temperatures promote extensive chemical weathering of exposed rock (BGS 2009.) It was first discovered and described by Berthier in 1821, within the Les Baux province, southeast France, from which the name bauxite was derived. ‘Karst-associated bauxites’ are those bauxite deposits that occur on, or within karstic structures, formed through the partial dissolution of carbonate rock layers.

1.3 The Greek Bauxite Deposits

Greece has long been a significant producer of bauxite to world markets, positioning itself as one of the few sources of bauxite for non-metallurgical markets. Recent annual production was around 2.2 - 2.3Mt making it the leading bauxite producer in the EU, and 12th biggest producer worldwide in 2012 (Newman 2012.) Most major bauxite deposits within Greece are situated within the Parnassos-Ghiona geotectonic zone, a relatively small geographic area situated within Central Greece, north of the Gulf of Corinth (Fig.1.1). Estimates of Greek bauxite tonnage vary, with reported values of 300Mt (Papastavrou 1986), 415Mt (Bardossy 1982) and 600Mt (USGS 2013), however proven reserves are currently at around 100Mt (Newman 2012), which at current production rates have a life of around 50 years.

The Greek bauxites belong to the Mediterranean-type Karst-associated bauxites, the most common and economic type of Karst-associated bauxite worldwide (Bardossy, 1982), of which
Greece holds the second largest reserves (Jamaica having the largest.) They are of the boehmitic and diasporic bauxite type, and have an average Al$_2$O$_3$ content of 55% (Valeton et al., 1987.) The bauxite typically occurs within three horizons intercalated with the Mesozoic age carbonate rocks of the Parnassos-Ghiona zone. Of the three layers, it is the middle and upper layers that are currently economic to extract.

This project focuses on a particular group of bauxite deposits within the Parnassos-Ghiona zone around Mt Iti and Mt Ghiona (Fig.1.1), which are presently within the concession zones belonging to the privately owned Greek bauxite producer Elmin S.A. Compared to the Australian, South

![Annotated satellite image of Central Greece showing the outline of the Parnassos-Ghiona zone in red, and the research area for this investigation in yellow.](image)

Fig. 1.1: Annotated satellite image of Central Greece showing the outline of the Parnassos-Ghiona zone in red, and the research area for this investigation in yellow.
American and African lateritic bauxites and the Chinese and Jamaican Karst-associated bauxites, the Greek karst-associated bauxites currently lack integrative, exploration-oriented, studies. As these deposits are mostly buried beneath many metres of carbonate rocks, with relatively limited surface exposure, they have attracted less attention from academic researchers.

1.4 Research aims and objectives

The aim of this thesis is to systematically study the texture, mineralogy, geochemistry, structure and overall lithology of the Parnassos-Ghiona zone bauxites and their carbonate host rocks, at various scales of observation, to produce integrated ore genetic and structural models of the Mt. Iti and Mt. Ghiona bauxite reserves. This would optimise exploration approaches within these ore bodies, and improve wider understanding of the formation of Mediterranean karst-associated bauxites. The specific objectives of this project are as follows:

Lithological Analysis

1. To collect representative samples of the bauxite ore bodies and host rocks from various locations across the study area.
2. To compare and contrast textural, mineralogical and geochemical features of the bauxite ore bodies at various locations and horizons within the research area, and to link these variations to formation events.
3. To investigate the formation processes of sulphide minerals within the Parnassos-Ghiona bauxites.
4. To investigate the cause and effects of epigenetic processes affecting the bauxite.
5. To examine the lithogeochemistry of the limestone host rocks adjacent to bauxite ore bodies, to assess their degree of alteration and the potential presence of “pathfinder” elements and features.

Structural Analysis

6. To collect a range of structural data across the research area from surface exposures and underground mines.
7. To use the structural data to develop and verify a regional structural model for the Elmin S.A. concession areas within the Iti and Ghiona mountains.
8. To develop several smaller structural models for structurally complex and important areas within this region.
9. To determine how the structural evolution has affected the locations, size, shape and economic viability of the bauxite ore bodies.

Remote Sensing

10. To test whether remote sensing methodologies applied to satellite imagery can be used to target exploration for bauxite ore bodies within this region. This includes multispectral image analysis and lineament analysis.

Ore genetic model

11. To combine the structural and lithological data into an ore genetic model for the research area, and critically compare this to existing models for the Greek and Mediterranean bauxites.

1.5 Contribution to mineral deposit science and exploration strategy

This thesis will advance scientific understanding of bauxite deposits in the following ways:

- It will test some of the main theories about the formation of ore textures, mineral assemblages, geochemistries and ore body structure of karst bauxites.
- It will provide detailed analyses on the epigenetic processes that affect the Greek bauxites, and surrounding lithologies, which has implications for other bauxites around the Mediterranean area.
- It will develop ore genetic and structural evolution models of Mount Iti and Mount Ghiona bauxites.

This thesis will contribute to exploration strategy of the karst-associated bauxites of Central Greece in the following ways:

- Build a regional specific structural model to show how the bauxite ore bodies are distributed underground and to show how faults and other structural features affect the shape and distribution of the ore bodies.
- The ore genetic model will show how the types of bauxite are distributed across the research area, and to pin-point the areas of highest grade/quality ore
- Evaluation of remote sensing methods will show whether these techniques can be used to locate bauxite ore occurrences within less explored regions of the research area.
1.6 The structure of this thesis

This thesis is structured into 9 chapters. Chapter 1 (current chapter) provides a context to the study and outlines its aims and objectives. Chapter 2 presents a summary of the geology of the research area and academic literature relevant to the study, and presents data and observations from geological fieldwork. Chapter 3 is a description and critical assessment of the methodologies used for this study. Chapter 4 is a study of the texture, mineralogy and geochemistry of the bauxites with particular reference to bauxite formation processes. Chapter 5 studies the formation of sulphide minerals within the bauxites and epigenetic processes affecting the bauxite. Chapter 6 is a study of the lithogeochemistry and alteration of the carbonate rocks surrounding the bauxites aimed at identifying potential ore ‘path-finder’ elements, and support the development of a comprehensive ore genetic model. Chapter 7 is an investigation of the geological structural evolution of the research area, and its effects on bauxite formation and structure. Within this chapter a structural model for the research area is presented and its implications are discussed. Chapter 8 investigates the use of remote sensing as a tool for bauxite exploration within Greece. Chapter 9 is a discussion chapter that combines the finding of this thesis with previous studies to produce an ore genetic model for the Parnassos-Ghiona bauxites. Chapter 10 is the thesis conclusion, summarising the main findings, examining the implications of the findings to ore exploration and suggesting areas of further work.

1.7 Bauxite as a Global Resource

Bauxite uses

The aluminium industry consumes around 90% of all bauxite mined globally, as bauxite is currently the only mined source of Aluminium metal. Bauxite however has many additional uses in its raw form, such as cement production, metallurgical flux, refractories and abrasives (Fig. 1.2). Alumina is pure white, has a Mohs hardness of 9, is chemically inert, thermally conductive and is an electrical insulator. It is widely used in industrial applications often offering a cheaper substitute to high cost materials, such as industrial diamonds in abrasives.

Aluminium is one of the most important metals used by modern societies. Its combination of physical properties allows it to be used in a wide variety of products, many of which are indispensable to modern life. It is light weight and electrically conductive allowing for its use as aluminium wire in long-distance transmission of electricity. Aluminium’s strength, light weight, and workability have led to increased use in transportation systems, including light vehicles, railcars, and aircraft, as efforts to reduce fuel consumption have increased. Its excellent thermal
properties and resistance to corrosion have led to its use in air conditioning, refrigeration, and heat-exchange systems. Finally, its malleability has allowed it to be rolled and formed into very thin sheets used in a variety of packaging (Menzie et al., 2010.)

**Bauxite production and consumption**

In 2012, bauxite was mined in 27 countries with a total production of 263 million tonnes (Fig. 1.3A). 90% of production came from nine countries, with the other eighteen contributing less than 1% each. For several of the highest producing countries, bauxite contributes a significant percentage to their GDP (Jamaica, Guinea, Guyana – around 10%, Suriname – around 30% (Meyer 2004.))

Fig. 1.3B shows the annual global bauxite consumption per capita from 1970 to present in blue, with the annual percentage change in bauxite consumption shown in red. The graphs are based on data published by the British Geological Survey (1970 - 2011). Driven by increasing demand, world bauxite production has risen substantially in the past 40 years, from 58Mt in 1970 to 263Mt in 2012 (Fig. 1.3A). Between 1970 and 1999 bauxite consumption never exceeded 22kg per capita, with an average of 19.5kg per capita. Since 1999, consumption has increased almost every year, reaching 35.6 kg per capita in 2011. Over the 10 years from 1998 to 2008, before the 2009 global recession, bauxite consumption was growing at an average rate of 5.25% per year, with annual growth ranging between <1% and 12%. Between 1970 and 2011, world population has grown steadily by around 1-2% per year as shown in Fig. 1.3C and so this recent increase represents an increasing demand for bauxite.

The consumption of bauxite and aluminium in a country is related to the GDP per capita of the country. Countries with a GDP per capita of less than $5000 consume less than 5kg of aluminium per capita, between $5000 and $15000 consume 5 and 10kg per capita, and countries with a GDP per capita of $25000 or more consume between 15 and 35kg of aluminium per capita. The change in aluminium consumption accompanied with GDP growth can be dramatic (Menzie et al., 2010 and references therein.) The 2009 global recession is a marked global economic decline that caused a drop in international trade and decreasing commodity prices. Global bauxite production was affected from 2008, which only saw a small rise of 0.5% compared to the previous year’s 12% growth. This was followed by a drop of 8% in global production. In the three years following 2009, production grew by 12.4%, 8.8% and 5.7% for 2010, 2011 and 2012 respectively, which appears to mark a return to pre-recession growth levels.
Fig. 1.2: Examples of the uses of bauxite, alumina and aluminium (BGS 2009).
Fig. 1.3: A. The growth in world bauxite production between 1970 and 2012. B. The change in bauxite consumption per capita from 1970 to 2012 in blue, with the annual percentage change in bauxite consumption per capita in red. C. World bauxite consumption per capita change versus world population change from 1970 to 2012. (Produced using data from the CIA World factbook, BGS World Mineral Production reports 1978 – Present.)
Primary versus secondary aluminium

Secondary aluminium is the aluminium recovered from scrap metal and currently accounts for 25% of global aluminium consumption. Recovering the aluminium is a simple process of remelting the metal and separating the aluminium. The process requires around 6% of the energy required for primary aluminium production, and around 10% of the capital cost. It also produces far less gas emissions with no PFC gases, and very little solid waste. The economic and environmental benefits of secondary aluminium are why there is a significant emphasis on recycling since the 1960s when aluminium packaging use was greatly increased (Schlesinger 2006, Menzie et al., 2010.)

The amount of aluminium available for secondary production can vary between countries of varying GDP, which has important implications for aluminium recycling. Countries with lower GDP tend to use more aluminium for electrical end uses. Countries with high GDP tend to use more aluminium for transport end uses. Aluminium use in packaging is not affected by the GDP (USGS 2010 and references therein.) Aluminium in electrical systems is typically in service for long periods of time and so the amount of aluminium available for recycling in countries with lower, but rapidly growing incomes, is likely to be delayed relative to countries with higher incomes. Transport end uses such as automobiles typically have in-service time periods of about 10 years giving higher income countries a larger supply of aluminium scrap available for trade or recycling. The transition from lower to higher incomes thus is accompanied by an increased availability of relatively easily recoverable aluminium (Menzie et al., 2010.)

Future Bauxite Demand

In the short term, Menzie et al., (2010) estimated a growth of around 4.4% per year in bauxite production from 226Mt in 2010 to 270Mt in 2015. Since publishing their report production growth has so far exceeded their estimates, with production of 248Mt in 2011 and 263Mt in 2012, compared with predicted 235Mt and 246Mt respectively.

In the long term, prediction is more difficult owing to a combination of several unknown variables; however Menzie et al., (2010) predicted a demand of 91.9Mt of aluminium in 2020 and 119Mt in 2025. Given the current primary aluminium/ bauxite production ratio of around 0.18, this will equate to a demand of 380Mt bauxite in 2020, and 490Mt in 2025, assuming that a constant 25% of aluminium demand is fed by secondary aluminium.
Future bauxite demand will be driven by increasing population and increasing bauxite consumption per capita. As consumption per capita remained stable up until 1999, the increase in demand up until then is likely to be due to population increase. After 1999 the significant rise in consumption per capita is likely to be due to the development of several countries’ economies and the increase in bauxite consumption that accompanies such growth, in particular the BRIC countries (Brazil, Russia, India and China), which are currently responsible for around 27% of world consumption, but are predicted to consume around 45% by 2025.

In theory, as more and more countries are developing, gaining a higher GDP and building better and longer lasting infrastructure, the use of bauxite globally will move from long life applications such as infrastructure, to shorter life applications such as transport. The increasing availability of secondary aluminium will decrease the demand for bauxite, as well as reducing energy demand, capital costs and waste production associated with aluminium production. Until this happens, the increasing demand for Bauxite and Aluminium will have to be met by increasing primary aluminium production and bauxite mine output.

**Future Bauxite production trends**

The future trends in bauxite consumption were investigated by Meyer (2004) by analysis of records of 70 currently operating bauxite deposits and the published materials on 100 bauxite deposits currently under exploration to investigate and compare ‘geological signatures’ of the bauxite deposits. Meyer found that, compared to currently (meaning 2006) working deposits, the future resources will have the following:

- A lower ore grade with the median value moving from 45.6 to 42.3 $\text{Al}_2\text{O}_3$ Wt%, and a higher bauxite/$\text{Al}_2\text{O}_3$ recoverable ratio.
- Future mines will potentially have larger mean bauxite reserves however they will require greater land usage.
- $\text{SiO}_2$ and $\text{TiO}_2$ contents may also be greater in future bauxite prospects.

While these changes may affect the annual demand for bauxite, particularly for the aluminium industry, Meyer concludes that there is sufficient potential to maintain the current level of bauxite quantity and quality for the next 20 years by currently known reserves.
1.8 Greek Bauxite

The ore grade of the Greek bauxites can vary over relatively short distances as a result of changing ore mineralogy and ore geochemistry. Syngenetic and epigenetic alteration of the bauxite, widely observed within the Parnassos-Ghiona ore bodies, may produce both beneficial and detrimental effects on ore grade.

Beneficial alteration includes de-ferrization, which is the removal or iron from the ore deposits, leaving bauxite that is relatively enriched in alumina up to grades of around 70% Al₂O₃. Detrimental effects include the formation of iron sulphide minerals at the expense of iron oxide minerals within the bauxite. Sulphides can create major problems during firing of bauxite in blast furnaces and so their presence in bauxite can significantly lower its value as a commodity.

The different alteration types observed within the bauxite ore are not uniformly spread across the current research area, and certain processes are known to have only affected certain regions. Understanding the causes of ore grade variation and modification, and the extent to which it affects the ore in different areas would have important economic implications in exploration and extraction for the Elmin S.A. concessions and the wider Greek Bauxite region. It would also have scientific importance in helping explain and understand the genetic history of these bauxite deposits.

1.9 Elmin S.A.

Elmin S.A. is one of three companies that produce bauxite in Greece, producing various grades of bauxite almost entirely for industrial purposes (Fig. 1.4, the bauxite mined is not used for aluminium production.) The company is currently exploring and extracting bauxite from within its concessions around Mount Iti and Mount Ghiona, within the Parnassos-Ghiona zone (Fig. 1.1.) Elmin S.A. has some 108 privately owned and rented concessions across the two mountains. In 2010, Elmin S.A. produced 420,000 tonnes of bauxite, 80% of which was exported worldwide. The end use of this bauxite is shown in Fig. 1.4.

The different uses of bauxite can require different ore compositions with respect to the relative amounts of the four main bauxite constituents (oxides and hydroxides of Al, Ti, Fe and silica), and other minor constituents such as calcium and potassium. The required composition for a particular end use is often very specific, and only allows for a few wt% variation in each component. Additionally, elements such as sulphur and phosphorus, sometimes known as penalty elements, are never desirable in bauxite, and their presence can incur fines from clients.
It is therefore important that the bauxite composition is regularly checked, from the exploration and extraction stage, to the transport and processing stage and also when stockpiling the ore, in order to maintain full control on the quality of bauxite being produced. This is achieved, to a high standard, by Elmin S.A. through daily analysis of bauxite samples using XRF technology; however, the natural heterogeneity of bauxite deposits can make this task potentially problematic. The causes and implications of this heterogeneity will be explored in this thesis.

![Uses of bauxite produced by Elmin S.A. in 2010 (after O'Driscoll 2011)](image)

**Fig. 1.4**: The major end uses of bauxite produced by Elmin S.A. in 2010.

References


Chapter 10: Conclusions

10.1. Introduction
This chapter summarises the main findings of this investigation and briefly discusses their implications to ore genesis and ore exploration within Greece. Suggestions for further work are also given.

10.2. The main findings of this investigation
This investigation focused on the karst-associated bauxite deposits of Mount Iti and Mount Ghiona, in the Parnassos-Ghiona zone, Central Greece, with the aim of advancing knowledge regarding the ore genetic history and structural evolution of the region to aid ore deposit science and bauxite exploration. The main conclusions are:

1. The complex pisolitic and clastic textures of the bauxites, particularly in the third horizon, can be explained through a complex, cyclical process of deposition, pisolith formation, re-working and destruction during transportation of the bauxites from mafic and ultra-mafic source rocks to the karstified carbonate platform. This investigation has proposed a model for the formation and genetic relationships between these textures which can be applied to similar deposits worldwide.

2. Mineralogical analysis of the bauxites from across Mount Iti and Mount Ghiona has identified a wide range of Al and Fe phases within the second and third horizons which can be linked primarily to variability in redox conditions. There is also evidence to suggest that the dominant Al phase (boehmite or diaspore) within karst bauxites of the Parnassos is primarily controlled by redox conditions during crystallisation from an original bauxite gel phase.

3. The iron sulphide minerals found within the third horizon bauxites can be split into at least three categories of authigenic pyrite, replacement pyrite and vein pyrite. These have distinctly different trace element concentrations and sulphur isotope compositions, indicating 3 separate phases of sulphide formation. In addition to pyrite, trace pentlandite, bravoite and galena were identified.

4. In agreement with previous research, it is concluded that oxidation of pyrite and the resulting acidic fluids are responsible for the bleaching alteration observed in the
third horizon ore bodies. Further to this, a genetic relationship is proposed between the bleaching and the iron rich deposits found at the base of the ore bodies and within fractures. A model is developed to account for precipitation of these iron deposits, which explains many of their textural features.

5. The bleaching process has also led to the alteration of the footwall limestones surrounding some third horizon ore bodies that are significantly enriched in iron and several trace elements. This alteration can be detected for up to 50 metres from an ore body, and could be used as a useful tool in future ore body exploration. Portable XRF equipment and analysis has shown utility in rapid assessment of ore grade and tracking of alteration halos around ore deposits.

6. The structural evolution of the Parnassos-Ghiona geotectonic zone has a strong control on the orientation, inclination and dislocation of ore bodies. This investigation has shown that compressional deformation during the Eocene has created southwest verging anticlines and synclines in the Parnassos-Ghiona carbonates along the northern edge of Mount Iti, which have led to inclined, vertical and even overturned ore lenses within this region, and west dipping thrust faulting across the northern Mount Ghiona area which has inclined and imbricated the ore horizons. Later extensional deformation has fragmented and offset ore bodies, and provided conduits for fluids responsible for pyrite oxidation and bleaching alteration of the bauxite. Lineament analysis of remotely sensed LANDSAT 7-TM data has been shown to be useful in identifying the major structural trends within the Parnassos-Ghiona zone, which aided the development of structural interpretations.

10.3. Further work
The results of this investigation have developed knowledge about the Parnassos-Ghiona bauxites from both an ore deposit science perspective and an ore exploration perspective. The suggestions for further work would both complement the findings of this investigation and previous research, and contribute to better exploration practices for karst bauxite deposits within the Mediterranean bauxite belt.

1. The lineament analysis methods presented in chapter 6 should be applied to the Parnassos-Ghiona zone as a whole in order to better understand the overall geological structure of this zone, and to extend the structural model to encapsulate all bauxite deposits within this region.
2. Modern geophysical methods should be tested on the geological units of this area, including systems designed for underground surveys, to investigate whether these methods could be used to identify bauxite-limestone contacts, thus enabling exploration drilling to be targeted more precisely.

3. Further investigations into the extent and intensity of the footwall limestone alteration around the third horizon should be carried out on drill core samples that extend away from bauxite ore bodies to formerly identify, and possibly model using drill core software, the extent style of footwall alteration.

4. Preliminary results presented in chapter 7 of the fold structures found within the Mount Iti flysch deposits suggests that they show similar deformation features to the underlying carbonates. It is suggested that they may be used to identify the extent and style of deformation in the underlying bauxite and limestones.
Chapter 2: The Geology of the Karst-associated bauxites of the Parnassos-Ghiona zone

2.1 Regional Background

Greece, like most of the Mediterranean, has a complex geological structure resulting predominantly from the convergence of the Eurasian and African continental plates during the early Palaeogene, known more commonly as the Alpine orogeny. As such, the Greek landmass forms part of one of the major mountain chains of the Alpine system; *The Hellenides*, which stretch for 1100km from the edge of the Dinarides in the North to the Taurides in southern Turkey.

Like most of the Alpine system, the Hellenides have been split into isopic zones and sub-zones which are widespread groups of rock that have a common formation and/or deformation history (Fig. 2.1). These were originally continental margins and continental fragments, separated by deep troughs or oceanic basins, all of which can be hundreds of kilometres long, and several kilometres thick (Higgins, 1996.) The isopic zones can be broadly grouped into two categories; the *inner (or internal) zones* and the *outer (or external) zones*, the difference being that the inner zones have been affected by Alpine regional metamorphism, whilst the outer zones have not (Smith & Moores, 1974.) The internal zones were predominantly continental fragments of the Eurasian plate; separated by the oceanic lithosphere of the Vardar zone. Now the internal zone consists predominantly of gneisses and minor marbles with a post Maastrichtian sedimentary and volcanic cover (Lambrakis & Marinos, 2003.)

The external zones developed on the margin of the Apulian micro-continent, an extensive Mesozoic, shallow to deep-water, carbonate platform that was sub-divided by rifting in the late-Jurassic into deep basins and shallow carbonate ridges. These divided sections became the isopic zones of the External Hellenides.

To the east of the Apulian margin was a passive continental margin that bordered the Pindos Ocean, now known collectively as the Pindos zone, which separated the Apulian and Eurasian margins (Lambrakis & Marinos, 2003). It was the closing of the Pindos Ocean that led to the collision of these two margins, relicts of which are found along the suture zone of the internal and external Hellenides (Doutsos et al., 2006.)
2.2 The Parnassos-Ghiona Zone

The Parnassos-Ghiona geotectonic zone differs from the other zones of the external Hellenides as it only covers a relatively small section of central Greece, between the Pelagonian zone to the east, and the Pindos zone to the west (Smith & Moores, 1974, Mettos et al., 2009.) To the north the zone is bounded by the Sperchios Valley Graben, and by the Corinth Gulf Graben in the south (Fig. 2.2). The zone forms a topographic ridge within the Hellenides and has a tectonic contact with the adjacent units. Its disappearance in the northern areas of Greece may be due to tectonic overlap by the adjacent zones (Moores & Fairbridge, 1997.) The detailed geology of the Parnassos-Ghiona zone (PGZ) is described in section 2.3 below.

2.3 The Geology of the Parnassos-Ghiona Zone

The Geology of the Parnassos-Ghiona zone

The Parnassos-Ghiona zone represents a 1800 to 2000 metre thick sequence of epicontinental, massive, shallow-water limestones and dolomites, of neritic or pelagic facies, of Triassic to Cretaceous age. It is thought to have formed as an isolated carbonate platform in the Pindos Ocean, which was floored by Triassic oceanic and/or transitional crusts and deep-sea sediments. The limestones contain three intercalated karst bauxite horizons at definable stratigraphic and temporal intersections, shown in Fig. 2.3.

The carbonate sequence is unconformably overlain in places by a 100 - 150 metre thick sequence of Palaeocene red shale that grades upwards into an Eocene flysch and molasse sequence of alternating clayey-sand and conglomerate layers, formed during Palaeocene to Eocene orogenic activity (Laskou & Economou-Eliopoulos, 2007; Smith & Moores, 1974; Doutsos et al., 2006; Moores & Fairbridge, 1997; Valeton et al., 1987.) The carbonate and flysch sequence has been over thrust from the NE by nappe sequences of the Pelagonian zone (Fig. 2.2). At present, the nappe covers the majority of Mount Iti and parts of Mount Parnassos. This nappe sequence contains Jurassic age platform carbonates of the Pelagonian zone and several flysch sequences, both of which act as a basal unit for an ophiolite sequence of mid-Triassic age oceanic crust. The Ophiolite is composed primarily of lherzolite and harzburgite and is known as the Iti Ophiolite; one of many ophiolite sequences found across Greece (see Fig. 2.1.). These Pelagonian nappe sequences are thought to have been emplaced as a single unit during Eocene overthrusting onto Mount Iti.
Figure 2.1: The Geotectonic Zones of Greece, showing the internal and external Hellenides, separated by the Pindos Suture, the modern day relict of a closed, ancient ocean, in which the Parnassos-Ghiona zone, shown in pale blue, formed. Adapted from Hejl et al., (1997).
Stratigraphy

The following sequence has been derived mainly from information from the 1:50 000 scale Amfissa and Lamia geology maps provided by the Institute of Geology and Mineral Exploration (IGME), Greece, as well as geological information from various studies on the region (Hose, 1978; Mistardis, 1978; Smith & Moores, 1974; Petrascheck, 1989; Laskou & Economou-Eliopoulos, 2007; Doutsos et al., 2006; Mettos et al., 2009; Kalaitzidis et al., 2010). It lists the Parnassos-Ghiona units from oldest to youngest, and a stratigraphic column of this information is shown in Fig. 2.3. The thicknesses are approximations based on previous studies.

- The basal unit of the Parnassos-Ghiona zone is a 600m thick, upper Triassic, crystalline dolomite, dolomitic limestone or limestone of white or grey colour. This section only forms a small outcrop in the southern part of the study area near the town of Amfissa. It has no direct relationship with bauxite deposits.
- An early to middle (Bathonian) Jurassic, 500m thick layer of dark coloured, bituminous, compact and crystalline limestone that becomes oolitic in the upper layers. The middle and lower layers contain gastropods and bivalves (species not specified) and *Pindae* in the lowest layers. The upper contact is generally unconformable, with overlying bauxite lenses,
- The First bauxite horizon, Oxfordian to Kimmeridgian (Late Jurassic) in age.
- An Oxfordian to Kimmeridgian age, 300m thick layer of compact, thickly bedded, dark grey limestones, occasionally with white spots. The lower contact is sharp and unconformable with the first horizon bauxite and the upper contact is an erosion surface, often karstified; sometimes only gently undulating. This unit is the footwall to the second horizon bauxite.
- The Second bauxite horizon, Kimmeridgian to Tithonian in age.
- A 400m thick sequence of Tithonian to Cenomanian ‘Intermediate’ limestones. These can be blocky or thinly bedded. The lower strata in contact with the second bauxite horizon tend to be reddish, marly limestones with a concretionary structure. The middle layers are of oolitic limestone. The upper layers, directly below the third bauxite horizon, are usually white, microcrystalline limestones. The lower contact is mostly sharp and unconformable with the second bauxite horizon. The upper contact is an erosion surface, is heavily karstified and forms the footwall to the third horizon bauxites.
- The Third bauxite horizon, Cenomanian to Turonian in age.
- An 80m thick layer of Turonian to Senonian (Late Cretaceous) micro-crystalline limestone. The lower layers, directly above the third bauxite horizon are dark-grey in colour and bituminous in composition. The upper layers are white and crystalline.

- A 50 to 70m thick layer of Senonian to Palaeogene thinly bedded limestone of white-brown colour, sometimes reddish, greenish or yellowish with chert nodules. The upper layers tend to be concretionary. The limestone grades conformably upwards into red shales of the flysch complex.

- 70-100m of Palaeocene flysch deposits that include red calcareous shales, sandstones and conglomerates, containing clasts of limestone, serpentine, granite, diorite and flysch material.
Figure 2.2: Simplified geological map of the Parnassos Ghiona zone and surrounding geology. The Parnassos-Ghiona zone has been overthrust by the Pelagonian nappe sequence from the NE, covering much of Mount Iti, and protecting much of the Eocene flysch deposits (shown in orange) from erosion. The stratigraphy of the bauxite bearing carbonate sequence is shown in Figure 2.3. The four main mountains: Iti, Ghiona, Parnassos and Helicon are also labelled within the zone. The red box indicates the study area for this project. Adapted from Mettos et al., (2009)
Current formational theories suggest that the limestone sequence accreted in a shallow marine environment that underwent three interruption phases, during which emergence of the carbonate platform allowed karstification and bauxite deposition (Hose, 1978; Mistardis, 1978; Smith & Moores, 1974; Petrascheck, 1989; Laskou & Economou-Eliopoulos, 2007; Doutsos et al., 2006.) The intercalation of these bauxites means that the limestones provide the hangingwall and/or the footwall to certain horizons (often the hangingwall limestone of one bauxite horizon will be the footwall of the next bauxite deposit higher in the sequence.) The footwall limestones of each horizon are described as very pure, often with a creamy-white colour. The transgressive, hanging-wall of each horizon has been described as well bedded, dark in colour and rich in organic material.
Hose (1978) draws similarities between the Mediterranean Karst bauxites and Jamaican Karst Bauxites which have formed on Palaeogene limestones, on island arcs in the Pacific Ocean, suggesting that the Mediterranean bauxites have likewise formed on island arcs during subduction and micro-plate collisions during the Mesozoic. Hose also suggests that for the limestone to emerge from the sea, block faulting or doming could produce a stable island with conditions suitable for bauxite formation.

### 2.4 Mediterranean Karst-associated bauxites

The Parnassos-Ghiona bauxites are a typical example of the **Mediterranean-type Karst bauxites** which occur all around the Mediterranean region in Turkey, Spain, France, Italy, Serbia and Montenegro (former Yugoslavia), Austria, Hungary, Romania and Greece. Combined, these form the Mediterranean belt (Hose 1978.) The karst bauxites of the Caribbean, Pacific and Irano-Himalayan bauxite belts are also exclusively of Mediterranean-type, and the East Asian and Uralo-Sibero-Central Asian belts also contain some examples of Mediterranean-type bauxites. The North American belt is the only belt that does not contain examples of Mediterranean-type karst bauxite. Bardossy (1982) describes Mediterranean-type karst bauxites as ‘karst bauxites in the strict sense’ meaning that these represent the classic model for karst-bauxite deposits. They are typically well defined karst infills with a wide variety of sizes and shapes, but stratiform, lenticular and sinkhole type and transitions between the three are the most common. In Greece it is the composite sink-hole type and the smaller ‘nest and bag’ structures that are predominant (Nia 1971, Bardossy 1982.) Other karst bauxite types tend to be intercalated with clays, silts and other sediments (Ariege, Timan and Kazachstanian types) (Bardossy 1982.)

### 2.5 A summary of current understanding of the Parnassos-Ghiona Bauxites

The bauxites of the Parnassos-Ghiona zone occur in three stratigraphic horizons (see Fig.2.3), of which only the third (B3) and some localised occurrences of the second (B2) are economically exploitable to date. The occurrences of the first horizon (B1) have so far proven to be uneconomic. The B1 horizon occurs at the boundary between the mid- and late Jurassic (Oxfordian to Kimmeridgian) limestones, the B2 during the Kimmeridgian-Tithonian (late Jurassic), and B3 during the Cenomanian to Turonian-(Late Cretaceous) (Laskou & Economou-Eliopoulos, 2007; Kalaitzidis et al., 2010). This study focuses on the B2 and B3 horizon ore bodies that exist within the Iti and Ghiona mountains on the western side of the Parnassos-Ghiona zone, within the concessions of Elmin S.A. A detailed geological map of this research area is shown in Fig. 2.4.
The second bauxite horizon (B2) has been described by Valeton et al. (1987) as an ‘up to several metres thick bauxite layer, situated on a little deepened karst relief or even a non-karstified emersion surface’. In the south-eastern areas of the Parnassos-Ghiona zone, around Mount

Figure 2.4: A detailed geological map of Mount Iti and the northern section of Mount Ghiona, to show the distribution of second and third horizon bauxites and associated carbonate horizons within the study area of this investigation. (Based on geological maps by IGME 1960.)
Helicon, the bauxite is interbedded with a marine biogenic limestone, rich in gastropod fossils, indicating a marine depositional environment. The bauxite was deposited during exposure of the carbonate platform during the Kimmeridgian to Tithonian stages of the Late Jurassic Epoch with at least one return to marine conditions indicated by the marine gastropod band in south-eastern areas (Valeton et al., 1987).

The third bauxite horizon has been described by Valeton et al. (1987) as a continuous layer, of 1-10 metres thickness on top of the karstic footwall surface. The B3 footwall is the most intensely karstified of all horizons, with the depth of the karst structures increasing from the southeast to the northwest. The variation in the B3 karst relief led Valeton et al. (1987) to distinguish two types: the high intensity Otavi-type and the low intensity Helicon-type. The majority of the research area falls into the Otavi-type karst relief.

The bauxite horizons also differ in texture, mineralogy and geochemistry, and this will be discussed in chapter 4, however several key features of the bauxite deposits will be discussed below.

The bauxites exhibit various colours from deep red to altered, grey-white or ‘bleached’ bauxites. The term ‘bleaching’ of the bauxite has been used by many workers to describe the event(s) that have converted the red-brown bauxite to a grey-white bauxite (plus orange, pink and yellow intermediary stages) that makes up around 30% of the Parnassos-Ghiona bauxites (Laskou & Economou-Eliopoulos, 2007.) The bleached zones are irregular, but show some tendency to occur at the top of the bauxite lenses and the transition between bleached and unbleached bauxite may be marked by a sulphide-bearing bauxite layer as indicated in Fig. 2.5 (Laskou, 2005; Kalaitzidis et al., 2010.) This bleaching has been argued to be related to pyrite oxidation, producing acidic fluids that could mobilize the iron, however this has not been confirmed.

Broadly speaking, the bauxites of the Parnassos-Ghiona zone can be divided into two types based on the dominant iron type; the ferric type which is rich in Fe$^{3+}$ and therefore iron oxide minerals, and the ferrous type which is rich in Fe$^{2+}$ encouraging the prevalence of iron sulphide minerals which are the focus of chapter 4. These have been the subject of several studies including Laskou (2005), Laskou & Economou-Eliopoulos (2007) and Laskou et al. (2010). While most of the bauxite within Iti and Ghiona falls into the ferric category, ferrous bauxite is present, particularly within the third horizon of Mount Iti.
As well as the various shades of red, yellow and white bauxites, there are also areas where the bauxite can have a greenish colour. This is attributed to the presence of chlorite minerals within the bauxite, in particular chamosite and clinochlore (Bardossy, 1982).

The sulphide bearing bauxites are often found in close association with organic material, usually in the form of coal. Within the Iti and Ghiona mining districts, the bauxite ore bodies are often locally overlain by a thin, unconformable coal layer. Kalaitzidis et al. (2010) identified the presence of this layer above the B3 horizon in the Pera-Lakkos underground bauxite mine, currently worked by Delphi-Distomo Mining Company. They determined that the coal occurs at a maximum thickness of 50cm and is present in association also with the bleached bauxite, but also occurs as layers directly between the hangingwall and footwall limestones in zones absent of bauxites. They

Figure 2.5: A stratigraphic log from the Pera-Lakkos ore body, presented by Kalaitzidis et al. 2010 to show the relationship between the red and bleached bauxites and the sulphide bearing ‘transitional zone’. The overlying coal layers are also shown. This model is also described in Laskou 2005.
note the presence of a thin yellow-coloured layer of Fe-oxides/hydroxides and clay minerals between the coal and bleached bauxite. Inter-layers of coal with shale can occur locally within the hanging wall.

2.6 Observations of the bauxite in the Iti and Ghiona Mountains

Through extensive underground mapping and logging of 13 ore bodies across the research area, the following stratigraphic logs and ore body models have been created. The locations of each stratigraphic log are shown on the geological maps in Fig. 2.6 A and B, and the full schematic logs in Fig. 2.7. The objective of this section is to develop the existing ore body models and add new information from currently understudied ore bodies around Iti and Ghiona. This information has been summarized in Table 2.1.

Observations from the bauxites of Iti and North Ghiona

By comparing the stratigraphy of the second and third horizons of Iti and Ghiona (Fig. 2.7) the following differences have been recognised. The second horizon on the whole is more aphanitic (fine grained with compact texture (Bardossy 1982.)) than the third horizon bauxites, and typically develops a strong prismatic or columnar fracture pattern. Silicified cream coloured bauxites and some chloritized, green bauxites are common in both regions (Fig. 2.10 E and F.) The second horizon bauxite rests on typically pale grey, micritic limestone in both Iti and Ghiona. The upper layers can show a transitional contact with the overlying, well bedded, hangingwall limestone. The presence of gastropod fossils, bauxitic marls at, and above, the contacts, and the lack of organic matter suggest that this horizon may have been deposited in, or at least quickly covered by, a shallow marine environment, which would agree with the model for deposits elsewhere in the Parnassos-Ghiona zone.

The third horizon bauxites generally show a pisoidal texture, with clear evidence of bedding within the individual ore bodies. The overlying hangingwall was seen to be dark-grey and bituminous in Mount Iti, with a strong petroleum smell when broken. In Mount Ghiona, the limestone was more medium grey, with a general absence of organic material. The third horizon coal deposits that were reported by Kalaitzidis et al. (2010) in Pera Lakkos, western Mount Ghiona, extend to the third horizon bauxites of Mount Iti, both as an accumulation directly above sulphide bearing bauxites, and as thin beds within the immediate third horizon limestones. The coal in Iti can be up to 50cm thick and occurs mainly at the edges of the ore bodies, grading
Figure 2.6: A. Geological map of the northern edge of Mount Iti. B. Geological Map of the northern edge of Mount Ghiona. On each map the locations of the studied ore bodies are indicated by numbers; dark red for second horizon, light red for third horizon. (Based on maps published by IGME 1960.)
laterally into organic clay material towards the centre of the ore bodies. Of the ore bodies around
north Ghiona, none were found in association with organic matter in the quantities found in Iti.
Some ore bodies had a small <1cm layer of organic rich clay on top of the ore. No organic matter
was found in association with the second horizon bodies of either Iti or north Ghiona.

Ore body alteration (bleaching) was seen in varying degrees across the third horizon, and
produces similar results across the research area. Bleaching is most extensive in the northern
Ghiona third horizon deposits where iron mobilization was seen in bauxites near the contact with
the hanging wall, but can occur throughout an ore body, aided by faulting. In both cases, the
altered bauxites show layering of the various altered bauxite types (pink, yellow, white) in several
repetitive cycles (Fig. 2.10A), with increasingly finer layering closer to the hangingwall contact or
fault. In some cases near prominent faulting, entire sections in the order of around 5-10m³ can be
converted to white, low iron bauxite. Bleaching was not seen to any significant extent within the
second horizon bauxites.

The second horizon shows extensive silicification throughout the bauxites, more noticeably in
Mount Iti. This process can create cream coloured bauxite with oval red, unaltered patches still
visible (Fig. 2.10F.)

Sulphide-bearing bauxites were found only in Mount Iti deposits, in association with organic
material (Fig. 2.10D.) Some minor sulphides were found in association with green chloritized
bauxites in Ghiona. The amount of sulphide-bearing bauxite can vary between ore bodies, some
thinner sections being completely sulphidized, whereas with thicker ore body sections, the
sulphidation is typically confined to the upper layers.

At the base of several ore bodies, particularly in Mount Iti, and also along faults in Mount Ghiona
(Fig. 2.10B), is a hard, iron rich, crust-like deposit, described as a ‘black crust’ by Valeton et al.
(1987). This crust was always found in association with bleached bauxite, and when found at the
base of a deposit; it was separated from the footwall by a layer of soft, powdery calcite.
<table>
<thead>
<tr>
<th>Bauxite Horizon</th>
<th>Bauxite Age</th>
<th>Location</th>
<th>Bauxite types</th>
<th>Hangingwall</th>
<th>Footwall</th>
<th>Organic matter</th>
<th>Fossils</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iti</td>
<td>Mainly ferrous, sulphide-bearing grey bauxite at the top of ore bodies with ferric red bauxite lower down. Extensive bleaching common</td>
<td>Sharp contact, dark-grey, organic matter rich limestones</td>
<td>Pale grey, often altered to a reddish-orange colour, with channel-like and sinkhole-like karstic structures</td>
<td>Thick layers (up to 50cm) of organic matter present directly above bauxite ore bodies</td>
<td>Fossil roots in bauxite, beneath organic matter layer</td>
</tr>
<tr>
<td>Third Horizon</td>
<td>Cenomanian - Turonian</td>
<td>Ghiona</td>
<td>Mainly ferric, red, bleached white, yellow and orange bauxites. No ferrous, sulphide-bearing bauxite found</td>
<td>Sharp contact, often sheared, medium grey micritic limestone</td>
<td>Pale grey, often altered to a reddish-orange colour, with channel-like and sinkhole-like karstic structures</td>
<td>Thin layers (up to 1cm) of organic rich clays above the bauxites</td>
<td>None found</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iti</td>
<td>Mainly Ferric bauxite with frequent silicification</td>
<td>Gradational contact, some pink bauxitic marls, moving up into pale grey micritic limestones</td>
<td>Pale grey micritic limestone, moderately karstified structures</td>
<td>No organic matter found</td>
<td>Gastropod fossils at bauxite-hangingwall contact</td>
</tr>
<tr>
<td>Second Horizon</td>
<td>Kimmeridgian - Tithonian</td>
<td>Ghiona</td>
<td>Mainly ferric red bauxite with silified patches. Some minor bleaching at bauxite-hangingwall contacts</td>
<td>Gradational contact, pink bauxitic marls, moving up into pale grey micritic limestones</td>
<td>Pale grey micritic limestone, moderately karstified structures</td>
<td>No organic matter found</td>
<td>None found</td>
</tr>
</tbody>
</table>

Table 2.1: A summary of the major features and characteristics of the bauxites of Mount Iti and Mount Ghiona, separated by horizon.
Figure 2.7: Series of schematic stratigraphic logs (this study) to show the variations of orebody geology across Mounts Iti and Ghiona. The logs depict second horizon ore bodies from Iti (1), and Ghiona (2,3), and third horizon ore bodies from Iti (4-8) and from Ghiona(9-11). The logs are not to scale.
4. Dark grey, well bedded bituminous limestone
   - Sulphide bearing coal layer
   - Grey, sulphide rich, pisolithic bauxite
   - Thin, yellow clayey bauxite layer
   - Red pisolithic bauxite
   - Yellow/orange altered limestones

5. Bituminous rich, well bedded limestone
   - Thick coal layer at the edge, becoming more clay rich towards the centre
   - Bleached white/grey bauxite close to the edge of the bauxite, and along fractures.
   - Grey sulphide bearing pisolithic bauxite some red/orange oxidation staining.
   - Red/orange altered karstified limestone

6. Dark grey/black bituminous limestone
   - Thin coal bands interlayered with bituminous limestone
   - Thick, sulphide bearing coal
   - Organic rich clay with preserved roots
   - Karstified limestone with bauxite filled fissures. Limestone also shows several degrees of alteration including pink/red staining
   - Dark grey, sulphide bearing bauxite. Some orange/brown oxidation along fractures. Pisolithic texture with fine grained matrix.
7
- Dark grey/black, micritic bituminous limestone with extensive calcite veining.
- Matrix supported fault breccia, mainly limestone clasts in orange clay.
- Red/brown orange clay with a thin organic rich clay and coal layer at the top.
- Bleached grey pisolithic bauxite.
- Mottled yellow/grey pisolithic bauxite with black staining along fractures.
- Red/pink pisolithic bauxite with dark red pisoids.
- Iron rich iron precipitation at bauxite base.
- Micritic, white footwall limestone with red/orange clayey fracture fills.

8
- Well bedded, bituminous and clay rich, micritic limestone.
- Thin, well bedded, clay layer with some organic material.
- Red pisolithic bauxite, becomes aphanitic and clayey towards the top.
- Yellow pisolithic bauxite.
- White, low iron, pisolithic bauxite. Slightly powdery and crumbly texture.
- Pink, low iron, pisolithic bauxite.
- Iron rich, pisolithic bauxite. Dark brown, iron rich patches present.
- Heavily altered red/orange footwall limestone, micritic.

9
- Medium grey, well bedded limestone.
- Organic rich clay layer.
- Bleached pisolithic bauxite with white/pink matrix.
- Brown/red pisolithic bauxite, clear stratigraphy, layers of increasing and decreasing pisolith size.
- Pisolithic bauxite with white/pink matrix (partially bleached).
- Brown/red pisolithic bauxite, clear stratigraphy, layers of increasing and decreasing pisolith size.
- Red/yellow altered limestone, possible silicification.
10

Medium grey limestone
Clast supported fault breccia of angular limestone clast at the top, bauxite clasts at the base
Bleached white pisolitic bauxite close to hanging wall fault contact, and deeper in bauxite along fractures and faults
Yellow pisolitic bauxite
Red pisolitic bauxite
Red/brown pisolitic bauxite
Orange/yellow altered and silicified limestone

11
Well bedded, medium grey micritic limestone
Thin clay layer with some organic matter
Repetitive, layered white, yellow and red bleached bauxite increasing in repetitions closer to the hangingwall.
Red pisolitic bauxite, bleaching can penetrate deeper via faults and fractures.
Red/ yellow altered, silicified, brecciated footwall limestone

Lithologies

<table>
<thead>
<tr>
<th>Sulphide bauxite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
</tr>
<tr>
<td>Coal</td>
</tr>
<tr>
<td>Red bauxite</td>
</tr>
<tr>
<td>Yellow bauxite</td>
</tr>
<tr>
<td>White bauxite</td>
</tr>
<tr>
<td>Chloritized bauxite</td>
</tr>
<tr>
<td>Breccia</td>
</tr>
<tr>
<td>Fossiliferous horizon</td>
</tr>
<tr>
<td>Pisolitic</td>
</tr>
<tr>
<td>Limestone</td>
</tr>
<tr>
<td>Bituminous Limestone</td>
</tr>
<tr>
<td>Red altered limestone</td>
</tr>
</tbody>
</table>
Observations from the karstified footwalls of Iti and Ghiona

The second horizon footwall tends to be fairly shallow karst, generally consistent with the gently undulating karst terrain described by Valeton et al., (1987). Within the third horizon of Mount Iti, several of the ore bodies lie within elongate, channel-like karst structures. The karstified footwall limestones in these channels does not show the typical clint and grike features of sinkhole karsts, but instead have horizontally suspended limestone pinnacles surrounded by bauxite (Fig. 2.9). These structures would have formed through predominantly horizontal fluid flow, such as in a stream or river. These features were not found in the third horizon ore bodies in Mount Ghiona; however some ore bodies do have an elongate, channel-like form.

In both the second and third horizons of Iti and Ghiona, it was seen that the bauxite does not completely fill the karst void in the footwall to the top. That is the karst hole is never ‘overflowing’ with bauxite material. The remaining space is occupied by overlying coals and clays, and quite commonly by laterally confined limestone units. An example of this feature is shown in Fig. 2.8.

The footwall limestone of the third horizon can be altered to red/orange colours for several meters beneath the footwall-bauxite contact, and either side of the ore bodies; each third horizon ore body studied showed at least some degree of footwall alteration (Fig. 2.10C.) The alteration is a mixture of brecciation and pseudo-brecciation (in-situ breccia development through dissolution and re-distribution of the carbonate), intense silicification of the limestone, staining of the limestone to orange, red, and black colours and deposition of goethite, kaolinite and other clays within fractures. There are often fissures filled with bauxitic material penetrating for 1-2 metres beneath the main body of the ore, and the footwall can have intense calcite veining. This alteration is far less prominent in the second horizon, with most ore bodies resting on unaltered, pale grey limestone.

Implications for exploration and extraction

The geological differences between ore bodies of the second and third horizon and between Iti and Ghiona can have important implications for exploration and extraction of the bauxite.

- Alteration (“bleaching”) of the bauxite, which significantly increases the ore grade, is most prominent and extensive in the third horizon ore bodies of Mount Ghiona. Mount Iti does show some bleaching; however the thick layers of flysch and overlying thrust sheet units have apparently protected and preserved the ore body, maintaining its high sulphide content. In both areas the bleaching is most associated with faults and fractures. This means that Ghiona is likely to have a higher average Al₂O₃ grade. Further geochemical
analysis of these zones will reveal more information on the process that causes the bleaching, and also which elements, other than iron, are mobile during this process.

- It is likely that the hangingwall above the bauxites cannot be traced laterally. Therefore, while the bauxite-hangingwall (and bauxite-footwall) contact is a first-order exploration element, caution needs to be applied due to lateral facies change of the sedimentary lithologies.

- Footwall alteration, seen beneath third horizon bauxites may act as a (albeit spatially limited) proximity indicator for individual ore bodies, and may allow for greater accuracy for drill hole planning. Geochemical analysis of the footwall limestone will determine if the alteration zone extends outside the visible alteration of the limestone, potentially identifying certain indicator elements within the limestone surrounding the ore bodies.

- Several of the ore bodies have a faulted upper contact with the hangingwall limestone. This is the result of tectonic activity in the region and tends to produce a layer of hangingwall-bauxite breccia in a clayey matrix. This layer is soft and unstable, and can form a structural problem during mine development. Other structural problems can occur near zones of faulting, and in areas of thick overlying coal deposits and interlayers clay or coal beds with the hangingwall limestone.
Figure 2.8: Photo and diagram to show the partial infilling of karstified limestone by the bauxite material, and the development of laterally confined layers of clays and hangingwall limestones. 1-Karstified footwall limestone, 2- bauxite ore body, 3- the laterally confined hangingwall limestone units, 4-The laterally continuous hangingwall units.

Figure 2.9: Sketched examples of karstic structures seen within third horizon ore bodies of Mount Iti. These elongate, horizontal lenses of karstified limestone suggest a lateral karstifying fluid flow such as a river or stream.
Figure 2.10: A - layering of red, yellow and white bauxites at the bauxite-hangingwall contact of a third horizon ore body in mount Ghiona. The layering suggests a repetitive and prograding bleaching process. B - The hard, iron rich crust developed along several fractures within bleached white and yellow bauxites from a third horizon ore body in mount Ghiona. C - Red stained, brecciated and silicified footwall limestone from directly beneath a third horizon ore body in mount Ghiona. D - Thick coal layer above a sulphide bearing ore body from the third horizon bauxite in Mount Iti. E - Green chloritized bauxite found at the top of a second horizon ore body in Ghiona. F - Cream coloured silicified bauxite within second horizon ore body from mount Iti.
2.7 Conclusions

Geological field investigations of the ore bodies around Mount Iti and Ghiona in the Parnassos-Ghiona zone in Central Greece have revealed the following.

1. The second and third horizons show evidence of distinctly different depositional environments, with gastropod fossils and bauxitic marls in the second horizon suggesting a shallow marine palaeoenvironment (at least in its terminal phase); and coals and organic rich clays above the third horizon suggesting a more terrestrial, swampy environment. These observations support previous studies on the bauxites.

2. The coal deposits found in association with the third horizon bauxites are only seen within the Iti sections, with thin organic rich clays more common in Ghiona. This may suggest that the swampy conditions in Mount Iti may grade into a more lagoonal environment in north Ghiona. This is also supported by the channel-like features seen in the karstified footwall in Mount Iti, compared with the flatter sinkhole karsts seen in Mount Ghiona.

3. The footwall limestone of most of the third body horizons shows varying degrees of alteration, including clay filled fractures, distinctive red/orange colouration of the limestone, brecciation and pseudo-brecciation and silicification. Further work (presented in Chapter ??) will determine if this alteration is sufficiently extensive and distinct to be used as an exploration tool.

4. Distinct variations in bauxite colour and mineralogy have been seen between the second and third horizons and between Iti and Ghiona. Sulphide-bearing bauxite is confined to Mount Iti bauxites; Ghiona having mainly iron oxide-rich bauxites. Silicified bauxite is common in the second horizon bauxites of both Iti and Ghiona. Chloritized bauxite has been recognised in all horizons, in both Iti and Ghiona, but never in significant volumes. Bleached bauxite is seen in the third horizon, and is more extensive in Mount Ghiona, probably due to the protection that the Iti bauxites have from the overlying flysch deposits and thrust units.

References


Chapter 3: Methodology

3.1 Introduction
This chapter will provide details of each of the analytical methods used within this investigation; the various samples and sample preparations used for each method; the equipment and analytical parameters of each method; the accuracy and precision of each method; and details of the purposes of each method to the investigation and justifications of methods where appropriate. The methods presented here cover the investigations into mineralogy, geochemistry, texture and isotope studies, and are used throughout chapters 4, 5 and 6. Chapters 7 and 8 have their own separate methodologies sections, due to the differences in the type of data used for those chapters.

3.2 Microscopy
A combination of transmitted and reflected light microscopy of 30 thin sections was used to investigate the various textures of the bauxites and surrounding lithologies.

3.2.1 Sampling
Samples of the major bauxite types present in the study area, as identified in the field, were selected for thin sectioning. Samples were selected from the second and third horizon bauxites, of Mount Iti and Mount Ghiona, to assess the lithological, textural and mineralogical variability of the bauxites.

3.2.2 Equipment
For transmitted light microscopy optical observations were made using a Nikon Eclipse 400 petrological microscope, and a Nikon stereomicroscope. A digital camera was attached to the microscopes while in use.

3.2.3 Purpose of method
Microscope analysis of the bauxites was used primarily to identify the textural features of the bauxites in order to develop the ore genetic models for the deposits, in particular, the pisolithic and clastic textures of the bauxites (chapter 4), and the various textural occurrences of pyrite within the sulphide rich bauxites (chapter 5). Transmitted light was found to be the best method to examine the ooid and pisolith structures on account of the varying optical properties of the individual pisolith layers. Reflected light was useful for examining the darker iron rich zones, fine grained bauxites and
the more crystalline iron minerals (hematite, pyrite etc.) Microscopy was also used for mineral identification, and to support X-Ray Diffraction mineralogical analyses (see section 3.3).

3.3 X-Ray Diffraction
The mineralogical compositions of the bauxites, and surrounding lithologies, were determined using X-Ray Diffraction (XRD) analysis.

3.3.1 Sampling
84 samples of bauxite and associated lithologies were analysed for mineralogical composition. The samples were selected to represent the wide range of textural and colour variations seen within the second and third horizon bauxites. The samples were crushed in a tungsten carbide ball mill until uniformly powdered. If further grinding was required, an agate pestle and mortar was used until a consistently fine particle size was achieved. The samples were then mixed to ensure mineral homogenization before a sub sample of around 5-6g was extracted and mounted in a stainless steel sample holder for analysis.

3.3.2 Equipment and analytical parameters
The samples were analysed using a P’Analytical X’Pert Pro X-ray diffractometer, using Cu Kα radiation generated at 40kV accelerating voltage and 40nA beam current. Samples were scanned between 5 and 70° at steps of 0.008°, for a total scan time of 12 minutes. The diffractogram for each sample was interpreted using the X’Pert HighScore Plus software package that statistically scores the match between database peaks and the sample peaks. Manual peak comparison and identification was then used to verify automatically chosen peaks; to locate and interpret any unidentified peaks; and to identify and remove any mis-identifications that can be inherent in an automatic system. The 84 analyses were then categorized using cluster analysis.

3.3.3 Cluster Analysis
Cluster analysis is a method of exploratory data analysis which separates a large data set into groups or clusters, where observations of variables within a cluster are as similar as possible, while differences between clusters are maximized. This method can be used effectively as a tool to better understand the multivariate (in this case mineralogical) behaviour of a data set, especially as it is becoming common practice to make many different measurements on increasingly large sample sets in geological studies (Parks 1966; Pirkle et al., 1984; Templ et al., 2006.) However, as only minor
variations in a data set (such as the addition or deletion of a variable or a sample) can lead to considerably different groupings, it can never be used as a ‘statistical proof’ of the relationship between variables or observations (Templ et al., 2006.)

Cluster analysis was carried out using PANalytical’s HighScore Plus software which automatically sorted the data into the clusters of closely related spectral patterns (before peak identification.) The software also highlighted the most representative spectral pattern of each class, and the two most different scans of each class, which are presented as the representative and ‘end member’ samples of each group in the results section in chapter 4. The software also allowed easy identification of outliers of the analysis. (Macchiarola et al., 2007).

Each resulting cluster was classified mineralogically, by identifying the minerals detected, and then the amounts of each detected mineral, within each sample, were quantified using the Rietveld method. This method compared the calculated diffraction patterns from each sample with experimentally derived diffraction patterns, and by running through a series of least-squares iterations, with varying experimental and physical parameters, the software calculates a profile that is a ‘best-fit’ for the sample profile. The quantities of each mineral within this ‘best-fit’ profile are then accepted as representative of the true quantities within the sample (Macchiarola et al., 2007.)

3.3.4 Purpose of method
The results of XRD analysis have been used within this study to identify the mineralogical assemblages of each bauxite horizon, and to identify any significant spatial and temporal differences between the bauxite orebodies with respect to the major minerals present (i.e., the major Al, Fe, Ti, Si phases). This method allows rapid and accurate detection of major mineral components, including polymorph minerals (i.e. boehmite vs diaspore), which may be difficult to identify in thin section. Cluster analysis of the data can reveal if there are any relationships between the formation of certain mineral phases. Rietveld analysis can effectively distinguish between mineral phases, even if they only have subtle differences in X-Ray diffraction signature, and it can produce quantitative values for phases present in quantities of <1% (Macchiarola et al., 2007.)

However, the XRD spectra cannot differentiate between syngenetic, diagenetic and epigenetic minerals, nor identify whether a certain mineral phase is confined to a particular textural feature of the bauxites and other lithologies. As diagenetic and epigenetic processes have been shown to play a significant role in bauxites development within the Parnassos-Ghiona zone, XRD analysis alone in not
sufficient to provide a full mineralogical paragenesis analysis. The Rietveld quantifications are also strongly affected by the crystallinity of each mineral phase; phases of low to no crystal form would not register within the analysis. As previous research has shown that the crystallinity of iron phases decreases due to epigenetic alteration (Valeton et al., 1987), it is likely that certain phases may be ‘undetectable’ for this reason. Therefore, it is important to note that the mineral quantities presented from XRD analysis may not be absolute weight percentages of each sample, but will be relative weight percentages of the crystalline phases within the sample.

To provide a full assessment of the mineral paragenesis of the bauxites, XRD analysis is supported by petrological and microscope studies in order to enhance the understanding of each stage of mineral formation, and identify when and how each major phase has formed. Additionally, the minor and trace mineral phases, in particular, the detrital mineral components that have remained unchanged throughout bauxite formation were also analysed via SEM analysis, and the mineralogical phases interpreted from their geochemistry.

3.4 Portable X-Ray Fluorescence

Over 200 analyses of major element data of the bauxites and surrounding limestones were acquired in-situ using a portable X-Ray Fluorescence analyser.

3.4.1 Sampling

Rather than collecting rock samples and the subsequent lab processing required for conventional bench-top X-Ray Fluorescence (XRF), Portable XRF (PXRF) can produce element composition data in the field from direct measurements of selected samples or the in-situ rock surface. Each analysis was performed on a fresh area of rock, which was exposed using a geological hammer, and then cleaned with water and tissue paper. If necessary, a steel wire brush was also used to remove any dirt.

Bauxite deposits and the surrounding limestone were analysed using PXRF. Data collection along horizontal and vertical transects was favoured in order to show elemental variability through bauxite ore bodies, and changing geochemistry within the host limestones. The sample intervals along each transect were chosen depending on the length of the transect, and the feature(s) that were being analysed. Each sample location was analysed at least twice, and an average taken of the measurements.
3.4.2 Equipment and analytical parameters

An X-Met 5100 Portable X-Ray Fluorescence (PXRF) analyser, designed by Oxford Instruments was used to measure major element contents. When analyzing bauxite, the PXRF was programmed to use a mode designed for mineral exploration, which recorded most major elements and some heavy metals. The elements recorded in this way were: Al, Si, Ti, Fe, K, Ca, Mn, S, and P. When analyzing limestones, the PXRF was programmed to use a mode designed for standard geology and soil analysis. Elements recorded in this way were: Ca, K, Ti, Mn, Fe, Cu, Zn, As, Rb, Sr, Zr, Ni, and Pb.

3.4.3 Data accuracy and precision

Analytical accuracy of the major element data was determined using a set of 14 CRM standards of bauxite and rock matrices with high Al and Fe. Post-collection calibration was applied to the data based on the y=mx+c equation, determined via a bivariate plot of the measured vs published values for each element. An example of this calibration method is shown in Fig. 3.1, and tables of the calculated calibration factors for the analysed elements, for both modes, are presented in Appendix 2. The Limits of quantification for the elements (i.e. the lowest content of an element that the equipment could detect) analysed by PXRF are given in Tables 3.1 and 3.2.

<table>
<thead>
<tr>
<th>Limit of Quantification (PPM)</th>
<th>Ca</th>
<th>K</th>
<th>Ti</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Rb</th>
<th>Sr</th>
<th>Zr</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>129</td>
<td>379</td>
<td>58</td>
<td>12</td>
<td>45</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3.1: Limit of quantification values for identified elements within the Parnassos-Ghiona limestones.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>K2O</th>
<th>CaO</th>
<th>TiO2</th>
<th>Cr2O3</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>P2O5</th>
<th>SO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Quantification (wt%)</td>
<td>0.106</td>
<td>0.188</td>
<td>0.009</td>
<td>0.003</td>
<td>0.002</td>
<td>0.005</td>
<td>0.002</td>
<td>0.009</td>
<td>0.019</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 3.2: Limit of quantification values for the major elements within the Parnassos-Ghiona bauxites.

3.4.4 Purpose of method

Data collected in this way have been used in investigating the major element variations along vertical transects through ore bodies, and for identifying potential pathfinder elements within the limestones.
surrounding the ore bodies. This method, while lacking the range of detectable elements of its bench-top counter-part, was preferred due to its in-field use and the ability to collect a large data set of geochemical analyses in a relatively short amount of time, without the need for extensive sample collection and laboratory preparation.

3.5 Inductively Coupled Plasma-Mass Spectrometry

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to quantify the content of trace elements and rare-earth elements (REE) within the bauxites and surrounding lithologies.

3.5.1 Sampling

40 different samples of bauxite, including red, yellow, bleached white, sulphide and chloritised bauxites, from the second and third horizons, in Mount Iti and Mount Ghiona, were used for ICP-MS analysis. 2 kg of each sample was crushed in a tungsten carbide ball mill until uniformly powdered. If further grinding was required, an agate pestle and mortar was used until a consistently fine particle size was achieved. The samples were then mixed in a clean sample bag with a spatula, to ensure homogenization before a sub sample of around 0.05 to 0.1 grams was taken for analysis.
3.5.2 Equipment and analytical parameters

Trace elements and REEs were determined after open acid digestion (HF+HNO₃+HClO₄) by quadrupole inductively coupled plasma mass-spectrometry (ICP-MS) (Agilent 7700x) and (Ti, Sr and Ba only) by inductively couple plasma atomic emission spectroscopy (ICP-AES) (Thermo iCap 6500 Duo) at the Natural History Museum, U.K. Arsenic was determined by ICP-MS either with unpressurised collision-reaction cell (CRC) or by pressurizing CRC by 5ml/min He depending on the content of interfering REE in the sample. V, Ni, Cr, Cu, Zn and middle to heavy REE were determined with CRC in He mode (5ml/min). This minimizes formation of polyatomic interferences (CeO⁺/Ce⁺ <0.2%) and further mathematical correction was applied for Eu, Gd, Tb (cf. Ferrat et al., 2012).

3.5.3 Data accuracy and precision

The analytical accuracy was checked by comparison to the USGS standard rocks W-2 (diabase), BCR-2 (basalt) and a GSJ standard lake sediment JLK-1, and was found to be within ±5% for all REEs and most other elements. The analytical error for each analysed element is presented in Tables 3.3 and 3.4.

| Element | Sc | Ti | V  | Cr | Ni | Cu | Zn | As | Sr | Zr | Nb | Mn | Ba | Tl | Pb | Th | U  |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Limit of Quantification (PPM) | 0.03 | 4  | 0.08 | 1  | 0.4 | 0.3 | 0.6 | 0.14 | 5  | 0.2 | 0.2 | 0.08 | 2.5 | 0.08 | 0.1 | 0.028 | 0.095 |

Table 3.3: The limit of quantification of trace elements analysed by ICP-MS analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Y</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Quantification (PPM)</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
<td>0.04</td>
<td>0.008</td>
<td>0.003</td>
<td>0.005</td>
<td>0.003</td>
<td>0.006</td>
<td>0.02</td>
<td>0.003</td>
<td>0.005</td>
<td>0.004</td>
<td>0.003</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 3.4 The limit of quantification of REE analysed by ICP-MS analysis.

3.5.4 Purpose of application

The results of ICP-MS analysis were used for several different objectives of this investigation. A comparison of trace element and REE contents of the second and third horizons, from Mount Iti and Mount Ghiona, in chapter 4 is used to help identify the potential source material of the bauxites. In chapter 5, samples of white, bleached bauxite, yellow bauxites, green chloritized bauxites and red bauxites, and ferric precipitate material from the third horizon of Mount Iti and Mount Ghiona, were analysed for their trace element and REE concentrations to compare and highlight element mobility.
during bleaching alteration, and to help identify mobilization processes. In chapter 6, the trace element and REE contents of the footwall limestones of the third horizon bauxites of Iti were analysed to identify the geochemical changes associated with footwall limestone alteration, and to propose a genetic relationship between bauxite bleaching and footwall alteration.

ICP-MS analysis was chosen for this investigation as it provides excellent detection capabilities for all of the trace elements and REEs analysed, allowing the more subtle element variations to be detected and interpreted with a high confidence level. Due to the cost and preparation time required for this method, only 40 samples were analysed within this investigation, and the conclusions draw from this data set will benefit from future expansion and population.

3.6 Electron Microprobe

Electron Microprobe analysis was used to quantify the trace element geochemical content of pyrite and iron oxy-hydroxide minerals.

3.6.1 Sampling

Five samples of sulphide-bearing bauxites, and one sample of ferric iron precipitate material, were used for this analysis to include a range of pyrite occurrences, and the ferric iron precipitate minerals. The samples were prepared as thin sections. Analyses were performed on individual pyrite or iron oxide crystals, with enough surrounding material to avoid contamination from adjacent minerals.

3.6.2 Equipment and analytical parameters

Electron Microprobe analysis used a Cameca SX100 Electron Microprobe at the Natural History Museum, London, with a spot size of around 4-5 microns.

The analysed elements used within this study are Ti, Cr, Al, As, Ni, and Si. The average detection limits for these elements are presented in Table 3.5, and the complete data set can be found in Appendix 5.

3.6.3 Data accuracy and precision

The analytical error of the electron microprobe data is shown in Table 3.5.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ti</th>
<th>Cr</th>
<th>Al</th>
<th>As</th>
<th>Ni</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of quantification (ppm)</td>
<td>182</td>
<td>191</td>
<td>115</td>
<td>230</td>
<td>244</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 3.5: The limit of quantification of Electron Microprobe results.
3.6.4 Purpose of method
Electron Microprobe analysis was used in chapter 5 to accurately quantify the contents of trace elements substituted within pyrite, from the third horizon bauxites of Mount Iti, in order to identify any significant differences in pyrite geochemistry based on their textural occurrence and paragenesis within the bauxite. The method was chosen as it provides quantitative data with low detection limits for most elements (around 200ppm.)

3.7 Sulphur Isotope Analysis
Sulphur Isotope Ratio Analysis was carried out at the SUERC isotope analysis facility in East Kilbride, Scotland, in order to quantify the composition of sulphur isotopes within sulphide minerals of the third horizon bauxites. Analysis involved two separate methods, conventional sulphur isotope analysis first, followed by laser ablation sulphur isotope analysis to allow greater precision in sampling. The results from both methods are presented within chapter 5.

Conventional Sulphur isotope analysis

3.7.1 Conventional analysis sampling
Eleven hand-specimens of sulphide bauxite, from several different mines in the third horizon of Mount Iti, were chosen to represent the various forms of pyrite occurrences within the bauxite textures. Each hand-specimen contained more than one textural occurrence of pyrite and so several samples were extracted from each hand-specimen in order to compare these closely associated pyrites.

The pyrite was extracted from the samples to create a high purity sulphide sample using a high precision, diamond tipped drill capable of grinding out sulphide minerals, producing a powdered sulphide sample. The samples were cleaned with a dry brush between sample extraction to avoid cross contamination, and the work bench was swept and covered in clean paper before each sample was extracted.

3.7.2 Equipment and analytical parameters
Before isotope analysis, the sulphur was extracted from each sample as SO₂ gas. Around 5 to 10mg was utilised for isotopic analysis. Minor contamination by non S-bearing phases was tolerated, and has no isotopic effect on the final data. Sulphides were analysed by standard techniques (Robinson and
Kusakabe, 1975) in which SO\textsubscript{2} gas was liberated by combusting the sulfides at 1075°C, \textit{in vacuo}, along with Cu\textsubscript{2}O as an oxidising agent. As well as SO\textsubscript{2}, the gases produced contained moisture, non-condensable gases and some carbon dioxide. Transfer and purification of the SO\textsubscript{2} gas was achieved through using cryogenic methods along a glass vacuum line. These were a dry ice/acetone trap to remove moisture, liquid nitrogen cooled ‘cold finger’ to freeze the SO\textsubscript{2} whilst releasing non-condensable gases via vacuum pump and a controlled cooling/thawing Pentane trap to enable cryogenic separation of CO\textsubscript{2} from SO\textsubscript{2}.

The liberated gases were analysed on a VG Isotech SIRA II mass spectrometer, and standard corrections applied to raw $\delta^{66}$SO\textsubscript{2} values to produce true $\delta^{34}$S.

3.7.3 Data accuracy and precision

To ensure data accuracy and precision, three standards were employed; the international standards NBS-123 and IAEA-S-3, and the SUERC standard CP-1. Repeat analyses of these standards gave $\delta^{34}$S values of +17.1‰, -31.5‰ and -4.6‰ respectively, with a standard error around ±0.2‰ during the execution of these samples. Data are reported in $\delta^{34}$S notation as per mil (‰) variations from the Vienna Cañon Diablo Troilite (V-CDT) standard.

\textbf{Laser ablation sulphur isotope analysis}

3.7.4 Laser analysis sampling

Six samples of sulphide-bearing bauxite were prepared by hand as polished blocks using a series of polishing powders and final polish cloths. All of the samples were analysed by \textit{in situ} laser combustion.

3.7.5 Equipment and analytical parameters

The blocks were inserted into a sample chamber, which was evacuated and subsequently filled with an excess of oxygen gas (Fallick \textit{et Al.} 1992). The spatial resolution is determined by the minimum volume of SO\textsubscript{2} gas required for analysis (0.05–0.10 μmol), with minimum spot sizes of approximately <100 μm. Typically, samples were rastered under the laser beam to combust individual zones of pyrite and to allow separation of the different sulphide occurrences. The laser beam was a SPECTRON LASERS 902Q CW Nd:YAG laser (1 W power), operating in TEM\textsubscript{00} mode. The SO\textsubscript{2} gas produced by each laser combustion was purified in a miniaturized glass extraction line, using a CO\textsubscript{2}/acetone slush trap.
to remove water and a standard n-pentane trap to separate SO$_2$ and trace CO$_2$ (Kelley and Fallick, 1990). Determination of the sulphur isotope composition of the purified SO$_2$ gas was carried out on-line by a VG SIRA II gas mass spectrometer.

3.7.6 Data accuracy and precision
The reference gas in the mass spectrometer was calibrated by running a suite of international and lab standards regularly through the system. The standards employed were the international standard NBS-123 and IAEA-S-3, and SUERC standard CP-1. These gave $\delta^{34}$S values of +17.1‰, -31‰ and -4.6‰ respectively, with 1‰ reproducibility around ±0.2‰ at the time of these analyses. Data are reported in $\delta^{34}$S notation as per mil (‰) variations from the Vienna Canyon Diablo Troilite (V-CDT) standard. The laser extraction method results in a sulphur isotope fractionation between the host mineral and the SO$_2$ gas produced via combustion, which is mineral-specific (Kelley & Fallick, 1990). Experimentally determined fractionation factors are currently available in the SUERC system to apply correction to several sulphide/sulphosalt minerals, for example, pyrite (+0.8 ‰) and pyrrhotite (+0.4‰). Further discussion of the laser-induced fractionation is given in Wagner et al., (2002).

3.7.7 Purpose of Method
Both conventional and laser isotope analysis was used in chapter 5 to investigate the differences in isotopic composition of the different textural occurrences of sulphide minerals to help verify if they represent several phases of sulphide formation, and to help interpret the processes involved in the sulphide formation.

3.8 Scanning Electron Microscope
Scanning Electron Microscope analysis was used to investigate bauxite texture and major element geochemistry of the textural components of the bauxite.

3.8.1 Sampling
Eighteen separate samples of second and third horizons were analysed to investigate their texture and mineralogies. The samples were prepared in several ways. Several samples were prepared as rough surface chip samples that were broken off larger bauxite specimens and mounted into the SEM. The samples were used for textural analysis only, as the uneven surface can affect the intensity of the X-rays produced making geochemical analyses un-reliable. The roughly broken surface of the
samples did allow many minerals to retain their crystal shape making identification easier. The chip samples were cleaned of any dust or other surface particles and carbon coated before analysis.

Polished blocks of bauxite were hand prepared using aluminium oxide polishing powders and finished using polishing cloths. These were made to investigate the mineralogies of many different bauxite samples, and to provide a quick alternative to thin sectioning. They were again carbon coated before analysis.

Polished thin sections of a selection of the main bauxite lithologies from each horizon were produced for analysis with SEM methods, but also with standard microscopy, and electron microprobe work. These were carbon coated before analysis.

3.8.2 Equipment and analytical parameters
Two separate SEM systems were used for this investigation. The first was the Zeiss EVO LS15 scanning electron microscope with an Oxford Instruments Aztec energy dispersive X-ray spectrometer (EDS), with an 80mm X-max detector at the University of Brighton, which was used for mineralogical and textural investigations. Observations were made in back scattered electron mode (BSE) using an accelerating voltage of 20.00kV and a beam current of 15nA.

The second was a LEO 1450VP Scanning Electron Microscope at the University of Derby, UK. This SEM was used to analyse the geochemical compositions of the individual ooids and their surrounding matrix using an energy dispersive x-ray spectrometer (EDS), an accelerating voltage of 20.00kv and a beam current of 15nA.

3.8.3 Data accuracy and precision
The SEM data from each analysis, from both facilities, were normalized to 100%. To ensure accuracy, each spot analysis was carefully located to avoid potential mineral contamination, holes in the samples, and other features that may alter the results. Geochemical analyses were only used from analysis of polished thin sections or polished blocks.

3.8.4 Applications
SEM analysis was used to investigate the bauxite texture, in particular the fine grained matrix and growth structures of the major minerals; the major geochemistry of textural features such as pisolith cortices, bauxite clasts and bauxite matrix; the chemical composition of detrital mineral phases; and
to provide additional mineralogical identifications of trace minerals through interpretation of their chemical composition and mineral structure.

SEM was also used to investigate the geochemical compositions of the pisoliths within the bauxites (see chapter 4.) SEM was chosen instead of Electron Microprobe analysis for this as it was thought that the fine grained, clayey texture of much of the bauxite would not withstand the more intense electron beam used for microprobe work. This avoided any potential damage to the samples and unreliable data.

References


Macchiarola, K., McDonald, A.M. et Al. 2007. Modern X-ray diffraction techniques for exploration and analysis of ore bodies.


Chapter 4: The texture, mineralogy and geochemistry of the karst-associated bauxites of Mount Iti and Mount Ghiona

4.1 Introduction

The bauxite mineralogy, its geochemistry and its various textural features are all the result of the series of processes that have contributed to its genetic evolution; from the original parent lithology, through bauxitisation, transport and deposition, and then diagenetic and epigenetic alteration.

From an economic perspective, the characteristics of bauxite deposits can control the overall value and usability of the ore. The particular types of aluminium bearing and iron bearing minerals can affect the way in which the ore is processed, and the energy requirements for aluminium and alumina extraction. It also dictates the amount of \( \text{Al}_2\text{O}_3 \) available for separation (i.e. Al content in aluminium hydroxide minerals versus Al in aluminosilicate minerals.) The geochemistry of an ore body dictates the distribution of its elemental components and the relationships between certain elements, ultimately controlling the grade of the ore. The ore body texture can have implications for ore body hardness, crushability, and can control the extent of epigenetic processes.

This chapter presents an integrated investigation of the texture, mineralogy and geochemistry of the bauxites of Mount Iti and Mount Ghiona, which have been studied in a segregated manner to date. This integrated approach aims to provide comparative models for the two mountains to highlight important ore genetic and economic characteristics.

4.2 Literature Review

Studies into bauxite mineralogy, geochemistry and texture can be found for most deposits worldwide, for either scientific or economic reasons or a combination of both. Bauxites generally have a simple composition of mainly Al, Fe, Si and Ti oxides and hydrous oxides in varying quantities, along with smaller amounts of other elements with typically low mobility in earth surface environments. The mineralogies can vary between deposits both spatially and temporally, with multiple potential minerals forming to accommodate each element. These variations have been interpreted in several ways, mainly based on ore formation conditions, bauxite source and epigenetic overprints.

The Parnassos-Ghiona bauxites as well as other lateritic deposits within the Hellenides have been described by Valeton et al., (1987) as reworked, laterite derived facies deposited in a terrestrial to marine-epicontinental zone.
4.2.1. The texture of the Parnassos-Ghiona bauxites

The Parnassos-Ghiona bauxite ore (from all three horizons) has been described as being a mixture of coarse grained oolitic and pisoidal bauxite, sometimes interlayered with fine grained, earthy bauxite (Valeton et al. 1987, Laskou 2005.) These ooidal/pisoidal and fine grained bauxites are the most common textures of karst associated bauxite (Bardossy 1982.) Clastic, conglomeratic and breccia textures have also been recognised and have often been referred to as ‘relict’ textures, as opposed to the in-situ ‘neogenetic’ textures (Nia 1971, Valeton et al., 1987). Ooids and pisoliths are present in all three horizons of the Parnassos-Ghiona bauxites and are typically sorted, broken and sometimes altered or overgrown.

Valeton et al. (1987) suggested that the interstratification of coarse grained pisolith layers and the finer grained layers indicates periodical transport as ‘fanglomerates’ (a conglomerate of all sized clasts, deposited as an alluvial fan), by which the coarser bauxite represents high energy transport, and the finer grained bauxites represents low-energy transport conditions.

The second bauxite horizon is predominantly fine grained, dense bauxite. Pisolith and concretion rich bauxites are also present as several intermittent layers. The finer grained bauxite has a well-developed, vertical, rhombohedral cleavage.

The third horizon bauxites are mainly built up of coarse pisolith and clastic bauxite material, but can also contain some fine grained colloidal bauxite. Due to intense diagenetic overprint, the relict and neogenetic textures appear inseparable (Valeton et al., 1987).

4.2.2. Bauxite mineralogy

The mineralogy of the bauxite deposits have been investigated by several workers, using a range of analytical techniques including X-Ray Diffraction analysis and Laser µ-Raman analysis. The mineralogy of the bauxites varies considerably, not only between bauxite horizons, but it can be highly heterogeneous within a single horizon and even a single ore lens (Nia, 1971).

While there are differences in the published data for both mineralogy and geochemistry of the second and third horizon bauxites, there is a general consensus that the dominant Al phase in the second horizon is boehmite, while in the third horizon diaspore is the most common. Nia (1971) showed that within a single third horizon deposit there are zones of boehmite-rich and diaspore-rich bauxites, and areas where the two mix. It is unknown if this is also true of the second horizon bauxites.

Within the second horizon the main Ti-phase is anatase, the main Fe-bearing phase is either hematite or goethite, with pyrite, and Si is found mainly as kaolinite and other clay minerals. Other
minerals include chlorite group minerals and possible traces of serpentine. The finer, colloidal bauxite of this horizon tends to be richer in Si and therefore kaolinite (Valeton et al., 1987).

The third horizon iron minerals include hematite, goethite, pyrite (Valeton et al., 1987), maghemite (Gameletsos et al., 2007), magnetite and lepidocrocite (Kiskyras et al., 1978.) Titanium occurs mainly as anatase and silica as kaolinite, although in notably lower contents than the second horizon. Detrital zircon and monazite have also been identified (Valeton et al., 1987 and references there in.) Chamosite has also been identified within this horizon (Kiskyras et al., 1978).

Laskou & Economou-Eliopoulos (2007) identified epigenetic gibbsite within the B3 horizon bauxites in lesser amounts than both diaspore and boehmite, however no syngenetic or diagenetic gibbsite has been found by their investigations, or by other investigations into the third horizon bauxites. Interestingly, Peppas et al. (2002) defined the B1 horizon as being a hydrargillite type bauxite (the alternative name for gibbsite), based on studies of the Fokida mining district of S & B Industrial Minerals S.A., however this horizon has not been studied in great detail and so confirmation of this is difficult at present. Valeton et al. (1987) observed small amounts of gibbsite in epigenetic black crusts formed at the base of some second horizon ore bodies.

4.2.3. Bauxite Geochemistry

The current geochemistry of the bauxites is a function of the composition of the source material, and diagenetic and epigenetic processes (Valeton et al., 1987.)

The source material for the bauxites is thought to be, at least partially, ophiolitic material from the adjacent sub-Pelagonian zone. This is indicated by high content of siderophile elements such as Cr, Ni, and Co, that are common to the ultramafic compositions. The second horizon also shows increased content of lithophile elements such as La, Nd, Pb, Zn and Y, as well as Zr and high Ti, which Valeton et al., (1987) interpreted as an additional contribution from magmatic rocks. The third horizon, which also has a high siderophile element content, also shows evidence for contribution from acidic lithologies via presence of zircon, monazite, high Zr, Ga, Pb, Zn and certain REE.

The major elements, as with any bauxite, are aluminium and iron, which in both the second and third horizons occur in a wide range of contents, and always show a strict negative linear correlation with each other (Valeton et al., 1987.) Silica is present within both horizons also. Nia (1971) noted that silica within the bauxite is richer in boehmitic bauxites, but is also typically richer at the top of ore bodies, steadily diminishing towards the centre. Nia also described the occurrence of silica as ‘silica fields’, suggesting irregular, high silica zones within the ore. Titanium is again present in both horizons, typically having a positive correlation with aluminium.
Diagenetic effects have been described in depth by Valeton et al. (1987), but in summary involve the removal of silica and iron, and crystallisation of several aluminium and iron mineral phases. Epigenetic processes generally involve the downwards mobilization of Ba, Mn, Ni, Co, Cu, Zn and REE in both horizons.

4.2.4. Ooids, pisoids and clasts in bauxite

Ooids and pisoids in bauxite are concretionary structures that typically have alternating layers of aluminium rich minerals and iron rich minerals. They are common in lateritic and karstic bauxite deposits and have been described by Mongelli (2002) as ‘geochemical recorders of the environment of formation.’

Nia (1971) suggested that the pisoliths originate from ‘re-working of an in-situ bauxite area in the sediments at an early diagenetic stage’, and described the pisoliths as displaying a rhythmic differentiation of iron-aluminium hydroxide gel, caused by ‘periodic fluctuation of surface water’ and the resulting alternation in iron contents gave rise to concretions. Nia attributed the formation of the bauxite clasts to weathering and internal movements which created cracks that split the bauxite into small fragments supported by a soft matrix after the formation of the pisoliths.

Mongelli & Acqualedda (1999) studied ferruginous concretions within the Mediterranean karst bauxites of the Apulian carbonate platform, Italy, and suggested that pisolitic concretions formed at the expense of kaolinite in the matrix and are composed of alternating Al-bearing hematite and boehmite layers around an Al-bearing hematite core. They conclude that the pisoliths form within a pedogenic environment. It was also noted that boehmite may form in the cortices as opposed to Al-bearing hematite at lower values of water activity (e.g. during dry seasons), lower pH or local reducing conditions that promote the instability of hematite.

Mongelli (2002) in studying the same concretions of the Italian karst bauxites identified a 2-stage process for their formation; the first being the growth of the core in a ‘long period of wet tropical climate’, the second a much drier period that favoured boehmite stability which alternated with wetter periods promoting Al-bearing hematite stability. This cyclic growth may therefore be representative of seasonal or annual fluctuations in near surface conditions.

Studies of the pisoliths of the allochthonous Weipa bauxites of Northern Australia by Taylor & Eggleton (2008) identified several characteristic features such as cores of earlier re-worked bauxite, distinction of ‘inner’ and ‘outer’ layered cores, discontinuous or lenticular cortices and broken pisolith inner cores. These features led them to conclude that the pisoliths have a complex formation history involving the formation of loose bauxite particles that were later coated by kaolinitic layers,
which were subsequently weathered to aluminium hydroxides during periods of erosion, re-deposition and bauxitisation. This model therefore suggests a physical accretionary process for pisolith formation.

Anand and Verrall (2011) identified various morphologies that resembled fungal hyphae composed of gibbsite and Fe oxides, within pisoliths of the Darling Range bauxites, Australia. They conclude that the pisoliths were formed in part by the active precipitation of Al and Fe by fungi (as opposed to fungi replacement by Al and Fe.)

The models for pisolith formation are varied (Nia, 1971; Mongelli & Acqualedda, 1999; Mongelli, 2002; Taylor & Eggleton, 2008), from being a syn-sedimentary accretionary process, bacterially/fungally induced precipitation, or a diagenetic feature caused by fluctuating water activity through seasonal climate changes. The models all agree that the pisoliths have formed from the bauxite material, rather than being a clastic product from an unrelated source and subsequently bauxitised. If the pisoliths have grown from the bauxite, then they should have a similar geochemical composition, or at least a geochemical relationship, with the matrix from which they formed. If they are products of accumulation during transportation, then at least the inner sections of the pisoliths should show some compositional differences to the surrounding matrix. This hypothesis is valid unless the composition of the bauxite material has remained constant throughout transport.

4.2.5. The focus of this chapter

The information summarised above is largely derived from studies that have focused on bauxite deposits from the South-eastern areas of the Parnassos-Ghiona zone. The deposits of Mount Ghiona and particularly Mount Iti have received little attention, and the current models for regional bauxite formation have not been extended this far. Field evidence (Chapter 2) has already shown some distinct differences between the bauxites of Mount Iti and Mount Ghiona, as well as several ore bodies that question existing models for the occurrence of pyritic bauxite and bleached bauxite. This chapter assesses the textural characteristics, mineralogy and geochemistry of the Mount Iti and Mount Ghiona bauxites, and uses these data to classify, and examine the formation of, the bauxite ores and key features within them. Methods applied are detailed in Chapter 3.

4.3 Results

4.3.1 The texture of the Parnassos-Ghiona bauxites

The bauxites studied in this investigation were all found to be either mainly earthy or pisoidal in texture. The textures of the bauxite ore bodies sampled within this study can be defined by the
relative contribution of three main textural features present: earthy bauxite matrix; ooids and pisoids; and clastic bauxite material.

**Bauxite matrix**

The bauxite matrix in all cases, is an equigranular, microcrystalline mass of randomly orientated hydrous aluminium oxide minerals (boehmite or diaspore), with fine grained iron minerals and angular detrital mineral components. The crystal size is typically between 1-5µm, but larger (20-25µm) crystals of diaspore are present, although rare (Fig. 4.1). Texturally, the second and third horizons are very similar, the only difference being the occasional larger diaspore crystal in the third horizon, as opposed to the constant microcrystalline boehmite in the second horizon (shown in Fig. 4.1.)

![Fig. 4.1: Two backscatter electron images showing the microcrystalline, equigranular and randomly orientated crystal texture of the bauxite matrix. A. Second horizon boehmite bearing bauxite matrix including bright clasts of detrital mineral components. B. Third horizon diaspore bearing bauxite matrix, with a large clast of goethitic bauxite in the centre, large crystals of diaspore within the matrix (centre left), and bright, authigenic, euhedral pyrite crystals. (He – Hematite, Bo – Boehmite, Di – Diaspore, Py – Pyrite.)](image)

The lack of a preferred mineral orientation within the bauxite matrix (random arrangement) is a feature that can form from the very slow crystallisation of a gel-like pulp under quiet conditions (Bardossy 1982.) This suggests that the bauxite matrices may have both crystallised from a similar composition Al-rich ‘gel’, but under differing external conditions that dictated the species of hydrous aluminium oxide mineral that formed. This fine grained matrix was found throughout the bauxites.
Often the matrix has formed small rounded accumulations of earthy bauxite sometimes referred to as ‘peds’ which in many cases act as the starting point of ooid formation (Fig. 4.2.) These may form through weathering and mobilization of bauxites grains that gradually accrete into the peds (Taylor & Eggleton, 2008).

Bauxite Pisoids

The bauxite pisoids, whilst common, were very diverse texturally. They do all share some common features.

1. The pisoliths occur in a range of sizes from microcrystalline (classified as micro-ooids) up to 2mm in size (pisoids), with various sizes in between (ooids) (based on a definition by Bardossy 1982), however there is very little difference between them apart from size. Presumably, given enough time for growth, the micro-ooids would grow into ooids and then pisoids. The pisoids are generally round or sub-rounded in shape, however some can be rather irregular depending on their core shape (Fig. 4.3A), and others can be deformed to unusual shapes, probably by compaction whilst still soft (Fig. 4.3B.)
2. The cores of the pisoliths are in most cases rounded lumps of bauxite material with texture identical to that of the matrix. These can be small with respect to the rest of the pisolith, or they can account for the majority of the pisolith, with only a few thin cortices surrounding them. In some of the more altered bauxite, the cores can often be removed, perhaps from physical weathering rather than from a selective dissolution process. In several pisoliths the core can be a small detrital mineral grain or non-bauxite material (Fig. 4.3C), or small broken fragments of earlier pisoliths (Fig. 4.3D) which is very common, and clusters of well-formed and consolidated micro-ooids have been found as pisolith cores also. In pisolith D the edges of the broken pisolith core appear well rounded suggesting transport and abrasion of the fragment prior to re-concretion.

3. The cortices vary from a few tens to hundreds of microns in thickness and a single ooid can have any number between 1 and 12 cortices, but most have between 2 and 5. Most cortices are continuous and can be traces around the complete pisolith. Each cortex is typically homogenous, but it is common for one or more cortex within a pisolith to be discontinuous due to abrasion during weathering. These abraded layers indicate disconformities during pisolith growth. Significant textural differences between cortices can also indicate a change
of matrix composition (Fig. 4.3E.). The description by Bardossy (1982) that the layers become increasingly more spherical from the inner to the outer cortices is true for many of the pisoliths. The pisoliths are either suspended within the fine grained earthy bauxite matrix (matrix supported, Fig. 4.3), or have a ‘pisoid supported’ structure with interstitial earthy bauxite matrix (Fig. 4.4).

The incorporation of broken pisolith fragments as pisolith cores suggests multiple generations of pisolith formation separated by pisolith destruction and transportation. The variable cortex texture also suggests transport during pisolith formation.

**Clastic bauxite**

Clastic bauxite material is present in many samples of the bauxites, but never exceeding more than 10-20% of a sample. The clastic material is often of bauxite or near bauxite composition, although often being noticeably richer in iron than much of the surrounding bauxite.

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Fig. 4.4: A transmitted light microphotograph of an example from a third horizon ore body of the clastic bauxite texture typical of the Parnassos-Ghiona bauxites, showing multiple types of clast, and evidence for several stages of pisolith development and multiple stages of transportation. See text for an explanation of labels.

The bauxite clasts occur in varying proportions of the bauxite and display a range of fabric and features. Many clasts within the second horizon and a large proportion of those in the third horizon
show a massive or homogenous fabric, primarily reflecting a composition and texture similar to that of the matrix (Fig. 4.4A.) Many of the third horizon clasts show a ‘composite’ clast structure, meaning that they are composed of earlier bauxite pisoids and/or bauxite clasts (Fig. 4.4B.) This suggests that these are clasts of an earlier generation of pisoliths than those surrounding it.

The clasts range from being angular to well-rounded (Fig. 4.4C), which suggests that clasts can be transported after formation, causing abrasion and rounding. The clastic material can subsequently become the nuclei for further pisolith formation at the small scale, and larger bauxite pebbles can themselves become coated by pisolith-like cortices.

The textures identified within the Parnassos-Ghiona bauxite suggest formation of the bauxite through several phases of re-working of the different textural features. The ooid in Fig. 4.4D represents the complexity of this process. The ooid itself is made of a red bauxitic core with 10 alternating iron and aluminium rich cortices. These cortices are discontinuous on the top left side, suggesting that they have been worn away through abrasion during transport, assuming it formed as a spherical structure. The ooid must have then come to rest and been covered in a thin, complete iron rich cortex, followed by a thick aluminium rich cortex. It was finally covered by a thin iron rich layer (which covers all of the pisoliths within this clast), before the area around it was consolidated, weathered and liberated as a composite bauxite pebble. This pebble has been rounded by transport over (presumably) a significant distance, so much so that pisolith D is now protruding from the clast edge, suggesting a higher resistance to abrasion than the matrix. It was then deposited along with several other bauxite clasts, pisoids and earthy bauxite into the formation seen within Fig. 4.4. This evidence for multiple pisolith generation and several phases of transport contradicts suggestions by Nia (1971) and other models that suggest the pisoliths or clasts formed through post-deposition and diagenetic, in-situ, processes within the bauxite.

**Internal textures of pisoliths**

Within the individual pisoliths various textures can be observed which can help reveal the formation process of the pisoliths. Fig. 4.5 presents back scatter electron images of four different pisoliths from across the Parnassos-Ghiona third horizon bauxites. These pisoliths are composed of alternating iron rich and iron poor cortices. The terms ‘iron-rich’ and ‘iron poor’ are used as SEM analysis of the individual bands has shown that all cortices contain contents of aluminium but only the ‘iron rich’ cortices contain >5% iron. The textures of the ooids overall are very similar to the bauxite matrix shown in Fig. 4.1, in that they contain microcrystalline (< 5um), randomly orientated hydrous
aluminium oxide minerals (diaspore within the images shown), which is especially clear within the iron poor cortices (Fig. 4.5 A and D). Within Fig. 4.5 B and C, both the Fe-rich and Fe-poor cortices contain small dark and bright clasts which are the detrital components of the bauxite (e.g. anatase, chromites, see section 4.3.2), also typically found within the matrix. The texture is also consistent across the pisoliths indicating that these Fe-rich and Fe-poor cortices have formed after the matrix formed. The gradational and undulating edges of the cortices further support this interpretation. Pisoliths B and C in Fig. 4.5 have distinctly different cores (both texturally and compositionally) to the surrounding cortices, and in pisolith B there is a clear unconformity between the darker core and the immediate paler cortex surrounding it.

Fig. 4.5: A selection of backscatter electron images of four different pisoliths from across Parnassos-Ghiona third horizon bauxites, showing the internal textures of the pisolith structures. A. Pyrite rich pisolith from Mount Iti, B. Hematite rich pisolith from Mount Ghiona. C. Pisolith from Mount Ghiona. D. Pyrite bearing low iron pisolith from Mount Iti.
The Mineralogy of the Parnassos-Ghiona Bauxites

The mineralogies of the bauxites have been presented here, firstly as an overview of the variability of the mineral assemblages across Mount Iti and Mount Ghiona in both the second and third horizons based on the XRD data. This is followed by a more in depth exploration of how each of the minerals identified through XRD occur within the bauxite textures based on microscopy and SEM data and observations, and additional mineralogical identifications of the trace mineral components.

Variability in Bauxite Mineralogy

Temporal Variability

Fig.s 4.6 and 4.7 are the results of the cluster analysis of the second horizon bauxite analyses and third horizon bauxite analyses respectively. Comparison of these indicates the differences between the Late Jurassic second horizon bauxites and the Mid-Late Cretaceous third horizon bauxites.

Second horizon bauxites

Mineralogical data for the second horizon agrees with previous findings that the dominant aluminium mineral in the second horizon bauxites is boehmite, with only minor (5%) diaspore in isolated samples. No Gibbsite was identified in the samples studied. The only iron oxide mineral found was hematite, which occurred in significant quantities in three of the four clusters, and no iron sulphides were found.

Titanium oxide minerals were found in all clusters, mainly in the form of anatase. Rutile is also present, particularly in samples lacking in iron bearing minerals.

Silicate minerals present include kaolinite, present within 3 out of 4 clusters, with quantities of between 26 to 37%. Where kaolinite wasn’t found in a cluster, the chlorite mineral chamosite is present. Calcite was also identified in several samples with values between 1 to 4%.

Clusters 1 and 3 contain samples from both Mount Iti and Mount Ghiona, however, the chamosite bearing bauxites of cluster 2 are all from Mount Iti, while the higher boehmite bauxites of cluster 4 are samples only from Mount Ghiona. Groups 2 and 3, which are richer in silicate minerals, are composed of samples taken from higher elevations in the bauxite profiles, within 1 metre from the hangingwall contact. Notably, group 1 contains samples noted for their proximity to faults, perhaps suggesting some degree of bleaching and iron removal. Group 4, the more boehmite rich samples, all came from Mount Ghiona, from deeper sections within the bauxites, typically 2-3 metres below the hangingwall contact.
The cluster ‘outliers’ show that some samples are particularly rich in calcite which is to be expected within karst terrain; but the samples didn’t contain any other unusual mineral components. These samples came from locations directly beneath hangingwall contacts, suggesting an interworking of calcite during marine transgression.

**Third horizon bauxites**

Again, the third horizon data agrees with previous research that this horizon is dominated by diaspore as the main aluminium mineral, however, there are some samples that are clearly boehmite rich (cluster 4), which are representative of samples from the southernmost ore bodies of Mount Ghiona. Again, no gibbsite was identified in the samples studied. This temporal difference in hydrous aluminium oxide mineralogy will be discussed further in later sections of this chapter.

Iron has been identified in hematite and goethite as the dominant oxide forms and as minor magnetite and lepidocrocite. In some samples, iron occurs as a sulphide mineral in the form of pyrite in cluster 7. The magnetite component was found in several samples in cluster 7, perhaps linking its occurrence to the formation of pyrite. The goethite rich bauxites of cluster 6 are representative of samples taken from the top of sulphide bearing bauxite profiles where the bauxite has been exposed to oxidising conditions.

Titanium occurs predominantly as anatase, with only 1% rutile detected in the low iron bauxites of cluster 8, in a similar way to the second horizon.

Silicate minerals are overall less dominant within the third horizon, however kaolinite has been recognised associated with pyrite rich bauxites in cluster 7, and in some selected other bauxites associated with both boehmite and diaspore. Chlorite minerals were also found in 9 samples of cluster 2, mostly as chamosite, which are associated with sulphide minerals, as well as diasporic bauxite. Other minerals include calcite, which again is to be expected as ‘contamination’ through dissolution of the surrounding carbonate rocks. Quartz occurs as a trace mineral in a selected few samples.

When compared to the second horizon mineralogy, it is clear that the iron mineralogy of the third horizon is more diverse, having goethite, pyrite, minor magnetite and lepidocrocite present within the bauxites, as well as a selection of bauxites that are lacking in a crystalline iron phase, which indicates several processes of iron mineral evolution and formation under more variable conditions. Notably, both horizons show a small percentage of rutile within samples where an iron phase is either absent or present in small quantities. This may be due to ‘passive enrichment’ in crystalline mineral phases due to the loss in the dominant crystalline iron mineral phases, which would imply
that rutile is present throughout the bauxite in a low quantity. The presence of chamosite in the second and third horizons (and many other bauxites worldwide, Bardossy 1982) suggests that it forms under a particular set of conditions that are common to bauxites.
Fig. 4.6: The results of cluster analysis of mineralogy data from samples of the second horizon bauxites from the Parnassos-Ghiona zone.
Cluster 1 – Hematite/goethite bauxite

Cluster 2 – Chamosite bauxite

Cluster 3 – Diaspore/Goethite bauxite

Cluster 4 – Boehmite/kaolinite bauxite

Cluster 5 – High Diaspore/Goethite bauxite

Cluster 6 – Goethite rich bauxite

Third Horizon

N = Number of samples in cluster
Fig. 4.7: The results of cluster analysis of mineralogy data from samples of the third horizon bauxites from the Parnassos-Ghiona zone.
Spatial variability
Cluster analysis was performed again on the same dataset, however this time it was separated by location (Mount Iti versus Mount Ghiona) instead of by age (i.e. horizon).

Mount Iti
Mount Iti contains a mixture of boehmite and diaspore bauxite, dictated as above by the corresponding horizon, and no boehmite was found anywhere within the third horizon of Mount Iti. Chlorite minerals were found in most groups. Several samples were found to be enriched in pyrite, up to 32%. The dominant component in each cluster is hydrous aluminium oxide, with varying amounts of iron oxides or sulphides.

Mount Ghiona
The boehmite bauxites in Mount Ghiona are a combination of second and third horizon samples, which suggests that there may be a difference in overall formation process of the aluminium oxide minerals between Iti and Ghiona, perhaps relating to a variable depositional setting. Kaolinite appears to be more common within Mount Ghiona, particularly within the diasporic bauxites; however chlorite minerals are far less abundant as within Iti, perhaps suggesting an inverse relationship between the two minerals.

Comparison of both mountains
Both Mount Iti and Mount Ghiona have a cluster (5 and 6 respectively) that is noticeably enriched in diaspore and where iron minerals are absent, which in both cases represent the white, bleached bauxites. Both Mountains contain bauxite that is diaspore rich, with around 10% hematite and 2-5% anatase, which is characteristic of the red, unaltered bauxite. This study assumes this hematite rich bauxite, with either boehmite or diaspore, to be the main bauxite composition from which various processes led to the formation of the various mineralogical compositions. In Mount Iti, this cluster also contains a certain percentage of calcite presumably from surrounding rocks.

It is also important to note that only the third horizon of Mount Iti contains any identifiable iron sulphide minerals, as they are completely absent in all Ghiona samples.
Fig. 4.8: The results of cluster analysis of mineralogy data from samples of the second and third horizon bauxites from Mount Iti, within the Parnassos-Ghiona zone.

**Mount Iti**

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Number of Samples</th>
<th>Mineral Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>Goethite bauxite</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>Boehmite bauxite</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>Ferric Bauxite</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>Hematite rich bauxite</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>Absent iron phase</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>Goethite rich</td>
</tr>
</tbody>
</table>

*Note: N = Number of samples in cluster*
Fig. 4.9: The results of cluster analysis of mineralogy data from samples of the second and third horizon bauxites from Mount Ghiona, within the Parnassos-Mount Ghiona

Cluster 1 – Diaspore/Goethite bauxite

Cluster 2 – Kaolinitic bauxite

Cluster 3 – Boehmite/Kaolinite bauxite

Cluster 4 – Boehmite/Kaolinite bauxite with Hematite

Cluster 5 – Diaspore/Hematite bauxite

Cluster 6 – Diaspore bauxite, absent Iron phase

Mount Ghiona

N = Number of samples in cluster
4.3.3  Textural Controls on Mineralogy

Hydrous Aluminium oxide minerals

Hydrous aluminium oxide minerals occur as Boehmite and Diaspore. As previously shown, much of the matrix of the bauxite material is composed of micocrystalline (1-5 µm) hydrous aluminium oxide with detrital and authigenic components. Aluminium hydroxides also feature as layers within pisoliths and often serve as pisolith nuclei.

Iron minerals

The iron minerals identified in XRD analysis were also identified within the bauxites in thin section analysis and examples of their occurrence are shown in Fig. 4.10 below. Hematite was found as the dominant iron mineral throughout the red bauxites of both the second and third horizons within ooids and pisoids, within the matrix and within the bauxite clasts. Pyrite occurs within the third horizon bauxites of Mount Iti in several different forms that will be discussed in detail in chapter 4. Fig. 4.10 A shows some examples of pyrites within the bauxites, where they appear to

Fig. 4.10: Four reflected light images of the Parnassos-Ghiona bauxites to show the textural controls on some of the iron minerals detected by X-ray diffraction analysis. A- Pyrite occurring as various components, probably replacing earlier hematite rich features. B. Goethite replacing pyrite as a pseudomorphic, oxidation replacement process. C- Magnetite occurring as clastic material, possibly detrital in origin, or possibly an alteration product of hematite. D. Magnetite occurring as a veinlet fill. (Py – Pyrite, Di – Diaspore, Go – Goethite, He – Hematite, Mag – Magnetite)
form either replacing, or instead of, iron oxides. Goethite has mostly been found as a pseudomorphic product of earlier pyrite minerals, such as those in Fig. 4.10B. While most of the identified goethite occurs in this way, thin goethite rich layers have been found at the very top of some of the bauxite deposits in Iti and Ghiona. Magnetite was found less frequently than other iron oxides, and occurred either as rounded clasts of almost solid magnetite (Fig. 4.10 C), within some of the bauxites, or as clearly epigenetic veining within bauxites of Mount Iti (Fig. 4.10 D.) The magnetite clasts were found in bauxites that were overlain by bauxites of the same textures, except the clasts were pyritised. It is possible that this magnetite is detrital in its nature, sourced from an igneous magnetite rich body, and pyritised after deposition on the bauxite, or it may be that these clasts were hematite rich, and were converted to magnetite due to instabilities in a reducing environment, with a significant lack of sulphur. The magnetite veinlets show that re-precipitation of iron in veinlets occurred under reducing as well as oxidising conditions.

**Titanium minerals**

Titanium has been identified as small (10-20 µm), often isolated minerals, within the bauxite pisoliths (identified in Fig. 4.11) and within the bauxite matrix. The anatase occurs as euhedral crystals. It is difficult to identify from present data whether they occur preferentially with another mineral or whether they are randomly dispersed.

![Fig. 4.11: A backscattered electron image of a pyritised pisolith from Mount Iti, showing the location of anatase (An) as individual, euhedral/subhedral crystals.](image)
**Silicate Minerals**

**Kaolinite**

Kaolinite was widespread within the second horizon bauxites as compared to the third horizon. The second horizon is not entirely kaolinite bearing, but becomes kaolinite rich through an epigenetic silicification process. Kaolinite is found replacing much of the matrix within the bauxites (Fig. 4.12 A.) and partial replacement of some pisoliths and clasts (Fig. 4.12 B). This typically leaves a “blotchy” appearance of deep red and creamy white bauxite. The patches can be ellipsoidal, with the long axis perpendicular to the bauxite-hangingwall contacts, which indicates fluid flow perpendicular to boundaries associated with silicification.

**Chlorite minerals**

Chlorite minerals were found in both the second and third horizon bauxites in minor to trace amounts. The mineral is associated with different textures within each horizon. In the second horizon chlorite minerals were found as several outer cortices surrounding ooids, sometimes interlayered with other iron and aluminium minerals (Fig. 4.12 C.) It was also found as similar layered structures around bauxitic clasts (Fig. 4.12 D.) The growth of chlorite in the second horizon suggests deposition of the bauxite material in a reducing shallow marine environment. Reaction with iron during silicification may have caused precipitation of chlorite around the most iron rich structures (ooids and clasts.)

Within the third horizon, chlorite was found as an epigenetic mineral component replacing the matrix of areas within the bauxites. Fig. 4.12 E shows an alteration front within the bauxite where the red/orange matrix has been altered to the olive green colour of the chlorite. The chloritization seems to target the matrix and leaves the ooidal structures mostly un-affected, as shown in Fig. 4.12 F.

**Trace mineral and detrital mineral components**

Scanning Electron Microscope analysis identified several detrital components in the bauxites, and trace minerals that were not identified through X-ray diffraction.

Within the second horizon bauxites detrital zircon (Fig. 4.13 A), containing trace values of Hf and Sc (around 1.3% and 0.3% respectively); zoned Chromite (FeCr$_2$O$_4$), possibly in solid solution with magnesiochromite (MgCr$_2$O$_4$) as it contains around 6% Mg (Fig. 4.13 B); and Xenotime(YPO$_4$) (Fig. 4.13 A) were identified. There is also some evidence to suggest that detrital chromite may occur as grains with hercynite (FeAl$_2$O$_4$) as a substitution product of aluminium in place of chrome (Fig.
4.13 C.) Within third horizon samples, cubic galena was found as isolated crystals, and a form of Ce oxide, perhaps Cerianite (CeO) or hydroxyl-bastnasite (Ce(\text{CO}_3)\text{OH})], was found with up to 5 wt% Nd (Fig. 4.13 D.) While it is difficult to establish a percentage content value for these minerals, the rarity with which they occurred within the analysed thin sections suggests that they occur on the order of 0.01 to 0.1 wt% of the bauxites.

Fig. 4.12: A selection of images showing the textural controls on silicate minerals within the second and third horizon bauxites. A- Kaolinite forming as an epigenetic replacement product of the bauxite matrix. B- Epigenetic silification and kaolinite decomposing an iron rich bauxite clast. C- Chlorite (Chl) minerals forming as pisoidal-like cortices around well rounded bauxite clasts in the second horizon. D- More chlorite mineral formation as irregular layers around a bauxite pebble cluster within the second horizon. E- Chlorite forming as an epigenetic replacement of the bauxite matrix within third horizon bauxites. F- Chloritised bauxite where the matrix has been completely chloritised, however the pisoliths remain largely unaffected.
4.3.4 Bauxite Geochemistry

**Major element geochemistry**

The major element geochemistry presented here is based on data received from Elmin S.A. (full dataset is shown in Appendix 10). The data were obtained using X-Ray Fluorescence analysis of bulk bauxite samples from daily mine sampling using industry standard quality assurance and quality control procedures.

The major elements analysed were Al, Fe, Si, Ti, Ca, Na, K and S. Of these Na and S were either not detected in the samples, or occurred in quantities <0.1 wt% oxide and so were not considered major elements. The remaining elements are presented here as wt% oxide values.

The graphs in Fig. 4.14 show the differences in major geochemical compositions between the second and third horizons of Mount Iti and the third horizon of Mount Ghiona. Unfortunately the company data did not represent the second horizon of Mount Ghiona as mining of the second horizon in Ghiona was not carried out during the period of data acquisition.
All 5 graphs show distinct differences in element oxide contents between horizons and mountains. Iron oxide is overall highest in content within the third horizon of Ghiona, with the lowest within the third horizon of Iti. The iron data as a whole have a weak negative correlation with aluminium (as Al₂O₃, R² value of between 0.5 to 0.66), which is strongest within the data of the third horizon of Mount Ghiona (R² value of 0.66). Silicon oxide also shows a strong negative correlation (R² value of 0.59) with aluminium oxide. Both the second horizon and third horizon of Mount Iti show the highest contents of SiO₂, while Ghiona and some samples of Mount Iti show

Fig. 4.14: The major element geochemistry of the Parnassos-Ghiona bauxites based on data provided by Elmin S.A. The graphs show the relationships between Al₂O₃ and several other metal oxides within the second and third horizon bauxites. Sample numbers are: Third Horizon Iti – 58, Third Horizon Ghiona – 35, Second Horizon Iti – 62.
exceptionally low contents. Titanium oxides within the bauxites show a very strong positive correlation ($R^2$ value of 0.81) with aluminium oxides throughout the dataset, and have highest contents within the third horizon, which is linked to higher aluminium oxide contents in the third horizon. Potassium oxides are highest within the second horizon, with some significant contents within the third horizon of Mount Iti, and are depleted within the Ghiona bauxites. The mineral host for this potassium is suggested here to be clay minerals (based on earlier studies). Finally calcium (most probably in the form of CaCO$_3$, sourced from the surrounding limestones) is present in some of the analysed samples and is highest within the second horizon samples. It is clear that the second and third horizons both have a minor addition of calcium oxide.

Further analysis of this data set using statistical separation methods (i.e., discriminant analysis, principle component analysis etc.), may highlight more subtle differences within the data; however, here the major differences identified were deemed sufficient for this investigation.

Overall it is the third horizon of Mount Iti that shows the most variability in major element oxide contents. The second horizon of Mount Iti seems to be closest, geochemically to the third horizon of Mount Iti, either reflecting some geographical control on geochemistry, or that the third horizon of Mount Ghiona has undergone a separate process where potassium and silica have been greatly depleted.

**Geochemical variability at an ore body scale**

The results of major element analysis of several ore bodies using in-situ PXRF methods are presented here. The data were collected along vertical transects through the ore bodies to investigate the variability in geochemical composition through the ore bodies of different horizons. Data collection was restricted by outcrop size and accessibility; however all transects represent the variability from the contacts with the overlying hangingwall limestones down into the lower parts of the bauxite. As the bauxites of Ghiona show extensive epigenetic alteration, it was difficult to find an ore body that had an unaltered section, so the third horizon of Ghiona is not represented here, instead data from two separate ore bodies from Mount Iti are presented, and the geochemical variation of the Ghiona third horizon bauxites is discussed further in Chapter 5. The second horizon bauxites are represented in Fig. 4.15 as two transects one from Mount Iti and one from Mount Ghiona. The Mount Iti, second horizon, transect represents an ore body that has a gradational transition with the overlying hangingwall limestone, producing a layer of bauxite marl. As such, the top metre of this transect is very rich in CaO, where it has mixed with the bauxite.
Fig. 4.15: Two transects showing element variability along vertical transects through the second horizon bauxite ore bodies within Kokkinovrakos mine in Mount Iti (left) and Arkouda mine in Mount Ghiona (right.) Note the logarithmic scales. The x-axis on each graph represents the contact with the overlying hangingwall limestone. The contact with the footwall limestone could not be accessed.
It is assumed that the cause of the variable Al₂O₃, Fe₂O₃, TiO₂ and SiO₂ contents within the top metre of this bauxite is the addition of this calcium. While there does seem to be some correlation between Al₂O₃, Fe₂O₃, and TiO₂ within this transect, calculated values of correlation coefficient are inaccurate due to the massive variance in CaO content. Beneath the top metre of the bauxite the content become less variable, particularly for Al₂O₃ and TiO₂, and CaO contents decrease to <2wt%.

The Mount Ghiona, second horizon, transect represents an ore body that has been subjected to tectonic shearing along its hangingwall-bauxite contact. There was also some visible alteration along the top of the bauxite, penetrating about 70-80 cm into the ore body. This alteration is reflected in the elemental distribution shown in Fig. 4.15. All 5 detected elements show significant variation within the top metre of the bauxite. Notably CaO is depleted close to the thrusted contact, suggesting a leaching of CaO by circulating fluid along this fault. If bauxite marl was present here at one time, either tectonism or leaching has destroyed it. Deeper within the bauxite CaO was detected at content between 1 and 2 wt% which is similar to the bauxites of Mount Iti. Al₂O₃ and Fe₂O₃ show a strong negative correlation within this transect with a correlation coefficient of -0.79 (level for statistical significance of correlation with 12 degrees of freedom (n=14) at a 95% confidence level is 0.457 after Rollinson 1993.) SiO₂ also shows a significant negative correlation with Al₂O₃ with a coefficient value of -0.58. TiO₂ did not show any strong correlations with any of the detected elements.

Both transects show that within the second horizon bauxites the geochemical composition is most variable within the top metre of the ore bodies due to various processes interacting with the bauxite material. The bauxite beneath the top metres shows a more compositionally homogenous bauxite, with only minor variations in geochemical composition.

The third horizon bauxites are represented here as the transects in Fig. 4.16. The first transect represents a thin ore body that was analysed on a 10cm sampling interval. It has a small section of bleaching within the first 50cm from the hangingwall-bauxite contact, and red bauxite through the remainder of the transect. Major element contents show significant variability throughout the ore body. Within the upper 80cm, the depleted values of Fe₂O₃ and CaO are representative of the bleaching process, which will be investigated further in chapter 5. Due to this process the upper sections have become enriched in Al₂O₃ and SiO₂. Beneath this bleached section the contents of the detected components are still relatively variable. Al₂O₃ within the data show a strong negative correlation with Fe₂O₃ with a coefficient value of -0.90 (the level for statistical significance of
correlation for this case is around 0.47 after Rollinson 1993), which has produced the almost ‘mirrored’ \( \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) transect patterns.

The second transect is another third horizon ore body from Mount Iti, however the ore body has been uplifted and sharply inclined. The exposure and orientation of this ore body made it possible to analyse the full 15 metre thick ore body from hangingwall to footwall contacts on a 1 metre sampling distance. Therefore the transect is on a much greater scale than the other graphs (note the change in scale between the two transect graphs.) This ore body was not visibly affected by any alteration or obvious secondary element mobilization process.

This transect shows that at a larger scale the detected elements are still highly variable in content. \( \text{Al}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) still show a strong negative correlation coefficient value of \(-0.75\) (5% statistical significance value in this case is 0.426 after Rollinson 1993.) \( \text{TiO}_2 \) has a strong positive correlation coefficient of 0.82 with \( \text{Al}_2\text{O}_3 \) and a negative correlation coefficient of \(-0.52\) with \( \text{Fe}_2\text{O}_3 \).

\( \text{CaO} \) contents appear to be highly variable within the bauxite. The high values close to the top and bottom of the ore body can be attributed to its proximity to the hangingwall and footwall limestones. The clear peak at 6 metres and between 8 and 10 metres depth is hard to interpret. While the possibility of re-precipitated calcium due to circulating epigenetic fluids cannot be ruled out, no calcite fracture fills or deposits were identified during the field analysis. This peak may instead represent a depositional feature, where proximity to a marine environment and fluctuating sea level may have added calcium carbonate material to the bauxite. This peak would represent a ‘high-stand’ point in the sea level at the time. Carbonate layers have been seen within other deposits of the Parnassos-Ghiona zone, documented by Nia (1971.) The amount of calcium added is not enough to classify this layer as a bauxite marl or limestone, as found within the second horizon, but it is significant with respect to ore grade.

\( \text{SiO}_2 \) occurs in higher contents within the upper 6 metres of the bauxite (up to 27wt%). \( \text{SiO}_2 \) does not show any strong correlations with the other elements so it is likely that this is a real feature, rather than a product of constant sum effects. This zone is lower in \( \text{Fe}_2\text{O}_3 \), \( \text{TiO}_2 \) and \( \text{CaO} \), but still relatively rich in \( \text{Al}_2\text{O}_3 \), which suggests that the upper parts of this bauxite are more clay rich (kaolinite) with respect to the lower sections, due perhaps to a lesser extent of de-silicification and bauxitisation, or perhaps later silicification of the upper layers.

Overall the third horizon is much more variable with respect to the major element components compared to the second horizon. Elemental variability is highest within the upper sections of the bauxites, mostly within the first metre section beneath the hangingwall. This is either because of
depositional conditions and/or the susceptibility of this bauxite–hangingwall contact to shearing and fluid flow. The strict negative correlation of aluminium and iron described by Valeton et Al. (1987) has been identified within both horizons. The strong positive correlation between aluminium and titanium identified in Fig. 4.14 could only be identified at the larger scale of analysis and not within the smaller scale transects. The element correlations identified in these transect analyses have been summarised, for both horizons, in Table 4.1 below.
Fig. 4.16: Two transects showing element variability along vertical transects through the third horizon bauxite ore bodies within two ore bodies in Mount Iti. Note the logarithmic scales and the change in vertical scale units between graphs. The x axis on each graph represents the contact with the overlying hangingwall limestone. The contact with the footwall limestone could not be accessed for the left hand graph, but it is represented on the right hand graph by the 16 metre mark.
Trace element geochemistry

The contents of a selection of trace elements from 9 second horizon bauxites and 10 third horizon bauxites are shown in Fig.s 4.17 and 4.18 respectively (note the change of scale between graphs.) Samples of red bauxite were mainly chosen for this analysis as they represent the compositions closest to the original bauxite material, therefore any differences in trace element contents should reflect variability in the source materials. The full dataset can be found in Appendix 6.

The second horizon bauxites are represented by red bauxites from both Mount Iti and Mount Ghiona, and silicified bauxite from Mount Iti. A comparison of these in the graph in Fig. 4.17 shows that the samples of the red bauxites of Iti are richer in V, Cr, Cu and Zr than red bauxites of Mount Ghiona, and lower in Ni, Zn, Nb, and marginally lower in Ba. The other elements that were analysed either show little variation between Iti and Ghiona, or show a wide content distribution, that is not location dependant.

When compared to the red bauxites of Mount Iti, the silicified bauxites do not show any significant change in the trace element content, suggesting that the process of silicification did not cause any significant element mobilization within the bauxite, other than for silica.

A comparison of third horizon bauxites samples are shown in Fig. 4.18, and are represented by red bauxites from Mount Iti and Mount Ghiona , and sulphide-bearing bauxite from Mount Iti. The data show that the red bauxite samples from Mount Iti are lower in Cr, Ni and Sr than those of Mount Ghiona, and for many elements, tend to show the most variability in contents between samples (e.g. V, Ni, Zr, Mo.) The red samples from Mount Iti have higher As and Pb contents than Mount Ghiona.
The sulphide bauxite samples from Mount Iti have an increased Cr content compared to the red bauxite samples of Mount Iti. Notably, despite the identification of Ni-bearing sulphide minerals in chapter 4, section 4.4.3, there still appears to be a lower Ni content within the sulphide bauxites, suggesting that these minerals are still rare when compared to the abundant Fe-sulphide minerals.

The trace element data from Fig.s 4.17 and 4.18 were averaged, and the values for both the second and third horizon are plotted in the graph in Fig. 4.19 in order to compare trace element contents between horizons. (Once again note the change in scale between Fig. 4.19, and Fig.s 4.17 and 4.18.)

The averaged data shows that the samples from the second horizon are higher in Cu, Zn, Sr, Ba and Pb than third horizon bauxites, and lower in V, Cr, Ni, and As, and marginally lower in Zr. Sc, Nb, Th, U and Ta show very little difference between the horizons. The quite considerable differences between many of the elements within the red bauxites of the second and third horizon are likely to reflect variations in the source material composition, which support theories of differing source material between the horizons. The high contents of Cr, V and Ni within the third horizon bauxites suggest that the bauxite may have originated from more ultra-mafic sources, which are typically enriched in these elements. The lack of significant contents of these elements within the second horizon, and the higher contents of Zn and Cu, suggest a more mafic to intermediate source for these deposits.

**Rare-earth element geochemistry**

The rare-earth element (REE) contents within a selection of the Parnassos-Ghiona bauxites are presented as REE patterns in Fig. 4.20, with Y plotted as a pseudolanthanide with an atomic mass intermediate between Dy and Ho (following Bau 1995), along with statistical analyses of the patterns. The data have been separated by horizons, and each horizon contains several sub-groups based on location (Mount Iti and Mount Ghiona) and bauxite type. The second horizon bauxites mainly have a consistent pattern, with one exception within the Mount Ghiona samples. This sample contains up to 23000ppm of rare-earth elements, while a similar sample from the same ore body has a content of around 2200ppm, which is similar to the Iti samples. It is suggested that this REE enrichment of the samples is due to the presence of REE minerals within the bauxite, and should therefore be treated as an outlier in terms of total REE contents, however it has been included in the statistical analysis in Fig. 4.20.
Figure 4. 17: The variation in trace element contents within a selection of second horizon bauxites from the Parnassos-Ghiona zone.

Figure 4. 18: The variation in trace element contents within a selection of third horizon bauxites from the Parnassos-Ghiona zone.
The red bauxites of the second horizon of Mount Iti and Mount Ghiona have similar patterns. Silicification and other alteration of the bauxites has not affected the REE contents to any great degree, as the total REE contents, Ce, Eu and Y anomalies and the ratios of the LREE, MREE and HREE are very similar to the original red bauxites. All three sample sets have a positive Y anomaly, which is slightly less pronounced in Ghiona, and a constant negative Eu anomaly, which is also seen within the third horizon. The strong negative Ce anomaly within the red bauxites of Ghiona suggests a later enrichment of the other REEs.

Figure 4.19: Average values and variation in trace element contents within samples of different bauxites from both the second and third horizon bauxites of the Parnassos-Ghiona zone. The error bars represent one standard deviation of uncertainty around the mean.
Fig. 4.20: REE composition data from second and third horizon bauxites from the Pamassos-Ghiona zone, and comparative values of REE contents, anomalies and relative enrichments.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Location</th>
<th>Lithology</th>
<th>Total REE concentration</th>
<th>Average values</th>
<th>Average values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Min</td>
<td>Max</td>
<td>Average</td>
</tr>
<tr>
<td>Second</td>
<td>Iti</td>
<td>Red bauxite</td>
<td>1263</td>
<td>2004</td>
<td>1644</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silicified bauxite</td>
<td>1067</td>
<td>1852</td>
<td>1351</td>
</tr>
<tr>
<td></td>
<td>Ghiona</td>
<td>Red bauxite</td>
<td>2192</td>
<td>22911</td>
<td>12551</td>
</tr>
<tr>
<td>Third</td>
<td>Iti</td>
<td>Red bauxite</td>
<td>293</td>
<td>1140</td>
<td>636</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulphide bauxite</td>
<td>277</td>
<td>487</td>
<td>354</td>
</tr>
<tr>
<td></td>
<td>Ghiona</td>
<td>Red bauxite</td>
<td>650</td>
<td>2147</td>
<td>1183</td>
</tr>
</tbody>
</table>
Overall, the LREE are strongly enriched relative to the MREE and HREE within all of the second horizon bauxite samples.

The red bauxites of the third horizon are rather different in REE contents. The red bauxite samples from Mount Ghiona have an overall higher REE content than those of Mount Iti, in a similar way to the second horizon bauxites. Both red bauxite sets show positive Ce anomalies, however the anomaly is greater within the Mount Iti bauxites, suggesting mobility through oxidation processes. Y anomalies within the red Iti bauxites are strongly positive, whilst within the red Ghiona bauxites; this anomaly is either non-existent or is weakly negative, which suggests differences in the extent of REE transport by aqueous solutions (Bau 1995.). The sulphide bearing bauxites have the lowest contents of REE of all of the analysed bauxite samples, whilst also having a very strong positive Ce anomaly. This is suggestive of mobilisation of REE under oxidising conditions, promoting the relative stability and enrichment of Ce.

By comparing the second and third horizon bauxite samples, the second horizon bauxites appear enriched in LREE relative to HREE (especially within Mount Iti, in comparison to the third horizon). Throughout both horizons, the Y anomaly is always of a lower intensity within the Ghiona bauxites as opposed to those of Mount Iti. Notably the Eu anomaly is constant for all lithologies, perhaps suggesting that this is a feature of the source material that has not been altered through subsequent processes. REE analysis of bleached bauxites and associated lithologies is presented in chapter 5.

**Geochemistry of ooids**

While it is clear that the ooid structures are developed mainly by the alternation of iron rich and aluminium rich cortices, it is unknown where the two other main components, silica and titanium, are located within these structures. Fig. 4.21 shows the results from a Scanning Electron Microscope element map across several ooid cortices. The cortices are cut by a thin veinlet of iron sulphide minerals, and the core of the ooid has also been partially replaced by pyrite, however the iron within the cortices has remained as iron oxide.

As expected, the iron and aluminium phases show a distinct separation from each other with aluminium being the dominant phase. Titanium within the cortices occurs as distinctive anatase crystals that are concentrated within the iron rich zones. Silica, while more evenly distributed than titanium, still shows some preference to the iron rich areas. This suggests that during ooid formation the Si and Ti phases are preferentially located within the Fe rich cortices.
Fig. 4.21: The results of element mapping of a section of a pisolith within a third horizon bauxite from the Parnassos-Ghiona zone to show the content locations of Al, Fe, Ti, Si, S and O, along with a backscattered image of the mapping location (top left) and a reflected light photomicrograph of the analysed pisolith.
Comparing the geochemical variability within bauxites at different scales

If the ooid structures were formed in situ through geochemical self-organization, it is expected that the ooids would have a similar overall composition to the matrix or earthy bauxite material that they are situated within. The geochemistry of the individual ooid cortices is the product of the relative contributions of iron and aluminium in either (hydrous)oxide, or sulphide form, and subsequent geochemical changes linked to epigenetic processes. At the ore body scale, the grade of the bauxite is also governed primarily by the relative contributions of aluminium and iron, again in either (hydrous)oxide or sulphide form, which is subsequently altered by processes such as bleaching. It is possible that the same statistical variability in the content of these elements can be seen in the small scale ooid/pisoid structure, the larger scale ore body, and the regional scale bauxite ore body group. If this variability can be proved, it may be possible to predict the grade variability within an ore body, from in depth analysis of only a few samples.

Three samples of ooidal bauxite from Mount Ghiona ore bodies that have known geochemical contents were thin sectioned and carbon coated. Geochemical analysis was along transects across the ooids in order to analyse the variability with alternating layers, with care taken to ensure inclusion of all ooid cortices. Scanning Electron Microscopy was used to take point analyses representing each ooid cortex and the matrix, and raster analysis to analyse the entire ooid.

The data were accumulated for each ooid and plotted on graphs of Al. verses combined Fe and Si to illustrate the geochemical variability of aluminium and iron and silica. The line of best fit was calculated for each ooid transect and collectively these were plotted to illustrate variability between ooids and then compared to similar X-Y graphs showing the variability within an ore body.

Figs 4.22 and 4.23 show a selection of four of the ooids analysed for this investigation from a red, and a yellow bauxite, along with an X-Y plot of Al vs Fe+Si for each measurement along the ooid transect, a measurement of the composition of the whole ooid, and several measurements of the bauxite matrix surrounding the ooid for comparison. An average of the transect data is also given to compare with the measurement of the whole ooid. The other ooid analyses can be found in Appendix 4.

Within each example, the analyses for the ooid cortices, the whole ooid, and the matrix all lie along a linear trend line, which implies that there is a geochemical relationship between these textural components. This supports the theory that these ooids have grown out of the bauxitic material.
Fig. 4.22: The results from the analysis of two ooids from a yellow bauxite sample. The results are presented as plots of weight % element Al vs Fe+Si and an accompanying image of the analysed ooid. The results represent analyses of transects across the ooids, point measurements of the bauxite matrix, and a raster measurement of the whole ooid. The red arrow on the ooid image indicates the location of the analysis transect.
Fig. 4.23: The results from the analysis of two ooids from a red bauxite sample. The results are presented as plots of weight % element of Al vs Fe+Si and an accompanying image of the analysed ooid. The results represent analyses of transects across the ooids, point measurements of the bauxite matrix, and a raster measurement of the whole ooid. The red arrow on the ooid image indicates the location of the analysis transect.
The data for all of the analysed ooids have been plotted in Figs. 4.24, 4.25 and 4.26 for red, yellow and bleached white bauxite respectively. Within the red bauxite there is a near perfect linear trend between the compositions of the ooid layers, the matrix and the whole ooids. The graph also shows that while the ooid shells have a wide range of compositions, the ooids as a whole tend to be richer in aluminium as opposed to the matrix which is richer in iron and silica. Interestingly the matrix shows a similar geochemical variability to the ooids, again supporting a genetic link between the two, and suggesting there may be geochemical organisation on scales smaller than the ooids.

The data from the yellow bauxite (Fig. 4.26) show that the ooidal compositions have a very similar trendline to the red bauxite (to be expected as they are from the same ore body), however the matrix has been depleted in iron, which represents the partial mobility and removal caused by the onset of bleaching. Again, the whole ooids have a higher content of aluminium than the matrix, despite the partial iron loss.

The bleached bauxite analysis (Fig. 4.25) is depleted in iron (maximum measured content of 8.98 wt% Fe) compared to the red and yellow bauxites. While each component shows a relatively low Fe+Si wt% content, there is still variability along a linear trend.

![Geochemical variability within the ooids and matrix of a red bauxite](image_url)

*Fig.4.24: Geochemical variability within textural features of bauxites. The data represent analyses from 10 pisoliths from a red bauxite sample.*
Fig. 4.26: Geochemical variability within textural features of bauxites. The data represent analyses from 10 pisoliths from a yellow bauxite sample.

Fig. 4.25: Geochemical variability within textural features of bauxites. The data represent analyses from 10 pisoliths from a bleached white bauxite sample.
Fig. 4.27 shows the data from the graph in Fig. 4.24 with the addition of geochemical data from bulk bauxite analyses from across the ore bodies of Mount Iti and Ghiona. This has been plotted to show the relationship of geochemical variability at the small scale (oid) to the large scale (ore deposits.) There is a much greater variation within individual ooid layers than is seen at an ore deposit scale. However, the analyses of the entire ooids do show a similar distribution to the ore bodies.

4.3.5 Results summary

The data presented here are extensive and diverse. Data have shown that there are differences between the texture, mineralogies and geochemistries of the second and third horizon bauxites, and differences between Mount Ghiona and Mount Iti within the study area of this project. The main differences are summarised in Table 4.1 below. These differences are significant for both the ore genetic model and ore deposits science, and for mineral exploration and extraction. Within the next section, these data will be discussed along with previous research with an aim of explaining these results, and providing information towards modelling the overall bauxite formation.
<table>
<thead>
<tr>
<th>Bauxite Horizon</th>
<th>Age</th>
<th>Location</th>
<th>Bauxite texture</th>
<th>Mineralogy</th>
<th>Geochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Third Horizon</td>
<td>Mount I</td>
<td>Mainly pisolithic bauxite (up to 2 mm in size), with frequent broken and re-worked pisoliths; composite, rounded, bauxite clasts; fine grained (microcrystalline, equigranular) bauxite material.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cenomanian - Turonian</td>
<td>Mount Ghiona</td>
<td>Diasporic bauxite, some boehmite, rich in goethite, some hematite.</td>
<td>Rutile, Marcasite, Magnetite.</td>
<td>Highest average Fe₂O₃ (16.6 wt%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second Horizon</td>
<td>Mount I</td>
<td>Mainly fine grained (microcrystalline, equigranular) bauxite material; some pisolith structures and bauxite clasts.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Kimmeridgian - Triasian</td>
<td>Mount Ghiona</td>
<td>Diasporic bauxite, some boehmite, rich in hematite and kaolinite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount I</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 4.2: A summary of the main results from the investigations of the Parnassos-Ghiona bauxites in this chapter. |
4.4 Discussion

4.4.1 Pisolith formation

The textural evidence of the pisoliths within this chapter shows that the aluminium rich cortices are identical in texture to the surrounding matrix, as a micro-crystalline equigranular mass, with small fragments of detrital minerals throughout. The iron cortices appear irregular and the contacts between the cortices are irregular, in a way that suggests the iron has grown within the matrix, as opposed to being accumulated as a distinct layer.

The geochemical analysis of the ooids presented in section 4.3.4 showed that there is a consistent negative linear relationship between Al and Fe + Si contents of the ooids and surrounding matrix. The trendline of this correlation (e.g., the trendline for pisoliths and cortices in Fig. 4.24), represents the variation of compositions found within the pisolith cortices with respect to Al, Fe and Si contents. Where this trendline intercepts the X-axis represents a zone of pure Al, which in this case would be diaspore; the intercept on the Y-axis therefore represents a zone of no Al, most likely and iron or silica phase, e.g. hematite or quartz. The compositions between these two ‘end-members’ represent the various combinations that the pisolith cortices may have. If we assume the original bauxite material to be a homogenous gel, the development of this compositional trend may have formed from a process of geochemical self-organisation, where separation of Al and Fe during gel ageing created zones of predominantly Al and zone predominantly of Fe; the closer the separation process was to completion, the closer to an end member composition the zone became.

4.4.2 Bauxite pisolith formation as a Self-organizing process

The features in the pisoids suggest that the cortices have formed from mobilization of iron and precipitation in spherical layers within a hydrous aluminium oxide rich matrix. The similarity between the matrix and diaspore layers suggests that the aluminium component remained unchanged, and it is the iron was segregated and precipitated in spherical layers, in similar overall processes to reduction spot and liesegang band formation (Ortoleva 1987.)

Liberation of these pisoliths from the bauxite could be achieved through weathering and erosion, followed by transport into an environment where the pisolith formation process could continue. The transported material would be a mixture of ooidal structures with a matrix of more aluminium and iron as an amorphous gel. On deposition, cortex formation would begin, with the ooidal structures, or indeed, fragments of ooidal structures acting as nuclei for continued re-organization. The thickness of the relative ooid cortices would be dependent on the proportions
of those elements within the formational gel, the ease at which the Fe ions could accrete, and the amount of time allowed for self-sorting growth before the next stage of re-working. The remaining aluminium rich gel would be allowed to age and crystallise into the micro-crystalline mass found within the bauxite matrix, clasts and pisoliths, without affecting the pisolith structures to any great degree. This process is shown in Fig. 4.28.

4.4.3 Model for bauxite texture formation

The textural evidence presented in this chapter gives a rather complex picture of the formation of the various components of the bauxites indicating several cycles of deposition, consolidation and dissolution with further “reworking” of the bauxite material. This is followed by diagenetic, epigenetic and tectonic processes acting upon the bauxite since formation, (evidence of which will be discussed further in Chapter 5, including sulphur isotope analysis). Original bauxite textures are consequently difficult to distinguish.

This investigation treats the second and third horizon bauxites as texturally very similar bauxites, being composed of three main textural components; microcrystalline earthy bauxites, well developed and composite ooids and pisoliths, and clastic bauxite material( which either has a fine grained earthy bauxite texture, or a composite ooidal-pisoidal texture.) These three components are accompanied by detrital material, which is presumably from the source lithology, or lithologies included during transport.

Figure 4.28: A model for the geochemical self-organisational formation of pisolith structures within the Parnassos-Ghiona bauxites.
The overall textural differences (at an ore body scale) between the second and third horizon ore bodies reflect the relative contribution of these three bauxite textural features. The second horizon is rich in the finer grained earthy bauxite, with small amounts of pisoidal and clastic bauxite, giving it a finer, clay-like appearance over all, with a well-developed vertical prismatic fracture in both Mount Iti and Mount Ghiona. The third horizon bauxite is richer in pisolithic and clastic bauxites, which are either surrounded by or suspended within fine grained earthy bauxite. This gives it a coarser appearance with a more random fracture.

Here is proposed a model that explains how these three components, and thus the overall textures of the bauxites, can be formed through a cyclic process of bauxite deposition, self-organization and re-working.

The initial material was a mixture of poorly crystalline gel or pulp of near bauxite composition along with detrital material from lateritic bauxites and other lithologies. This is supported by the randomly orientated, micro-crystalline, equigranular bauxite matrix in both the second and third horizon, which is typical of formation from gel crystallisation (Bardossy, 1982.) If this gel were to age and crystallise without further re-working, fine grained earthy bauxite would form, similar to much of the second horizon. The gel itself contains significant amounts of small detrital minerals, which can now be seen distributed throughout the bauxite matrix, pisoliths and clasts. The gel was also unlikely to be homogenous, more likely being of variable composition, particularly in its Al and Fe content.

This pulp was deposited on river beds, meanders and other sites of deposition within fluvial terrains during a period of low energy conditions. This is where mobilization of particular elements in a geochemical self-organisation process separated the gel into iron rich and iron poor (aluminium rich) zones, which on the small scale created sphere-like structures around an initial nucleus, creating the pisolith structures. These initial pisoliths would be soft, as the aluminium components were probably still within a gel-like state. This is indicated by examples of plastic deformation seen within the pisoliths. There must have been some degree of consolidation of the material at this stage in order for the pisoliths to maintain their structure. Additionally, the thickness of the cortices would be dependent on the rate of accumulation of the individual cortices, and the ratio of Al/Fe (lower Fe forming thinner, iron rich cortices.)

An increase in energy conditions after this stage would have broken up this partially consolidated bauxite, liberating and fragmenting the ooids, and breaking the bauxite, with the harder areas forming clastic bauxite and the softer areas being broken down into the bauxite pulp.
Transportation would have rounded off the fragments and bauxite clasts, abraded softer ooid cortices, and broken down much of the bauxite texture into the finer, poorly sorted gel. On deposition of this bauxitic mixture in lower energy conditions, geochemical self-organisation could resume, using the fragmented and abraded ooids as nuclei for concretion. The alternating higher and lower energy conditions would resume and repeat during transport of the bauxitic material from its source area until its final deposition on the karstified limestone. On final deposition onto the karstic surface, the bauxite would be a mass of rounded, composite bauxite clasts, composite and broken ooids, which is the texture of the third horizon bauxites.

This model suggests that continuous re-working of the bauxite would ultimately lead to a conglomeritic mass of bauxite clasts with little to no earthy or free ooidal bauxite remaining. However, as this is not the case, either the process has not had sufficient time enough to continue until this conglomeritic bauxite is achieved, or that the liberated bauxite material must be easily broken down into the earlier components of ooids, earthy bauxite and even the poor crystalline gel material during transport. The surviving bauxitic clasts are typically iron rich for this reason as they are the harder and more resistant fragments that can survive this re-working. It is also thought that each increase in energy would have been linked to periods of faster and more turbulence flow of the transporting river(s), and most likely brought with it fresh, microcrystalline bauxitic material which became incorporated into the system. This model is summarised in Fig. 4.29.

### 4.4.4 Bauxite mineralogy and implications for ore formation

The bauxites of both horizons show variable mineralogies, with several mineral phases identified for aluminium, iron, titanium and silica. The necessary formation conditions for the mineral phases are discussed here with emphasis on the implications of their presence on bauxite formation. The Fe-phase mineralogy is discussed first, and then Al-phases.

**Iron Minerals**

A diverse array of both ferrous and ferric iron minerals were identified through XRD analysis. Within the second horizon, hematite is the only purely iron phase, whilst in the third horizon, pyrite, goethite ($\alpha$-FeO(OH)), lepidocrocite ($\gamma$-FeO(OH)) and magnetite were also identified. The formation of these minerals can occur in surface environments under specific Eh-pH conditions, shown within the Eh-pH plot in Fig. 4.30.

The second horizon bauxites contain hematite where the iron is in its trivalent or ferric state of Fe$^{3+}$ that forms within an oxygen rich environment. This gives the bauxite its distinctive red colour.
and represents formation within an oxidising environment. The same can be said of the red, hematite rich bauxite of the third horizon.

Pyrite was found, often quite abundantly within many of the bauxites of Mount Iti. Pyrite is a ferrous iron mineral meaning that it is in the divalent state (Fe$^{2+}$). Following Fig. 4.30, pyrite forms within a reducing environment, and so where it forms either instead of, or replacing hematite, it indicates the prevalence of reducing conditions within the bauxite. The size of the sulphide fields within the diagram is dependent on
Figure 4.29: A model for the formation of the textural components of the second and third horizon bauxites of the Parnassos-Ghiona zone
the amount of sulphur within the system, and if sulphur is low and CO$_2$ high then siderite would be the stable mineral at those conditions (Klein & Hurlbut 1993.) As siderite was not found and pyrite was, it can be assumed that the ore forming system was rich in sulphur during pyrite formation.

Goethite is present within the third horizon and is found mainly as a replacement product following pyrite (see Fig.4.10 of this chapter and chapter 4.) Goethite is a ferric iron mineral and represents oxidising conditions. After the formation of reducing conditions within the bauxites, the overall Eh conditions must have reverted back to more of an oxidising environment. The
formation of goethite instead of hematite may be reflective of high water activity conditions (see Fig. 4.31.)

Magnetite was found as magnetite clasts and as magnetite veinlets. The clasts of magnetite may be detrital in origin, as is common in many magnetite rich placer deposits, and wouldn’t necessarily reflect the deposition conditions. However the magnetite veinlets within the bauxites do prove that the low Eh, high pH conditions were possible during epigenetic processes; probably linked to circulating reducing, low sulphur fluids. It must be stressed here that magnetite veinlets are not extensive within the bauxites, and were found generally as isolated single veinlets. Pyrite and goethite veins are far more common.

Within the third horizon of both Mount Iti and Mount Ghiona, samples were identified that lacked any iron mineral phase. These are associated with epigenetic leaching of the iron, referred to as bleaching. This will be investigated in chapter 6.
Aluminium minerals

The mineralogical investigations of this study and previous studies (Valeton et al., 1987; Laskou & Economou-Eliopoulos, 2007) have identified that the second horizon bauxites are predominantly boehmitic, whilst the third horizon bauxites are predominantly diasporic, with some boehmite. The boehmitic bauxites have been found in association with hematite only, however the diasporic have been found with hematite, pyrite, goethite and magnetite, which indicates fluctuations in Eh-pH conditions as explained above.

The formation of boehmite and diaspor within bauxites has been a much debated topic, which has been well summarised in Bardossy 1982. One of the earliest theories was that that gibbsite, boehmite and diaspor formed as a sequence during increasing levels of dehydration caused by overburden pressure and deformation stresses to convert gibbsite to boehmite, and then stronger structural stresses and weak metamorphism to produce diaspor, followed by corundum at higher metamorphic grades. This theory (or amalgamation of theories) does not accurately explain the mineralogic distribution within the Parnassos-Ghiona zone as the boehmitic bauxites occur at a deeper setting to the diasporic bauxites, which would put the second horizon under greater pressure, and therefore greater dehydration.

Nia (1971) suggested that diaspor formed from an initial boehmite rich material in zones of good drainage where water percolation was intense, which explains how boehmite and diaspor can occur together within a single bauxite ore body. Conditions of this type would promote strongly oxidising environments which would not allow for the formation of the diverse iron mineral assemblages described in this chapter. If this is the main control on hydrous aluminium oxide development, it must be assumed that diaspor formation was completed before the development of the reducing conditions necessary for the formation of ferrous iron minerals.

Figure 4.32: A simple representation of the theory for the formation of different hydrous aluminium oxide minerals with varying Eh conditions. The assemblages of the second and third horizons are indicated also. (Adapted from Bardossy 1982.)
Several investigations suggest that bauxite mineralogy is controlled by the Eh-pH (Valeton, 1965; Coombes, 1969; Bardossy, 1967) with gibbsite forming at high Eh conditions, boehmite at a lower, but still positive Eh and diaspore forming under negative Eh conditions (Bardossy, 1982.) This is summarised in Fig. 4.32 below. This is in accordance with the formation conditions necessary for the iron minerals also found within the Parnassos-Ghiona bauxite deposits.

**Silicate minerals within the bauxites**

The second horizon was found to be distinctly rich in kaolinite often with visible alteration of the bauxites to a cream/pink, kaolinite rich lithology. Thin section evidence suggests that this was an epigenetic process, and a relationship with faulting, identified during field studies, supports this. The process of silicification is likely to be a simple reaction of the hydrous aluminium oxide with silica bearing fluid descending through the bauxite to create secondary kaolinite (Bardossy 1982.) The lack of any significant changes in trace or REE contents between silicified and non-silicified bauxites suggests that this was not a particularly ‘aggressive’ fluid with respect to Eh and pH, and may simply be from silica rich drainage water from over burden.

The chlorite group minerals identified were either chamosite or clinochlore, and show differences in occurrence between the horizons. Within the second horizon, chlorite minerals (chamosite mainly) occurs as pisolith-like cortices on pebbles and other detrital components, indicating a syn-depositional or syngenetic formation, or perhaps a direct replacement of earlier iron rich components. Chlorite group minerals contain iron in its divalent form (Fe$^{2+}$) which indicates that at least part of the second horizon was deposited within a reducing environment, with accessible iron and silica. Chamosite can also form at the top of the second horizon bauxite ore bodies, altering the top of the bauxites and infilling fractures. This is again indicative of reducing conditions at or shortly after deposition. There must have been a restriction at this time on pyrite formation, as there is clearly reduced iron within the system. This will be discussed in chapter 5. It must be stressed that chlorite minerals are not extensive within the second horizon bauxite, but occur sporadically in the modes described.

Within the third horizon, the chlorite minerals (again mainly chamosite, with possible clinochlore) are of an epigenetic origin. This indicates several processes. Firstly that iron was mobilized, and therefore in the divalent state. Silica was also mobile. Secondly, that formation of the chlorite must have been under reducing conditions within the bauxite, probably via a reducing fluid. This has several implications for epigenetic processes affecting the bauxite and will be discussed further in chapter 5.
It is likely then that the second horizon overall represents a bauxite formed within dominantly oxidising conditions, with very little fluctuation, producing a boehmite-hematite rich bauxite. The third horizon has formed under more variable Eh and pH conditions, that have given rise to ferric and ferrous minerals, and if Fig. 4.32 is accurate, diaspore formation.

4.4.5 Bauxite mineralogy and implications on exploration

The bauxite mineralogy has several implications on exploration practice:

1. Of the aluminium oxide minerals, boehmite requires less energy to process for alumina and aluminium extraction than does diaspore. In this respect the second horizon would seem a better option for alumina and aluminium production raw material. For non-metal uses of bauxite, the mineralogy does not affect the energy requirement.

2. The high kaolinite contents within the second horizon bauxite are detrimental to the ore grade, however, the majority of re-silicification was seen within Mount Iti bauxites, making Ghiona a more promising source of higher quality bauxite.

3. Mount Iti third horizon bauxites can contain sulphide minerals which are absent from Mount Ghiona. Due to problems caused by sulphide minerals during bauxite processing, they may need to be avoided during mining.

4. Bleached bauxite or bauxite with no iron mineral phases present is only found within the third horizon.

4.4.6 Bauxite geochemistry and implications for ore formation

Major element contents

This investigation looked at the major element content variability between the bauxite ore bodies of Mount Iti and Ghiona, the variability through individual ore bodies and the variability at a textural scale.

The highest average Al$_2$O$_3$ contents are found within the third horizon bauxites of Mount Ghiona at 57 wt%, compared with the third and second horizons of Mount Iti at 53 wt% and 50 wt% respectively. However the highest contents of Al$_2$O$_3$ detected were from samples from the third horizon of Mount Iti at 79.4 wt%, with 64 wt% in Mount Ghiona and 56.2 wt% in the second horizon of Mount Iti. The Mount Ghiona third horizon bauxites are also the lowest in SiO$_2$ and K$_2$O, however they are highest in iron.
Within individual ore bodies, there is notable variability vertically through the ore body. Within the second horizon, the variability is highest within the top of the bauxite ore body. There is a notable enrichment in Ca from mixing with the overlying limestone during marine transgression. Where the hangingwall-bauxite contact has been tectonically sheared in the upper sections of the bauxite such as along the northern edge of Mount Ghiona the bauxite is depleted in Ca, as well as Si and Fe, likely due to circulating fluids along the fault plane. Beneath this zone, the bauxite is relatively uniform in Al and Fe contents.

The major element contents within the third horizon bauxites are far more variable vertically through the ore bodies. There is a strong negative correlation between Al and Fe throughout the bauxite (also seen within the second horizon), however it is difficult to identify any significant zones of Al enrichment, except within the zones of epigenetic bleaching. Si is higher within the upper areas of the bauxite. Ca is rather variable throughout the ore bodies and may be attributed to intermittent marine transgression and addition of large amounts of Ca to the bauxite.

**Trace element and REE contents**

The trace element analysis of the second and third horizon red bauxites showed distinct differences between the second and third horizon bauxites. In particular the Ni, V, As and Cr contents are much higher within the third horizon than within the second horizon, while Cu and Zn are higher within the second horizon bauxites. This has led several researchers to suggest different source lithologies, or at least partially different lithologies for the bauxite horizons. REE again show distinct differences between the second and third horizons. The second horizon is overall richer in REE compared to the third horizon.

Silicification of the second horizon bauxites does not cause any major change in trace element contents except for possible depletion of Ni, Cr and Pb. Silicified bauxites also have the lowest REE contents of the second horizon.

Sulphide-bearing bauxites of the third horizon tend to be lower in Ni, V and Sr than third horizon red bauxites, which may be due to the mobility of these elements during sulphide formation. Sulphide-bearing bauxites tend to have the lowest REE contents of all bauxites studied, and showing large positive anomalies for Ce and Y, which may derive from continuous cycles of fluctuating Eh conditions during the formation of the sulphide minerals, as suggested by Laskou & Economou-Eliopoulos (2007, 2012.) The Ce would have been stable during oxidising conditions, while other REE would have been continuously leached by mobilising fluids.
4.4.7  Bauxite geochemistry and its implications for exploration

- Overall the third horizon is richer in $\text{Al}_2\text{O}_3$ than the second horizon, and will therefore be more economic.
- Sulphur, which is a detrimental product to the ore quality, has only been found in significant contents in Mount Iti. More sulphur-bearing bauxite ore bodies are likely to be encountered further beneath the flysch due to its protective cover, preventing the oxidation of the pyrites.
- Silicification of the second horizon bauxites in Mount Iti and Mount Ghiona has enriched the bauxite in silica, giving it a distinctive cream white appearance which should be easy to separate from stock piles.
- Calcium contents are high at the top of the second horizon bauxites, (unless leaching by fluids along sheared contacts has occurred), and calcium high zones have been identified within the third horizon bauxites. It is difficult to develop a specific rule for the distribution of calcium within the bauxite and so geochemical analysis will have to be used to determine its content within stockpiles.

4.4.8  The effects of the scale of observations on bauxite exploration

Nia (1971) showed that the third horizon Parnassos-Ghiona bauxites have a high geochemical and mineralogical variability within single ore bodies. The current investigation added to the idea of geochemical variability and heterogeneity within the ore bodies, showing the comparison between the second horizon and third horizon major element transects in Figs. 4.15 and 4.16. The major element contents within the third horizon appear far more variable than within the second horizon. It is suggested here that the cause of this observed difference is due to the processes of geochemical self-organisation that have formed the coarse ooid and pisoid structures predominantly within the third horizon. At the scale of geochemical observation, (which for the portable XRF analyser was around $1\text{cm}^2$) the coarser bauxite will vary geochemically due to element zonation, which is not as prominent within the finer grained, and therefore more homogenous at the scale of observation, second horizon bauxites. If portable XRF analysers are to be used for further study of these and other bauxites, these effects must be taken into account.
4.5 Conclusions

This chapter focused on the texture, mineralogy and geochemistry of the second and third horizon bauxites of Mount Iti and Mount Ghiona within the Parnassos-Ghiona zone, central Greece. From the data presented here, the following conclusions about these bauxites can be drawn:

1. The textures of the Parnassos-Ghiona bauxites are the products of a complex series of deposition, self-organisation and re-working of an original fine grained to gel-like pulp of near bauxite composition. This has produced earthy, pisolithic and clastic bauxite textures seen in both the second and third horizons.

2. The pisolithic textures of the bauxites are suggested here to form from geochemical self-organisation of iron into distinct spherical layers, within an aluminium rich gel-like matrix around nuclei of bauxite material (peds) or detrital minerals or clasts.

3. The third horizon bauxites are diasporic rich, whilst the second horizon bauxites are boehmite rich. It is suggested here that this has been controlled by the Eh conditions of the deposition and diagenetic environments, following suggestions by Valeton (1965), Coombes (1969), Bardossy (1967), supported by evidence in this chapter linking diasporic bauxite to the formation of sulphide minerals in swampy conditions.

4. The third horizon bauxites of Mount Iti are the only ore bodies within the study area to contain iron sulphide minerals at present, whereas all other bauxites contain iron oxides.

5. The major element contents of the bauxites show differences between the second and third horizons and between Mount Iti and Ghiona. The differences are suggested to be the products of bauxite clay content, and post deposition alteration.

6. The trace element contents again show marked differences between horizons, particularly the higher contents of Cu and Zn in the second horizon, and the higher contents of Ni and Cr in the third horizon, which is interpreted as representing differences in parent lithologies of the bauxites.

References


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Chapter 5: The formation of sulphide minerals within the Parnassos-Ghiona bauxites and subsequent epigenetic alteration associated with their destruction

5.1 Introduction
Sulphide-bearing bauxites are common throughout the Mediterranean bauxite belt e.g., Montenegro (Dragovic, 1989), Croatia (Sinkovec, 1994), Greece (Laskou, 2005; Laskou & Economou-Eliopoulou 2007, 2012), and are of interest as they indicate variations in redox conditions during the ore forming process, and can affect ore grade, ore quality and necessary processing methods for bauxite and aluminium producers. Similarly, epigenetic alteration of the bauxites can affect ore grade and quality, often having beneficial supergene enrichment-style effects.

This chapter details the location, texture, mineralogy, geochemistry and formation history of the sulphide-bearing bauxite found within the bauxites of the Duo Vouna region, Mount Iti. It will also investigate the processes of sulphide destruction and its effects on the bauxite ore, particularly the interaction between sulphide oxidation and bauxite alteration, and try to explain why the Mount Ghiona bauxites show extensive alteration (specifically bleaching), whilst apparently being devoid of sulphide minerals (see mineralogical investigations in chapter 4.).

Within this chapter, bauxites containing sulphide minerals will be referred to as sulphide bauxite, those without will be referred to as oxide bauxite.

5.2 Background

5.2.1 Sulphide minerals associated with bauxite
Sulphide minerals are not uncommon in karst-associated bauxite deposits, being present in many deposit groups worldwide. They are, however, something of an anomaly, being indicative of reducing conditions in the genetic history of an ore that is invariably associated with formation in oxidising weathering environments.

The dominant sulphide mineral found within karst associated bauxites is pyrite (FeS₂). This is typically of early diagenetic origin, however syngenetic types can occur. Epigenetic pyrite occurs less frequently. The pyrite minerals can be euhedral, anhedral or spherical (framboids), the last two of which are less common. Euhedral pyrite grains are usually less than 0.5mm in size, with
increasing grain size from the top of the deposit downwards in pyrite-bearing bauxite, and can often act as trace-element scavengers (Bardossy 1982, and references there-in).

Other sulphide minerals that can occur include in karst associated bauxites are bravoite ((Fe,Ni)S₂), marcasite (FeS₂), hydrotroilite (FeS·nH₂O), galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄) and niccolite (NiAs) (Bardossy 1982).

5.2.2. Economics of sulphide bearing bauxite

Historically, some sulphide bearing bauxite has been mined for its alumina and sulphuric acid potential (e.g. the Minjera bauxite, Croatia) (Sinkovec et al., 1994). At present, sulphur in bauxites is considered a harmful impurity, and almost always incurs penalty costs from ore processors if quantities are too high. Where bauxite is used for alumina production via the Bayer process, sulphur can take several forms including S²⁻ in the dissolving liquor, and can erode production facilities, interrupt production operations and requires an increased level of alkali consumption (Zhonglin et al., 2009.)

5.2.3. The Parnassos-Ghiona Sulphide Bauxites

Sulphide bearing bauxites within the Parnassos-Ghiona zone have only been reported in the third horizon ore bodies. Laskou (2005) describes their location as being ‘at the transition zone between red and grey type bauxites, characterised by abundant pyrite.’ This is true in several cases; however, sulphide-bearing bauxite can also occur in varying (> metre) thickness at the top of a bauxite ore, with red hematite bauxite at its base, or comprising the entire thickness of an individual ore body, as shown in chapter 2, Fig. 2.7, cross sections 5 and 6.

Textures

Sulphide-bearing bauxites within the Parnassos-Ghiona zone are mainly of the diasporic type (Laskou & Economou-Eliopoulos, 2007, see chapter 4.) The sulphide minerals can occur in several forms including framboidal aggregates, characterised as bacteriopyrites, and euhedral sulphides, in the forms of minute cubic and pyritohedron-shaped crystals which are found dispersed in the bauxite matrix. Anhedral sulphides can be found infilling cracks and pores, and can be replaced pseudomorphically by hematite or goethite. There are also occurrences of small kaolinite nests which contain numerous pyrite crystals, possibly forming during a secondary re-silicification process (Laskou 2005). Sulphide veins which cross-cut sulphide-bearing ores are also present (Laskou & Economou-Eliopoulos, 2007.) This vein mineralisation appears to be structurally controlled and along with sulphides, contains goethite, diaspor and is surrounded by kaolinite (Laskou & Economou-Eliopoulos, 2012.)
Mineralogy

The major sulphide mineral present is pyrite (Valeton et al., 1987; Laskou & Economou Eliopoulos 2007). Pentlandite and pyrrhotite, as well as other iron monosulphides are occasionally dispersed throughout the matrix of the red-grey bauxites, as fragmented and disaggregated crystals.

Geochemistry

Laskou’s (2005) study of a selection of representative sulphide and oxide bauxites from the Parnassos-Ghiona zone found that the sulphide-bearing bauxites had higher concentrations of As, Ba, Co, Cu, U, V and SiO$_2$ than hematite-bearing bauxites. The total REE content was found to be lower in the sulphide bauxite, 76ppm mean, compared to 260ppm mean in the hematite bauxite and La/Lu ratios are lower in the sulphide bauxite compared to the hematite bauxite (11.5 and 19.0 respectively.) La/Y ratios are lower in pyrite bauxite compared to typical bauxite.

Laskou (2005) determined that the pyrite crystals themselves are Co and Ni free, but have a range of Se contents up to 0.51%.

5.2.4. Formation of iron sulphides in sediments

Bauxite is a sedimentary ore, and so for the purpose of modelling iron sulphide formation, may be treated as a sediment. Sedimentary pyrite formation was modelled by Robert Berner (1970) using experimental and in-situ analysis of iron sulphide formation. His model is summarised here:

5.1 First organic matter and re-actable iron contained within or on fine grained detrital materials is deposited into relatively quiet water.

5.2 On burial, the organic matter fuels aerobic metabolism by organisms which removes dissolved oxygen (via respiration). With sufficient organic carbon supply the dissolved oxygen concentration in the sediment interstitial water can fall to such a low level that respiration must proceed using secondary oxidants (anaerobic respiration). Oxidants are consumed (or reduced) in the order nitrate ~ manganese oxides > iron oxides > sulphate. Therefore, in fine sediments with high rates of organic carbon burial anaerobic bacterial sulphate reduction of sea water sulphate occurs within sediments, forming H$_2$S. The concentration of available organic matter controls the rate of sulphate reduction and the concentration of H$_2$S that can be maintained (after loss by diffusion out of the sediments.)

5.3 The H$_2$S reacts with iron to form black, non-crystalline FeS, as greigite, mackinawite or pyrrhotite minerals (simplified equation shown below.) The amount of FeS that can form
is limited by the rate of production and concentration of the $\text{H}_2\text{S}$. Berner’s investigation
found that in most cases, iron was not a control on FeS production, presumably due to its
 crustal abundance.

$$\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+$$

(1)

5.4 Oxidation of some of the $\text{H}_2\text{S}$ creates **elemental sulphur** (plus $\text{H}_2\text{O}$.) Sulphur can also be
formed through the reaction of FeS and $\text{H}_2\text{S}$ with dissolved oxygen stirred into sediments
by burrowing organisms or storm action. The elemental sulphur slowly reacts with FeS in
the sediment to form **pyrite framboids** shown in reaction 2.

$$\text{FeS} + \text{S}^0 \rightarrow \text{FeS}_2$$

(2)

So for pyrite to form in sediments there needs to be a supply of re-actable iron, organic matter,
reducible sulphate to create $\text{H}_2\text{S}$, and elemental sulphur. Experimental work and investigations
have determined that it is organic matter which is the crucial component to eventual mono-
sulphide and subsequent pyrite production (Berner 1940.)

### 5.2.5. Major controls on iron sulphide formation in bauxites

With the exception of bauxites that have undergone some later epigenetic iron removal, iron is
readily available for sulphide formation and therefore should not play a major role in controlling
the amount of iron sulphides produced. The source of sulphate for sulphide generation in
sedimentary rocks is most commonly seawater, as fresh water has very low concentrations. If
seawater is the source, then as long as the bauxite is either in contact with seawater or brackish
water, or that occasional contact is achieved, then the amount of sulphate would not control the
sulphide development to any great extent. It is possible that detrital sulphates, magmatic sulphur
and other sources could also contribute to the sulphate source. Given the above, rate of organic
matter supply and burial will be the major control on sulphide development within bauxites.

Sinkovec et al., (1994) also concluded that in the Croatian bauxites of Minjera, Istria, the content
of organic matter was the main limiting factor of pyritization, as many of the deposits there are
not fully pyritised and still contain iron oxides.
**Organic matter the Parnassos-Ghiona bauxites**

Within the Iti and Ghiona mining districts, the bauxite ore bodies are often locally overlain by a thin, unconformable coal layer. Kalaitzidis et al. (2010) identified the presence of this layer above the B3 horizon of the Pera-Lakkos underground bauxite mine, currently worked by Delphi-Distomo Mining Co. They determined that the coal attains a maximum thickness of 50cm and is present in association with altered (bleached) bauxite (although bleached bauxite also occurs in deposits that are not associated with coal and vice-versa), but also occurs as layers directly between the hangingwall and footwall limestones in zones adjacent to bauxites. They also note the presence of a thin yellow-coloured layer of Fe-oxides/hydroxides and clay minerals between the coal and bleached bauxite. Inter-layers of coal with shale can occur locally within the hanging wall.

The major maceral (coal mineral) within the coal layer is vitrinite, with minor inertodetrinite and semifusinite, all of which were derived from herbaceous plants and algal material (Kalaitzidis et al., 2010). Non-coal minerals present include inter-layered illite and smectite, gypsum, iron sulphides (pyrite, pentlandite and pyrrhotite), goethite, carbonates and minor Al-hydroxides.

The sulphide bauxites occur in association with organic matter in variable forms and concentrations, with total organic carbon as high as 2.78 wt%, compared with around 0.06% for oxide bauxite (Laskou & Economou-Eliopoulos, 2007). Quite commonly, the organic matter is often preserved as coal deposits at the top of some third horizon bauxites and in some areas as coal and organic rich shales intercalated with the lower-most hangingwall limestones of the third horizon. Valeton et al. (1987) suggested that this represents ‘stagnating and reducing conditions in inundated coastal plains during tectonic downwarping.’ To date, no organic matter has been identified in association with the second horizon bauxites.

Kalaitzidis et al. (2010) studied the coal layer in detail to reconstruct the coal forming environment. Through several lines of evidence they determined that the peat, that formed the precursor to the coal, accumulated in mildly brackish mires under pure rheotrophic conditions, from fragmented organic material sourced from herbaceous plants and algae. Restricted circulation in this groundwater-saturated environment led to stagnant, anaerobic conditions during peat accumulation indicated by disseminated pyrite crystals. The presence of halite and sylvite along with the pyrite in the coals also indicates a marine influence.

The model for the overall environment is that these mires were part of a barrier bar system in a flood-tidal delta plain, where back-barrier lagoons of brackish waters were established above the
bauxite filled karstic depressions (Kalaitzidis et al., 2010.) At the end of peat accumulation there was ‘exposure and significant oxidation’ of the top of the coal layers, either syngenetically by wave action of the transgressing sea, or epigenetically by percolating drainage waters after more recent uplift.

From a regional perspective, Kalaitzidis et al. (2010) see the geotectonic setting of the coal as a ‘local variation on an emerged carbonate platform in a passive margin’, and not an extensive basin system. If this is correct, then the sulphide bauxites are also local variations within this environment.

5.2.6. Models for sulphide formation in the Parnassos-Ghiona Bauxites

Valeton et al. (1987) briefly mention the sulphide bauxites within the third horizon bauxite, describing the pyrite minerals as appearing as ‘a late-diagenetic precipitate in different levels within the sections in relation to the local syngenetic groundwater conditions.’ They interpret it as one of several mobilisation phases of iron during the bauxite formation, caused by reducing conditions and stagnating ground water, resulting in the growth of pyrite. Pyrite oxidation can also cause precipitation of secondary sulphates (Valeton et al., 1987) leading to multi-coloured bauxite ores.

Laskou (2005) also suggested a late-diagenetic process under reducing conditions for pyrite formation, noting that the transformation of iron sulphides to iron oxides is a repetitive process, indicating the fluctuation of Eh-pH conditions during this time.

Laskou & Economou-Eliopoulos (2007) identified at least two stages of bauxite ore transformation: the reduction of ferric iron to ferrous iron resulting in the formation of pyrite, followed by subsequent oxidation, replacing the pyrite crystals with goethite. They also state that the relative timing of diagenesis and sulphide bauxite formation remains unclear, but they do link the pyrite bearing bauxites to a fault controlled system, and an epigenetic stage of formation. They suggest a weakly oxidising condition for pyrite formation, based on the geochemistry of the sulphide bauxites, and put a strong emphasis on a bacterial control on the formation of the pyrite, and the oxidation to Fe-oxides.

Laskou & Economou-Eliopoulos (2012) is the first study to use systematic stable isotope analysis to investigate the origin of the sulphur in the pyrite from the Parnassos-Ghiona sulphide bauxites. The sulphur isotope ratios were determined using ‘whole rock samples’, which may have averaged several paragenetic stages within single analyses. The result was a range of δ³⁴S values from +10.2‰ in pyrite bearing red bauxites, to -30.2‰ in the grey sulphide bauxites. They
attribute this wide range of values to bacterial influence on the pyrite formation, drawing similarities with bauxites in Turkey which have similar $\delta^{34}$S ranges. Laskou & Economou-Eliopoulos (2012) also re-enforce a multi-stage pyrite formation process due to variable Eh-pH conditions indicated by coarser pyrite replacing framboids, and pyrite pseudomorphs after goethite.

**Formation of sulphides in other bauxite deposits**

Pyritic bauxites have been studied elsewhere within the Mediterranean Karst Bauxite belt. Presented here are studies from Croatian bauxites and the bauxites of Montenegro. Dragovic (1989) described the ‘red and white’ bauxites (oxide and sulphide respectively) of Montenegro. Dragovic identified that the primary material of the sulphide bauxites were the red oxide bauxites and suggested that the sulphides formed in a swampy phase, characterised by permanent waters and marshes above the bauxite accumulation basin. The reductive waters reduced the Fe$^{3+}$ to the more mobile Fe$^{2+}$ which was carried away at the surface, leaving an Al enriched ore, but in deeper sections of the basin the Fe$^{2+}$ reacted with H$_2$S (and elemental sulphur) to form pyrite minerals within the bauxite and clays. It is presumed that should the reductive waters not penetrate the very base of the deposit, the lowest levels would remain as red, oxidised bauxite. This model would create a similar ‘three-layered’ bauxite profile (see Fig. 5.1) to the Parnassos-Ghiona pyritic bauxite studied by Laskou (2005) where sulphide bauxite forms at the contact between red and white bauxites.

Sinkovec et al., (1994) studied the pyritic bauxites of the Croatian deposits and believed that pyritization was a two-stage process; the first part simultaneous with synsedimentary transportation in a low-lying coastal swamp terrain, where poorly-crystalline iron-monosulphides
formed in anoxic bauxite filled swamps by the process outlined by Berner. Pyritization of these iron-monosulphides was achieved through the addition of sulphur, presumably through bacterial sulphate reduction. A second phase of pyritization started after burial and compaction by swamp sediments through circulating seawater sulphate bearing pore waters, encouraging further growth of more crystalline pyrite, at greater depths within the bauxites.

5.2.7. Sulphide oxidation and bauxite alteration

Sulphide oxidation
Pyrite minerals are unstable under earth surface conditions, and on exposure to water and oxygen, will readily decompose (equation 3). This reaction releases the Fe$^{2+}$ from the pyrite structure and H$^+$ ions from the water molecules, which react with oxygen to form Fe$^{3+}$ and water (equation 4). This ferric iron reacts with the water to produce Fe(OH)$_3$.

$$\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$

(After McKibben & Barnes, 1986)

Studies have also shown that within aqueous pyrite oxidation can occur through reaction with dissolved oxygen and ferric iron, and ferric iron has been shown to be a direct oxidant in both aerobic and anaerobic conditions (Moses et al., 1987). Bacterial action has also been linked to pyrite oxidation, particularly by *Ferrobacillus ferrooxidans* (Silverman, 1967).

The overall net effect of these chemical processes is to release H$^+$ ions which lower the local pH, encouraging solubility of Fe$^{2+}$ and more importantly Fe$^{3+}$. Under more neutral and alkaline conditions the iron (III) hydroxide will precipitate as goethite and lepidocrocite, typically with distinctive yellow colour. These processes are also found in supergene enrichment zones of mineral deposits (Robb 2005), and are the main cause of acid mine drainage (Woo et al., 2013.)
Alteration of the bauxite

The most pervasive and noticeable alteration of the bauxite is the distinct change in colour from a red bauxite, to yellow, pink and white colours, often referred to as ‘bleaching,’ with the white bauxite representing the end product of this process. Bleaching-type alteration of the bauxite is associated with a decrease in iron oxides and a relative increase in aluminium hydroxides, sometimes to concentrations exceeding 60%. The bleaching process involved remobilization of iron (and other more mobile elements), descending movement, and re-precipitation to form concretions, lenticles and layers of pyrite in various levels within the bauxite (Valeton et al., 1987). Valeton et al., also suggest a similar process whereby secondary sulphates as opposed to sulphides are precipitated, as the reason for the crumbly texture of the grey bauxite in the first horizon. Nia (1971) identified that the bleaching is also associated with a loss in hematite crystallinity. The goethite that occurs where bleaching is most prominent is generally well crystallised. There is a general consensus throughout the literature that the bleaching does not affect the type of aluminium minerals present within the bauxite.

As for the effects of bleaching on the geochemistry of the bauxites, Laskou (2005) revealed that As, Ba, Co, Cu, U, V and Si are higher in the sulphide-bearing transition zones, meaning that the bleached zone is probably stripped of these elements. Ratios of La/Lu are lower in the sulphide bauxite than in the hematite bauxite (11.5 versus 19.0 respectively) and ratios of La/Y are constant throughout. Laskou interprets these ratios as being ‘consistent with an acid deposition environment’, based on Crici & Jurkovic’s (1990) study of REE in Croatian Triassic bauxites. It must be pointed out that Laskou’s conclusions were based on the analysis of only four bauxite samples (two sulphide, two hematite) and so the ratios described may not be a true representation of the deposits as a whole.

Alteration such as bleaching is common in karst-associated bauxite as a result of secondary diagenetic and epigenetic processes, replacing the original red to ochre colour of the bauxite by yellow, white, pink, purple, grey and green colours, sometimes with a mottled appearance. This is caused mainly by the partial dissolution and reduction of ferric iron and the formation of new clay minerals such as berthierine and chlorite (Bardossy 1999.) Bardossy (1999) also observed that bauxites that were covered by marshy sediments suffered diagenetic reduction. This would have leached the original iron oxide minerals and replaced them with iron sulphide minerals such as pyrite and marcasite.

Kalaitzidis et al., (2010) suggested that oxidation of the pyrite bearing coal above the bauxite produced an acidic solution (sulphuric acid) that penetrated through the top parts of the bauxite...
horizon, removing iron in solution. The oxidation of the pyrite could have occurred at the surface of the depositional environment or have been caused by an epigenetic process involving flowing meteoric waters.

Laskou & Economou-Eliopoulos (2007) suggest that micro-organisms could have played a major role in the bleaching process; their influence on redox conditions would control the formation of iron sulphides/oxides. Micro-organism activity can also control the re-mobilization and re-distribution of certain major and trace elements.

**Re-precipitation of the iron**

One of the main questions arising from the study of the bleaching process is what happens to the mobilized iron that is removed in such high quantities from the bleached bauxite. Valeton et al., (1987) describes the epigenetic migration of iron in both the second and the third horizon bauxites, re-precipitation as goethite near the footwall in ‘chemical traps’, created by the alkaline pH of the limestones. They also described ‘black crusts’ of Ba, Co, Cu, Mn, Ni, Zn and REE, several cm in thickness within the chemical traps of the second horizon. Gibbsite was also found within cleavage zones of the bauxite, and near to the base of the ore bodies. Laskou & Economou-Eliopoulos (2007) agreed that the highest REE concentrations are found near the footwall contacts.

This suggests that many elements were remobilized during the bleaching process, and transported vertically to the base of the bauxites where they were re-precipitated.

Iron rich deposits have been identified in the present study along fracture planes and at the base of several ore bodies in the third horizon of Mount Iri and Mount Ghiona. They have a banded, spongy texture and will be referred to as ‘Ferric iron precipitate’ for the remainder of this investigation.

**5.2.8. Knowledge gaps**

It is generally agreed that the sulphide bauxites of most regions are mainly pyrite bearing and their formation is linked to reducing conditions developed in swampy and marshy bauxite filled basins. While many different occurrences of pyrite have been described by previous researchers, none have investigated the paragenetic sequences of the pyrite in terms of timing of formation and the evolving geochemistry of the pyrite minerals. This investigation will build a paragenetic model for the pyrite formation and outline the geochemical differences between pyrites formed at each stage.
The sulphur isotope analysis presented in Laskou & Economou-Eliopoulos (2012) does not differentiate the $\delta^{34}\text{S}$ values of the various occurrences of pyrite that they, and other workers, have identified within the Parnassos-Ghiona bauxites. The wide range of $\delta^{34}\text{S}$ values they revealed may be further broken down by separation of what they describe as the sulphide veins which cross cut the sulphide-bearing zones versus the disseminated pyrites within the bauxite matrix. This may also be true of geochemical analyses performed by Laskou & Economou-Eliopoulos (2009, 2012.) This investigation will determine the $\delta^{34}\text{S}$ values of the various pyrites to aid paragenetic modelling and identify if any other sulphate reducing processes were operating, other than bacterial-reduction.

It is still under question what exactly caused the ‘bleaching’ of the bauxite, whether it was a product of a reducing depositional environment, a diagenetic process involving a change in pH/Eh conditions, or whether it was an epigenetic process, perhaps involving some form of reducing fluid. Secondary minerals formed as a result of these processes may help to distinguish which process was responsible for the bleaching, or indeed if multiple processes played a role. Sulphur isotope analysis of the sulphides may distinguish if these are the products of microbial action or have other origins, perhaps from the interaction of re-deposited iron and a fresh injection of seawater sulphate.

5.3 Results concerning sulphide-bearing bauxites

5.3.1 Sulphide mineral textures

For this investigation it was important to study the textures of the sulphide minerals within the bauxites and their modes of occurrence in order to distinguish any genetic relationships and paragenetic sequences of the sulphide minerals. This identified the following three categories of sulphide (pyrite), and this distinction was utilized for further analyses:

1. Disseminated pyrite which has grown in amongst the other bauxite textural features.
2. Replacement pyrite found replacing earlier iron rich textures. This is split into two sub-categories: ooid and pisoid cortices; and bauxite clasts.
3. Pyritic veinlets.

This classification is based on pyritic bauxite from Mount Iti only as this is the only place within the study area where pyrite was found in the bauxite. Textural observations by previous researchers of the sulphides within the Parnassos-Ghiona zone can also fit into these categories.
Disseminated sulphides

The disseminated sulphides are those that have features which are indicative of in-situ growth, which would include the euhedral variety identified by Laskou (2005.) These pyrites are found dispersed throughout the matrix of all grey sulphide bauxites analysed and are typically equigranular (although research on other bauxite deposits has found a steady increase in sulphide crystal size from the top of the bauxites vertically downwards (Bardossy 1982, and references therein)), euhedral and as Bardossy (1982) describes, are automorphic. The size range identified is between 50 to 100 µm. The crystals rarely appear within ooids and pisoid structures, and the outer edge can often appear skeletal (Fig. 5.2E.) The internal structure of these sulphides is typically zoned (shown in Fig. 5.2E.)

These disseminated minerals can cluster together and form up to 200 µm size euhedral sulphides, as shown in Fig. 5.2C, where the larger pyrite crystals have grown from several small crystals. The zone of very fine grained pyrite around the bright crystals in this image suggests that the euhedral sulphides have grown at the expense of some earlier sulphide phase. The visible, rounded outline of this pyrite zone suggests that this earlier phase was of anhedral structure. Fig. 5.2D shows disseminated sulphide development on goethite minerals, which suggests a change in redox conditions during iron mineral formation.

Also included in this group are the spherical, framboidal varieties, again identified by Laskou (2005), which represent the products of bacterial activity. Only one example of these bacteriopyrites was found in this investigation so they were not included in subsequent investigations; however they are shown in Fig. 5.2F.

Replacement Sulphides

Replacement sulphides are those that have formed as a replacement of previous textural features within the bauxites. These include sulphide rich layers within concretions, formed from the alteration of previous iron oxide rich layers, and pyritised bauxite pebbles where the iron rich matrix, typical of these pebbles, has been replaced by iron sulphide. The sulphides within this type typically display anhedral and massive textures, although in some cases, euhedral crystals can grow within bauxite clasts (Fig. 5.2C and D), and can represent either partial or complete replacement of an earlier textural feature.

a. Pyritic pisoliths

The pyrite within the pisoliths occurs as individual nuclei and cortices, however examples do exist where pyrite may have formed the original iron rich layers. The pyrite shows a massive texture
when compared to the more aluminium rich cortices, shown in Fig. 5.3D which suggests diagenetic re-crystallisation of the sulphide minerals. The ooids are never completely transformed to pyrite, and in comparison with non-sulphide bauxite, it is clear that pyrite selectively occurs within the hematite rich zones of the ooids. They can have between 2 and 10+ shells. Fig. 5.3A shows a large pyritised ooid within a red matrix, along with several other ooids. Pyrite has selectively replaced parts of the iron rich cortices, and the iron rich centre. Fig. 5.3B shows pyrite rich zones within an ooid that has been previously described as having formed in situ due to the textures and consistency in the aluminium rich cortices (see chapter 4.) Fig. 5.3C also shows multiple pyrite rich layers of variable thickness within ooids, as well as a pyrite rich core. Fig. 5.3E shows a fragment of a broken ooid that has been overgrown by pyrite (possibly pyrite replacing an earlier iron oxide phase.) There is also evidence for pyrite formation that precedes some ooid formation. Fig. 5.3F shows an ooid that has grown around euhedral pyrite crystals that appear larger than the disseminated pyrites within the surrounding bauxite matrix. This pyritic core may be the product of later alteration of an oxide phase to pyrite, and then re-crystallisation into the euhedral crystals; however it is difficult to imagine this happening without affecting the surrounding pyrites.
Fig. 5.2: Disseminated sulphides from pyritic bauxite in Mount Iti. A. Euhedral, disseminated, equigranular pyrites within the matrix of the sulphide bauxite. B. Disseminated pyrites surrounding ooid structures within the bauxite. They do not occur within the bauxite. C. Larger Euhedral pyrites formed through re-crystallisation of earlier, finer grained pyrite masses. (indicated by the red arrow.) D. Growth of pyrite onto goethite crystals suggesting changes in redox conditions during iron mineral formation. E. Clear zonation within the euhedral, disseminated pyrite crystals. The exterior of the crystals show some evidence of decomposition and skeletal structures. F. Framboidal pyrites grown in a matrix of bauxitic material. (Py – pyrite, Go – goethite).
Fig. 5.3: A selection of photomicrographs and backscatter electron images showing pyrite either forming or replacing ooid and pisoid structures. A. A combined transmitted and reflected light image showing an iron rich pisoid that has been partially replaced by pyrite. B. A backscatter electron image showing anhedral, massive pyrite rich ooid cortices alternating with microcrystalline diaspore rich cortices. C. A backscatter electron image of pyrite rich cortices and ooid core. D. The anhedral, massive pyrite growths within a diaspore matrix. E. Pyrite overgrowths on a fragment of a broken ooid. F. Euhedral pyrites acting as a nucleus for ooid growth.
b. **Pyrite in clastic bauxite**

The pyrite within the bauxite clasts also occurs as a fine grained crystal mass often replacing the matrix/groundmass of the pebbles and sometimes within structures within the pebbles such as ooids. Hematitic pebbles of ooidal bauxite are seen in many different samples of non-pyritised bauxite across the research area. They are evidence for bauxite formation in a region outside the current deposition area, and subsequent transport and re-deposition of the bauxite in its present location (see chapter 4 for a description of this process). The pebbles are always seen to be more iron rich than the surrounding bauxite material that hosts them. Their high iron content will also make them preferred sites for sulphidation, often resulting in the complete transformation of the iron oxide in the pebbles into iron sulphide (e.g. Fig. 5.4A and B). In many cases, remnants of the original oolitic texture of the bauxite pebbles are preserved due to low iron nuclei and oolite

![Fig. 5.4: Four microphotographs of pyritised bauxite clasts within bauxite from Mount Iti. A. Several pyritised clasts within a red, iron oxide rich bauxite, suggesting the blocks were pyritised before deposition. There are several veinlets also cutting the bauxite. B a large sulphidised, composite bauxite clast with an outer oxidised rim. This again suggests transport of sulphidised clasts before deposition. C. Large euhedral pyrite crystals replacing a goethite rich clast. The clast has been subsequently concreted by a layer of hydrous aluminium oxides. D. A partially oxidised pyritic bauxite clast, with other sulphides present around it. The clast is well rounded and is also covered by a concreted layer of iron oxide rich bauxite. (Py – pyrite, Go – goethite).](image)
Sulphidised bauxite clasts can occur within areas of the bauxite that have an entirely hematitic matrix, such as in Fig. 5.4A and B, which suggests sulphide replacement occurred prior to final transportation and deposition into more oxide rich environments. The distinctive oxidised outer edge of the clast shown in Fig. 5B also suggests some degree of transport and exposure to oxidising conditions after sulphide formation. The clast in Fig. 5C shows euhedral pyrite formation at the expense of a goethite rich zone within the clast. This clast has also been surrounded by a layer of diaspore after deposition. Fig. 5D shows a pyritised bauxite clast that has been partially oxidised and replaced by goethite. There is also an outer layer of red/brown hematite rich bauxite around the clast.

**Sulphide veinlets**

The third textural type is the sulphides found in veins and fissures within the bauxite, cross-cutting all previous textural features. Sulphides veinlets tend to be very fine grained, sometimes showing filament style pyrite crystals, especially when grown into void space. In hand specimen, most appear composed entirely of sulphide minerals and can be surrounded by several centimetres of wall rock sulphidation (Fig. 5.5A.) Some veinlets show a breccia-like texture (Fig. 5.5F) which also links their formation to tectonic activity. There is also evidence for several generations of veinlets, where one vein cuts and offsets another (Fig. 5.5B, E & F.) In Fig. 5.5B the pyrite veinlet is cut by a later goethite veinlet. As the pyrite appears relatively un-oxidised it is likely that the goethite veinlet was precipitated as an oxide, rather than being a pseudomorph. This could be linked to a later iron mobilization stage. These veinlets are epigenetic in origin and some examples suggest links with larger scale tectonic activity.

### 5.3.2 Sulphide Minerals in Mount Ghiona

While the mineralogical analysis of the bauxites of Mount Iti and Ghiona showed that sulphide bearing bauxites are confined to the third horizon of Mount Iti, there is evidence that the third horizon bauxite deposits of Mount Ghiona were formerly rich in sulphide minerals to a similar degree to those of Mount Iti, despite the lack of associated coal deposits.

The images in Fig. 5.6 show a range of features that suggest the early presence of pyrite in the bauxites. Cubic pseudomorphs of goethite after pyrite occur within the matrix between the bauxite ooids, similar to the euhedral pyrites in the Mount Iti bauxites, and are shown in 5.6A and 5.6b. The size range and distribution of these crystals are identical to those in Mount Iti. The
goethite rich layers within the ooids are also consistent with pseudomorphic replacement of massive pyrite cortices by the goethite. Fig.5.6C shows a massive pyrite growth which has partially converted to goethite along the outer edge and along internal crystal boundaries. Fig.5.6D shows cubic spaces in heavily bleached white bauxite, where the pyrite and any alteration products have been completely removed, and leaving distinctive void shapes. Where these pseudomorphic features exist, the bauxite is a distinctive yellow colour, and they are associated with extensive bleaching alteration elsewhere in the ore body.

Fig. 5.5: Four reflected and transmitted light photomicrographs and two backscattered electron images showing the sulphide veinlets within the Mount Iti third horizon bauxites. A A euhedral crystalline pyrite veinlet with goethite. The photo also shows a zone of sulphidation surrounding the veinlet (outlined in black.) B. A pyrite veinlet cut and slightly offset by a goethite veinlet. C.A partially oxidised pyrite veinlet. Goethite is replacing the pyrite here. D Growth of filament type pyrite minerals at the expense of magnetite rich bauxite clasts. The veinlet also contains silica as chalcedony. Two generations of pyrite veining, the thin set being clearly offset by the thicker vein, indicating an association with faulting. F. A breccia texture within a pyrite veinlet, suggesting fault association. (Py – pyrite, Go – goethite).
Sulphide Mineralogy

X-ray diffraction analysis of the sulphide bauxite presented in chapter three identified pyrite as the only sulphide mineral within the bauxites. Textural analysis of the bauxites also identified galena as a trace mineral component. Here further sulphide minerals have been identified from SEM and Electron microprobe imagery and geochemical analysis.

Disseminated sulphides

The disseminated sulphides were found to be entirely pyrite (within the exception of a few galena occurrences). The zonations found within most of these euhedral pyrites (Fig. 5.8) were analysed and showed that the only difference between the bright and darker layers is an increased quantity of aluminium, and therefore diaspore. This perhaps suggests that the growth of these sulphide minerals involves similar self-organisation processes as the growth of the ooids and pisoids seen within the bauxites, resulting in a similar iron-rich, iron poor zonation.

Fig. 5.6: A selection of transmitted and reflected light photomicrographs of bauxite samples from Mount Ghiona showing pseudomorphs of goethite after pyrite, identical to those in Mount Iti sulphide bauxites. A. Euhedral cubic goethite pseudomorphs after pyrite throughout the matrix of yellow bauxite from Mount Ghiona, cut by goethitic veinlets. B. Cubic goethite pseudomorphs after pyrite, surrounding goethite rich ooids. C. Pyrite crystals partially replaced by goethite, particularly along cleavage planes in the bauxite. D. Cubic void space within a white, bleached bauxite from Mount Ghiona, where pyrites haé been completely removed. (Pyrite – Py).
Figure 5. 8: A zoned disseminated pyrite, showing iron-rich and iron-poor zonation. No other sulphide minerals were identified with these disseminated pyrites. (Py – pyrite, Di – diaspore).

Figure 5. 7: Back-scattered electron image of a bauxite ooid, with a magnified section inserted. Interpretation of geochemical analysis indicates the presence of nickel bearing iron sulphide minerals (pentlandite and bravoite) with pyrite minerals. (Pe – pentlandite, Di – diaspore, An – anatase, He – hematite, Br – bravoite).
Replacement sulphides

Of the replacement sulphides, several occurrences of sulphide minerals other than pyrite were discovered. In Fig. 5.7 is an example where nickel rich sulphide minerals, mainly pentlandite \((\text{Fe},\text{Ni})_9\text{S}_8\) have formed within ooid cortices, which is surrounded by the more iron rich bravoite \((\text{Fe},\text{Ni},\text{Co})\text{S}_2\). No purely nickel sulphides such as millerite \((\text{NiS})\) have been identified anywhere within the bauxites.

Vein sulphides

The vein sulphides are rather variable in terms of bulk mineralogy, however, pyrite was the only iron sulphide mineral detected. Fig. 5.9 A is an example of a veinlet containing a crystal of galena, indicating that lead was also mobile during vein pyrite formation. Fig. 5.9 B is a more complex veinlet, of goethite, likely to be replacing pyrite (indicated by the small (<10 micron) residual pyrite crystal.) The original pyrite was inter-grown with titanium oxide laths (likely to be anatase) which also indicates that titanium was mobile during vein formation.

5.3.4 Trace Element Geochemistry of the sulphide minerals

The trace element geochemistry of the sulphides was investigated using electron microprobe analysis of 5 pyritic bauxite samples. The analyses were split based on sulphide textural type. The total number of analyses of each textural type was 56 disseminated pyrites, 71 replacement pyrites (49 from pisoidal pyrite, 22 from pyritic clasts) and 79 vein pyrites.
A range of elements were analysed for, but many returned values below detection limits. Of the analysed elements, Fe, S, Al, As, Cr, Ni, Si and Ti were identified in concentrations greater than their corresponding detection limits. Elements Mg, P, Ca, Co, Zn, Cu and Mn were not detected in significant quantities in any of the analysed pyrites. The results of these analyses are shown in Figs 5.10, 5.11 and 5.12 where a comparison is made of each textural type for a selection of detected elements, plotted against Fe to discriminate data groupings more clearly.

The results show that the different pyrite occurrences have variable trace element concentration, with some clear distinctions between the different groups. The disseminated pyrite has the highest concentrations of Ni and Al of the analysed pyrites, (up to 1.52 wt% and 7.46 wt% respectively), with significant values of Ti, Si and As (up to 1.95 wt%, 0.16 wt% and 0.19 wt% respectively). These samples are comparatively low in Cr (up to 0.05 wt%). The Al, Ti and Si concentrations likely represent the growth zonation within these pyrites, in which matrix was incorporated as fine inclusions within the crystal as it grew, shown in Fig. 5.7 as these elements do not typically occur as impurities within pyrite. The high Ni and As quantities are more likely to be as impurities within the pyrite crystal structure, scavenged from the surrounding sediment during precipitation. In replacement textures, the ooidal pyrites are also high in in Al, with a maximum concentration of 7.11 wt%, and contain Ti and Si concentrations up to 8.5 wt% and 0.11 wt% respectively, which are again likely to represent included hydrous aluminium oxides. These ooidal pyrites differ from the disseminated pyrites as they have much lower As and Ni concentrations (up to 0.08 wt% and 0.05 wt% respectively.) An explanation for this is that these sulphides have replaced earlier formed hematite, which would not contain either As or Ni as impurities, therefore making the pseudomorphed pyrite equally low in these minerals. Al and Ti could have occurred as impurities in the hematite, which could have contributed to the higher quantities found within this pyrite.
Fig. 5.10: The concentrations of Ni and Si within the various pyrite types within the sulphide-bearing bauxites. Both elements are plotted against Fe for easier comparison.
Fig. 5.11: The concentrations of Al and As within the various pyrite types within the sulphide-bearing bauxites. Both elements are plotted against Fe for easier comparison.
Fig. 5.12: The concentrations of Ti and Cr within the various pyrite types within the sulphide-bearing bauxites. Both elements are plotted against Fe for easier comparison.
The higher Cr quantities within the ooidal pyrite (up to 0.36 wt%) may be explained in the same way as the Al and Ti concentrations, especially if the original hematite contained minor amounts of Fe-chromite before sulphidation. The bauxite clasts show a very similar trace element concentration to the ooids, supporting the idea that these are related. The only difference is that the clast pyrites can contain up to 0.44 wt% Ni, which is significantly greater than the ooidal pyrites. This is likely to be due to a higher Ni content in the iron rich bauxite clasts overall, compared to the individual iron rich ooid cortices.

The vein pyrite is distinguished by its higher values of As (up to 0.33 wt%) and Cr (up to 0.85 wt%), and moderate Ni enrichment (up to 0.22 Ni wt%). Ti and Si were measured at values similar to the disseminated pyrites, and Al values can be rather high (up to 7.78 wt%). The most important aspect of this pyrite composition is that as the veinlets must have formed epigenetically, a proportion of the As and Ni within the ore body must also have been mobile during vein precipitation.

Overall the pyrite trace element geochemistries show variability between the different pyrite occurrences within the bauxite. The variability in trace element contents can be explained in terms of timing and whether they are disseminated with respect to the bauxite, or if they are replacing earlier textural features within the bauxite, thereby having a particular geochemistry imposed on them.

5.3.5 Sulphur Isotope Composition

Sulphur Isotopes

Oxidised and reduced forms of sulphur, as sulphate and sulphide minerals, are commonly present in sedimentary environments. The $\delta^{34}S$ values of sedimentary sulphides have been used as a tracer to evaluate the sulphate reduction processes, and for re-construction of palaeo-environments (Strauss & Schieber, 1990). Sulphur isotopic fingerprints in sedimentary pyrites result as a consequence of primarily Bacteria Sulphate Reduction (BSR) active processes, which take place over time in dynamically evolving open through closed system settings.

Many bacteria (mostly anaerobic) reduce either:

1. Small amounts of sulphates in order to synthesize sulphur-containing cell components (assimilatory sulphate reduction).
2. Large amounts of sulphates in order to gain energy and expel the resulting sulphide ‘waste’ (dissimilatory sulphate reduction), using sulphate as electron acceptor of their electron transport chain.

**Isotopic Fractionation associated with BSR**

Large isotopic fractionation associated with BSR processes produces sulphate that is enriched in δ$_{34}^{34}$S due to the preferential removal of δ$_{32}^{34}$S which, in turn, will lead to an increase in the δ$_{34}^{34}$S of subsequently formed pyrites (Chambers & Trudinger, 1979). Sedimentary sulphides are often significantly more depleted in δ$_{32}^{34}$S with respect to the contemporaneous seawater sulphate (Wortman et al., 2001; Brunner & Bernasconi, 2005).

**Open and Closed Systems Sulphur Isotope Fractionation**

In open systems, where the sulphur reservoir is continually replenished, sulphur isotope fractionations are generally larger than in closed systems, where the sulphur reservoir is progressively depleted (Riciputi & Hendry, 1997; McKibben & Riciputi, 1998).

The preferential removal of δ$_{32}^{34}$S will cause the δ$_{34}^{34}$S of the residual aqueous sulphate to increase which, in turn, will lead to an increase in the δ$_{34}^{34}$S of subsequently formed pyrite. Under closed-system process, after all sulphate has been reduced, the bulk isotopic δ$_{34}^{34}$S of the precipitated pyrite is expected to be equal with the δ$_{34}^{34}$S of the initial sulphate. However, the δ$_{34}^{34}$S of individual pyrite grains or pyrite assemblages is expected to be both lower and higher than the bulk composition, depending on when the pyrites formed during the evolution of the sulphate-sulphide system.

In a setting where the reservoir of sulphur available is finite (closed system), especially where the sulphur isotope fractionation factor between the starting and final sulphur species is large, significant isotopic variations may occur as a result of progressive fractionation processes.

Analysis of the sulphur isotope composition of the various pyrite textures will provide information as to the formation processes of the sulphides, whether they all formed during the same phase, or whether they represent several phases of sulphide formation in a dynamically evolving system.

**Sulphur Isotope Analysis**

Sulphur isotope analysis was conducted on 11 samples of sulphide-bearing bauxite, representing 3 different ore bodies within Mount Iti. The sulphides were selected for analysis based on their occurrence (disseminated, ooidal, clasts and vein) to test whether these textural classes exhibited different sulphur isotope ratios, and by ore body to test whether similar relationships could be seen between ore bodies, or whether each ore body acted as an isolated system after deposition.
A total of 29 isotopic measurements were obtained through conventional methods and 33 through laser ablation methods. While laser ablation analysis allowed a greater accuracy of sampling, comparison between both data sets showed little difference in $\delta^{34}S$ values and so these two data sets have been combined in Figs 5.13 and 5.14.

Fig. 5.13 shows the complete data set of 62 analyses separated by ore body. $\delta^{34}S$ distributions in samples from Duo Vouna and Kopresies both show a distinctive bi-modal pattern, with one mode situated between $-34\%$ and $-42\%$, representing analyses of predominantly disseminated pyrite, and a second at much heavier values centred on $+2\%$ in Duo Vouna and $+12\%$ in Kopresies, representing vein pyrites. The samples from the Viotier ore body show a contrasting distribution in that 18 of the 19 analyses produced $\delta^{34}S$ values clustered between the values of $-3\%$ and $-6\%$, with one analysis at $-34.8\%$.

The data from Duo Vouna and Koprisies has been combined in Fig. 5.14 to show the overall variation in $\delta^{34}S$ value with pyrite occurrence. The Viotier analyses have been excluded from this graph as they are considered to be an anomaly that will be discussed later in this section. It is clear that, in the other two ore bodies, the disseminated pyrites have a consistently light $\delta^{34}S$ compositions compared with other forms of pyrite in the samples. Values for the disseminated pyrites range from $-44.3\%$ to $-28.2\%$, with a median value of $-39.2\%$. This range is consistent with bacterially reduced sulphide formation in a system with abundant sulphate (Kaplan & Rittenburg, 1964.)
Table 5.1: The complete data set from conventional and laser ablation isotope analysis of pyrite minerals from within the Parnassos-Ghiona bauxites, separated based on textural occurrence. Two analyses of coal sulphides are also provided.
The vein hosted pyrites identified in Duo Vouna and Kopresies have a δ^{34}S composition range from -4.8‰ to +12.2‰ with a median value of +4.3‰ which are significantly heavier than the

![Graph of Duo Vouna](image)

Number of samples = 5

- Authigenic Sulphides
- Replacement Sulphides - Ooids
- Replacement Sulphides - Clasts
- Vein Sulphides

![Graph of Kopresies](image)

Number of samples = 3

- Authigenic Sulphides
- Replacement Sulphides - Ooids
- Replacement Sulphides - Clasts
- Vein Sulphides

![Graph of Viotier](image)

Number of samples = 3

- Authigenic Sulphides
- Replacement Sulphides - Ooids
- Replacement Sulphides - Clasts

Fig. 5.13: The δ^{34}S values of pyrite within the sulphide-bearing bauxites of Mount Ili within the Parnassos-Ghiona zone. The values are separated based on ore body and by textural occurrence of the sulphide minerals.
disseminated pyrite and closer to the Cretaceous seawater sulphate $\delta^{34}$S value of $+14$ to $+18\%$ (Kampschulte & Strauss, 2004.) If the vein pyrites are bacterially reduced sulphides, then these would represent values expected within a closed system, where fractionation has proceeded for a significant amount of time, such that the available sulphate is enriched in $^{34}$S.

Pyrites within bauxite clasts show a wide range of values from $-43.5\%$ up to $+11.7\%$ with no significant ‘clustering’ around any particular set of values. This range of values would again be indicative of a closing or closed system with a limited sulphate source that becomes steadily heavier (enriched in $^{34}$S) as more $^{32}$S is reduced out of the system. The ooidal pyrites are only represented here by two analyses that have values of $-25.1\%$ and $-27.0\%$, close to the disseminated pyrites. If more analyses were performed, the ooidal pyrites may be expected to show a similar distribution to the clast pyrites, given that they are both replacement types, however it is difficult to draw further conclusions at present.

The clustering of the three types of sulphides within the Viotier samples suggests re-setting of the $\delta^{34}$S values within this ore body. A proposed mechanism for this resetting is by intense oxidation converting the iron sulphides to iron oxides and soluble sulphates, mixing of the re-mobilized

Fig. 5.14: The $\delta^{34}$S values of the sulphide minerals within the Parnassos-Ghiona zone sulphide-bearing bauxites, (excluding the data from ‘Viotier mine’ in Fig. 5.13) The $\delta^{34}$S value of seawater sulphide during the late Cretaceous is indicated on the graph by ‘SW.’
sulphate with new seawater sulphate, followed by reduction and re-sulphidation of the iron oxides to pyrites with the new and highly confined $\delta^{34}S$ values. The one analysis of disseminated pyrite that gave a value of $\sim$-36‰ is interpreted as a relict sulphide that survived this extensive re-setting.

### 5.3.6 Sulphide minerals results summary

The data presented in this section show that the sulphide minerals within the Parnassos-Ghiona bauxites have a relatively complex paragenesis, and show significant differences in textural occurrence, mineralogy, trace geochemistry, and sulphur isotope composition. The main differences have been summarised in Table 5.2 below.

<table>
<thead>
<tr>
<th>Textural Occurrences</th>
<th>Sulphide Mineralogy</th>
<th>Trace Element Geochemistry</th>
<th>$S$ isotope range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major</td>
<td>Trace</td>
<td>Ni, As zoned with Al rich layers</td>
</tr>
<tr>
<td>Disseminated</td>
<td>Pyrite</td>
<td>-</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td>Pentlandite, Bravoite</td>
<td>Cr</td>
</tr>
<tr>
<td>Replacement</td>
<td></td>
<td></td>
<td>Ni, As, Cr</td>
</tr>
<tr>
<td>Ooid</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Clast</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Vein</td>
<td>Pyrite</td>
<td>Galena</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: The main findings of the investigations into the sulphide minerals of the Parnassos-Ghiona bauxites.

### 5.4 Results concerning epigenetic alteration of the bauxite

This results section will present data and information regarding the extensive epigenetic iron removal (hereafter referred to as ‘bleaching’) and epigenetic chamosite formation within the third horizon bauxites of Mount Iti and Mount Ghiona. The products of the bleaching, both bleached bauxite and the re-precipitated iron materials, are also investigated.

#### 5.4.1 Textural analysis of bleached bauxite

The SEM electron backscatter images in Fig. 5.15 shows a comparison of red, yellow and bleached bauxite textures from within the bauxite of Mount Ghiona. Fig. 5.15 A is a red, pisolitic bauxite where the iron rich (hematite) minerals are clearly seen as the brighter zones, throughout the majority of the matrix, and as pisolith cortices. The darker zones are iron-poor. Fig. 5.15 B is an example of yellow bauxite. Within this yellow bauxite there is a clear redistribution of iron as
multiple, thin, parallel veinlets, running throughout the matrix of the bauxite. These veinlets are composed of goethite and appear far more frequently than pyritic veinlets do. In the top left-hand corner of the image is a cluster of bright pyrite minerals, with many pseudomorphs of goethite,

Fig. 5.15: Three back scattered electron images of bauxite from Mount Ghiona showing the textural changes associated with bleaching. A. Red bauxite with iron rich matrix and pisolith cortices. B. Yellow bauxite showing the development of goethitic veinlets, and earlier pyrite crystals. C. Bleached bauxite showing a lack of iron minerals, with mainly pale grey diaspore. The dark areas represent void space left by iron removal. (Di- diaspore, He – hematite, Py – pyrite.)
which have not been detected in the red bauxite. Fig. 5.15C is an example of white bleached bauxite. This sample is almost fully depleted in iron, leaving diaspore rich pisoliths seen as the pale grey zones, mainly within the ooids. The darker areas are predominantly void space within the sample, created by the removal of iron.

The bright minerals are either small crystals of residual iron sulphides or oxides, or detrital components of the bauxite as shown in chapter 4.

5.4.2 Mineralogical change resulting from bleaching

XRD were performed on a suite of 9 bauxite samples showing the red, yellow and bleached bauxites. Representative results are presented in Fig. 5.16, and the full analyses can be found in Appendix 1.

The mineralogical analysis shows that the change from red bauxite to white bauxite is simply a complete removal of crystalline hematite. Yellow bauxite is rich in goethite. The origin of the goethite within the bauxite has already been indicated to be primarily from the pseudomorphic

![Image of mineralogical analysis]

**Fig. 5.16:** Mineralogical analysis of red, yellow and bleached white bauxites presented as three pie charts showing the relative crystalline mineral components of each bauxite type as detected by XRD analysis. These are accompanied by a photo of the three bauxite samples with a 15cm pencil for scale.
alteration of pyrite into goethite through oxidation. This indicates that this yellow, goethitic/limonitic bauxite is the product of near complete oxidation of pyritic bauxite, and the residual pyrite and pseudomorphic goethite in Fig. 5.15B also confirms this.

5.4.3 Textural analysis of ferric iron precipitate

In ore bodies that have undergone significant bleaching, the iron can accumulate as discrete masses, (as opposed to simply enriching nearby ore), typically along fracture planes within the bauxites or as layers of iron oxides at the base of the ore body. This ferric iron precipitate is typically hard, dark brown in colour and exhibits liesegang banding-type structures when accumulated in large masses at ore body bases (Fig. 5.17A and B). The contact with the footwall

Fig. 5.17: A selection of sample photos and transmitted and reflected light photomicrographs showing the texture of the ferric iron precipitate found at the ore body base and along faults within the bauxite. A. A sample of ferric iron precipitate from Mount Iti. B. Example of ferric iron precipitate found within a mine in Mount Iti showing typical liesegang banding structures. C. A transmitted light image showing alternating goethite (Go) and calcite (Ca) rich bands within the precipitate. D. An example of the precipitate material that has been partially replaced by pyrite (Py) within an ore body in Mount Iti.
limestone has a layer of finely powdered calcite around 5-10cm thick.

In thin section, the goethite rich layers are seen to be interlayered with crystalline calcite layers (Fig. 5.17C), likely to be sourced from the acid dissolution and eventual re-precipitation of carbonate footwall material. In some cases the goethite liesegang-type bands are interlayered with, or are replaced by, pyrite (Fig. 5.17D) suggesting a re-establishment of reducing conditions after precipitation.

### 5.4.4 Mineralogy of the ferric iron precipitate

X-ray diffraction of a selection of these iron precipitates has identified goethite as the major iron mineral forming these layers. Samples from fracture planes within bauxites typically show some quartz content, supporting the idea of silica removal as well as iron removal during bleaching. Samples of the precipitates from the footwall contact contained large amounts of calcite, and in some cases gibbsite. The white friable material was also analysed and was found to contain up to 24% gibbsite along with calcite. The presence of gibbsite within the iron precipitates and re-precipitated calcites, when none were found within the bauxites themselves, suggests that it is epigenetic gibbsite, and that in order to form the gibbsite, some aluminium was mobilized from the diasporic bauxite during the bleaching process. It is possible that this aluminium has come from digested aluminosilicate minerals such as kaolinite, rather than dissolution of hydrous aluminium oxides.

![Ferric iron precipitate from fault through the bauxite](image1)

![Ferric iron precipitate from the base of a bauxite](image2)

![White mineral from the contact between the ferric iron precipitate and the footwall limestone](image3)

**Fig. 5.18:** Mineralogical analyses of the ferric precipitate material from faults within the bauxite and at the contact between the bauxite and the footwall limestone. The third pie chart represents a soft, friable material found in-between the ferric iron precipitate and the footwall limestone.
5.4.5 Geochemical change resulting from bleaching

The data presented in this section illustrate the geochemical alteration and element mobility during the bleaching process.

**Major element concentrations**

The concentrations of $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{TiO}_2$ and $\text{SiO}_2$ throughout a simple bleached bauxite profile are shown in Fig. 5.19. This profile shows an example of a bleached bauxite sequence in which the overall process is seen in quite simple terms. Throughout the sequence it is clear that $\text{Al}_2\text{O}_3$ is enriched within the white bauxites where iron has been removed. Iron is enriched towards the base of the section where the bauxite had dark brown patches, which suggests that the iron...
removed from the bleached bauxite has been re-precipitated within the red bauxite deeper down the section. TiO$_2$ and Al$_2$O$_3$ show a close relationship with each other throughout this section.

**Trace element mobility during bleaching**

Trace element concentrations of the various altered bauxites were determined using ICP-MS analysis. Two sets of samples, the first set from Mount Iti and the second set from Mount Ghiona were used. The first set represents the full bleaching process from red bauxite, the oxidised yellow bauxite, and the white bleached bauxite and a sample of ferric precipitate from fracture planes within the bleached bauxite. The second set shows a similar suite, however instead of an iron precipitate, a sample of green chloritised bauxite found in association with the bleached ore was included. This sample was included in order to investigate whether the formation of epigenetic chlorite within the third horizon bauxite is linked to the re-mobilization of iron through bleaching. The results of both sets of analyses are shown in Figs. 5.20 and 5.21.

Comparing the red and bleached bauxites from each set it is possible to determine some of the geochemical changes occurring when red bauxite is bleached. There is a loss of Ni, Cu, Zn As, Ba and Pb, common to both sample sets due to bleaching, and an enrichment of Cr, Zr, and Sr within the bleached bauxite in relation to the red bauxite.

The ferric iron precipitate is enriched in Ni, Cu, Zn, As, Ba, Pb and Th relative to the red bauxite. As these elements are depleted from the bleached bauxite it is more evidence that the ferric precipitate has formed through direct removal of material from the bauxite and subsequent deposition elsewhere. Cr, Zr and Nb are much lower in the ferric iron precipitate compared to the bleached and red bauxites which suggests that these elements were relatively immobile during bleaching. The chloritised bauxite shows a different distribution of trace elements to the ferric iron precipitate; however it is still enriched in Ni, Cu, Zn, As and Pb and depleted in Cr, Zr and Nb relative to the associated red bauxite, which suggests a similar formation process to the ferric iron precipitate. The yellow bauxites are similar in many ways to the associated red bauxites; however there is a clear enrichment in As in both sample sets. They are also both high in V and Pb. This could be due to the inclusion of these elements within the goethite minerals within the yellow bauxite, or/and the enrichment associated with sulphide bauxites as shown in chapter 4, section 4.4.4.

**REE mobility during bleaching**

In order to examine bauxite alteration and iron remobilisation processes in more detail, REE concentrations were also determined for the bleached bauxite sample sets 1 and 2.
Fig. 5.20: Trace element concentrations in a set of four third horizon bauxite samples from Mount Ghiona, representing the overall bleaching process and epigenetic chloritised bauxite.

Fig. 5.21: Trace element concentrations within four third horizon bauxite samples from Mount Iti, representing the overall bleaching process and the resulting ferric iron precipitate.
Total REE concentrations vary between all samples, however in both data sets the yellow bauxite is enriched relative to the red or bleached bauxite. However, it is the iron precipitate and the chloritised bauxite that have the greatest enrichment in REE, containing more than the combined concentrations of the associated samples in each data set. Within these iron enriched samples the LREE are greatly enriched relative to the HREE, and also relative to the MREE. Within the red, yellow and white samples, LREE also seem to be enriched relative to the HREE and MREE, in particular in the yellow bauxite of sample set 1.

The red bauxites within each sample set are taken to be the most unaltered lithology for REE comparison. In both sets there is a positive anomaly in Ce, a negative anomaly in Eu, and, while there is no anomaly in set 1, there is a minor negative anomaly in set 2. The yellow bauxites have more differences between the two samples; however the negative Eu anomaly is of the same intensity to other samples, there is a variable but clearly negative anomaly in Y, and a negative or slightly positive anomaly in Ce. The bleached bauxites have a large positive Ce anomaly, a negative Eu anomaly and no significant anomalies in Y. The iron precipitate analysis and the chloritised bauxite sample show almost identical anomaly patterns within the REE spectra. They both have a large negative anomaly in Ce, a negative Eu anomaly and a negative Y anomaly.

Comparing the white bleached bauxites and the re-precipitated iron samples indicates that during bleaching not all of the REE were mobile. The strong positive Ce anomaly in the white bauxites and the strong negative Ce anomaly in the iron rich samples suggests that Ce was not mobile during bleaching, whilst most other REE, (especially LREE given the huge enrichment relative to HREE) were mobile. Ce has therefore become passively enriched in the white bauxite, whilst the fluid carrying the re-mobilized iron was depleted in Ce. The same is true for Y. This indicates that the Ce was in its insoluble Ce$^{4+}$ state, as opposed to its soluble Ce$^{3+}$, which suggests that the bleaching process was an oxidising process. Eu anomalies are identical in each lithology across both sets, indicating that the bleaching process has no effect on Eu.

The similarities in total REE enrichment, negative Y anomaly and negative or reduced Ce anomalies between the iron enriched samples and the yellow bauxites suggests that these too are linked. It is suggested here that during pyrite oxidation and alteration to goethite, REE in the circulating acidic fluids were captured by the goethite minerals, enriching the yellow bauxites in REE. As Ce and Y are not mobile during this process, the goethites forming during this process are not enriched in these elements.
Fig. 5.22: The REE concentrations within two sets of bleached bauxite samples to show the mobility of the various elements during the bleaching process, and to compare the epigenetic products of ferric iron precipitate and chloritised bauxite. The tables beneath each graph show quantitative analysis of the REE patterns.
5.5 Discussion

5.5.1. The formation of sulphide minerals within the Parnassos-Ghiona bauxites

This investigation has presented evidence to show how the pyrites within the Parnassos-Ghiona bauxites can be grouped into three main types which are: disseminated sulphides, replacement sulphides of ooids and bauxitic clasts, and vein sulphides. There is textural, geochemical and isotopic evidence which suggests that these sulphides did not form at the same time, but are part of a paragenetic sequence that evolved during the history of the bauxite. The various sulphide occurrences are summarised in Fig.5.23 along with the sulphur isotope ranges. In this section a suggested explanation for the formation of these sulphides is given.

Considering the very light δ34S values of the disseminated pyrites, and given a natural evolution of δ34S values in a closed system sulphate reservoir undergoing bacterial reduction of sulphate, it can be assumed that these were the first pyrites to form. Their position within the matrix of the bauxite, always outside the pisolith and clasts, suggests that these pyrites formed after the processes of deposition, pisolith formation and re-working had ceased. The system was in a low energy condition at this stage, with sufficient organic matter and abundant iron in the soft, earthy
bauxite matrix. The high trace element content of the disseminated pyrites (shown in section 5.4.4) is a further indication that they are, as Bardossy (1982) described, ‘trace element scavengers’, particularly of As and Ni, which would be expected of newly formed precipitates growing in the porous, soft bauxite. The zonation seen within these pyrites probably formed through alternating periods of increased and decreased pyrite formation, and the bauxite rich zones support the theory that these formed while the bauxite was still soft.

As the system evolved, and the amount of pyrite within the bauxite increased, the eventual consumption of much of the readily sulphidised iron compounds in the matrix would have driven sulphide formation to utilize other sources, such as the iron present within more consolidated pisoliths and bauxite clasts. This represents the second stage of pyrite formation. During this phase, the already depleted sulphate source became greatly enriched in $^{34}$S as indicated by the wide range of values within the pyritised clasts, eventually moving into positive $\delta^{34}$S values. This phase could continue without any major change in tectonic activity or environment conditions.

Finally fracturing of the lithified (or at least partially lithified) bauxite allowed for vein pyrite formation. There is also some evidence to link these vein structures to tectonic activity such as a brecciated vein fills. During vein formation, aside from iron and sulphate within the system, the trace element analysis showed that As, Cr and Ni were all mobile, and were incorporated within the veinlets.

If the sulphate for these veinlets was re-mobilized by oxidation of earlier disseminated pyrites, then it would be expected that the $\delta^{34}$S values would be in the same range as the disseminated pyrites, which they clearly are not, so another explanation is needed. If the vein pyrites are the product of bacterial reduction as stated by Laskou & Economou Eliopoulos (2007, 2012) from a fresh source of seawater sulphate, it would also result in a lighter $\delta^{34}$S value close to that of the disseminated pyrites. It follows that the sulphate source for the vein pyrites must have been heavily enriched in the $^{34}$S isotope. It is therefore likely that the sulphate was sourced from remaining heavy isotope rich pore fluids within the bauxite after the formation of disseminated pyrite and replacement pyrites. The fluid may have been liberated by fracturing during tectonic activity, and the iron sourced from the remaining iron oxide rich bauxites.

This model accepts seawater as the sulphate source and reduction by bacterial processes. However, inorganic reduction via thermochemical sulphate reduction (TSR) may also be a potential method by which the vein sulphides have formed. TSR occurs at temperatures of at least 100-140°C which would form only after burial, at around 5-6km depth (given a geothermal
gradient of 25°C per km.) The coal overlying the sulphide bauxites has been determined to have $T_{\text{MAX}}$ values of between 418 and 433°C (Kalaitzidis et al., 2010) which shows that the bauxites have been exposed to temperatures high enough to establish a TSR system. However, further evidence is needed to determine the sulphate reduction process operating during the formation of the pyrite veins. It can be said with some confidence that the disseminated pyrites and the replacement pyrites are the products of bacterially reduced sulphate fuelled by organic matter in and above the bauxite deposits (Machel 1998).

**What controls the accumulation of organic matter in bauxites**

The coal deposits found above the third horizon bauxite ore bodies within the third horizon of Mount Iti are the products of organic matter derived from terrestrial plants, and accumulated in a swampy terrestrial environment (Kalaitzidis et al., 2010.) The development of this terrestrial environment allowed the growth of the plants, and the suitable swamp conditions for organic matter accumulation and preservation. However, these conditions are not matched further south within Mount Ghiona which suggests that this organic matter preserving environment is not laterally continuous.

As there is evidence of sulphides having formed within the Mount Ghiona bauxites, there must have been a supply of organic matter to these ore bodies, but the lack of coal suggests that the organic matter was quickly decomposed, and/or was present in a relatively lower concentration than in Mount Iti. It may be that the Ghiona ore bodies were deposited into a shallow marine environment in contact with the swampy terrestrial plains. This allowed organic matter to be transported from the swampland into the shallow marine environment, and more importantly, to fuel bacterial sulphate reduction, the establishment of a reductive water column, and pyrite formation.

There is evidence for reducing conditions being present within the second horizon (syn-genetic chlorite minerals, see chapter 4, section 4.4.3); however sulphide minerals have not formed within this horizon. As iron would be in sufficient supply, the likely barrier is therefore a lack of organic matter. This may be due to deposition of the bauxite in entirely shallow marine conditions, preventing the growth and development of terrestrial plants, and/or a faster marine transgression after bauxite deposition again preventing growth and accumulation of organic matter, and the development of a reductive sediment column.
These late Cretaceous coals formed during a time in Earth’s history of intensive coal accumulation, responsible for some of the largest coal deposits worldwide including the Lena coalfield in the U.S.S.R., which is considered the biggest in the world (Vereshchagin 1961.)

5.5.2. Ore texture formation model and pyrite formation

With reference to the model for the formation of the bauxite textures within the Parnassos-Ghiona zone proposed in section 4.5.3 of Chapter 4 of this thesis, the pyrites can be seen to occupy specific intervals in the texture cycle.

The disseminated pyrites are only found within the matrix of the bauxites suggesting that the majority came after formation of the ooids and pisoids. This would make them a diagenetic growth after final deposition. However, some ooids are found to contain euhedral pyrite crystals as nuclei, suggesting that some must have been present during ooid formation. Perhaps these disseminated pyrites began forming before the bauxite reached its final destination, so that ooids could utilize them as growth nuclei, however they would require a source of sulphate. Overall it is clear that they grew once the sediment column was stable and when a reducing environment had been established.

Within the clasts there is evidence for sulphidation of the iron before and during transportation, as well as post-deposition alteration and re crystallisation. Within each of the sulphide occurrences described here, goethite has been found as a pseudomorphic replacement product of oxidation of the sulphides, sometimes within separate ore bodies, different levels within an ore body, and within singular examples of sulphide occurrences.

All of the veinlets show evidence of epigenetic formation as they cut across the bauxite textures, such as ooids and clasts. Therefore the veining occurred after at least partial lithification of the bauxite.

As the textures of the red and the sulphide-bearing bauxites are identical, sulphidation of the bauxite doesn’t apparently interrupt the bauxite development. They represent the action of the same textural forming processes, but in a different environment that creates different mineral assemblages. The processes of ooid formation, bauxite re-working etc must be the same in all bauxite types.
5.5.3. Ghiona sulphides
The evidence presented here for sulphide minerals having existed in Mount Ghiona bauxites explains why bleaching is possible in Mount Ghiona, with the apparent lack of sulphide minerals. In geological terms, Mount Iti represents the bauxites of Mount Ghiona before they were so heavily oxidised. Comparing the different deposits across the two mountains it is possible to see ‘snapshots’ of the bauxites at different stages in their life cycle from initial deposition, sulphide formation and then destruction and associated bleaching. Given enough time (geologically) the ore of Mount Iti will progress to mineralogies and geochemistries similar to that of Mount Ghiona. Up until present the evolution has been slowed by the overlying flysch and overthrust units acting as a protective cap against meteoric waters.

5.5.4. Epigenetic alteration of the bauxites
This investigation has focused on the epigenetic processes associated with the intense iron removal within the bauxites, creating ‘bleached’ white bauxites, and briefly investigates the epigenetic chlorite mineral formation seen within some third horizon bauxites.

The bleaching process
The mineralogical and geochemical data presented here shows that bauxite bleaching is not a gradual change from red to orange, to yellow to white bauxites, but is a more complex process involving several stages. Based on data from this investigation and previous investigations the following model is proposed to explain bleaching and how the various types of bauxite may form from this epigenetic process.

1. The process starts through oxidation of pyrite minerals typically found at the top of the bauxites, by oxygen rich meteoric fluids descending along faults and fractures formed during tectonic deformation. This produces pseudomorphic goethite, and thin goethitic fracture fills with a distinctive limonitic yellow colour, creating the yellow bauxite.
2. The breakdown of pyrite minerals releases sulphur that combines with oxygen and hydrogen to form $\text{H}_2\text{SO}_4$ (sulphuric acid) which decreases the pH of the local environment, and any fluids present. At low pH-high Eh conditions iron would only be stable in its mobile $\text{Fe}^{2+}$aq form.
3. Continued descending vertical movement of this low pH-high Eh fluid would allow it to penetrate into the red oxide bauxite beneath the sulphide-bearing bauxite, where
destabilization of the hematite would occur, mobilizing the iron. Continued percolation of
the fluid would remove this iron, creating the white bleached bauxite.

This interpretation, if valid, shows that:

1. Decomposition of pyrite does play a role in the bleaching, most likely through the
   formation of sulphuric acid during sulphide decomposition.
2. The iron removed from the sample during oxidation of the pyrite could either have been
   in the form of pyrite or hematite to be removed.

With regards to the occurrence of white, low-iron bauxite, this investigation agrees that white
bauxite is the product of a process of predominantly iron-removal from the bauxite ore. Here this
process is investigated in detail and a more complex model is proposed for the process of de-
ferriginization of the bauxite. The model proposed by Laskou & Economou-Eliopoulos of
bleaching that places the white bauxite above a layer of sulphide rich bauxite on top of red
bauxite does not account for many of the bleached structures seen within the Parnassos-Ghiona
bauxites. Within Mount Iti and Mount Ghiona there is evidence that epigenetic, fault associated
bleaching is the more predominant process.

**Controls on the extent of bleaching**

The bleaching process involves potentially large volumes of fluid, indicated by the vertical
propagation of the bleached zones, and the focusing of bleaching around faults and fractures. It
also relies on the interaction of the fluid with sulphide minerals. Given these conditions, the
following controls on bleaching have been determined:

- **The original volume and distribution of sulphide minerals** formed within the bauxite
  controls the amount of sulphuric acid produced, and therefore the amount of iron that
  can be mobilised. As shown in Mount Ghiona, sulphide-bearing bauxite doesn't
  necessarily occur with coal deposits on top, but the presence of coal would more than
  likely indicate sulphide-bearing bauxite.

- **Faults and fractures** greatly enhance and focus fluid flow, intensifying the bleaching.

- **The more exposure to meteoric waters** the bauxite has, through thin overburden and
deeper penetrating faulting, allows a sufficient supply of bleaching fluid and oxygen.

- **Porosity and permeability** of the bauxite can not only aid penetration of the bleaching
  fluid, but it is likely to control the efficiency of the iron removal and re-deposition
  elsewhere. As bleached bauxite is more porous and permeable than red bauxite, it would
allow more fluid flow and thus more bleaching. It is therefore representative of a positive feedback mechanism.

5.5.5.  Bleaching alteration at different scales of observation

Bleaching alteration at the Ore Body Scale

Fig. 5.24 shows a section through a bleached bauxite deposit demonstrating the relationships between the red, yellow and white bauxites. At the top of the bauxite is a 0.2 metre layer of high iron clayey bauxite. Beneath this is a 0.35 metre thick layer of yellow goethite rich bauxite. It is proposed that this layer formed through the oxidation of pyrite rich bauxite and formation of yellow limonitic goethite, which produced sulphuric acid, thereby increasing the acidity of pore fluids and descending meteoric fluids. Given the horizontal nature of the ore zones within the bauxite, it is interpreted that the acidic fluid descended vertically through the ore.

The 0.1 metre thick zone beneath the yellow bauxite is a thin band of white/grey low-iron bauxite. It is suggested that this has been depleted in iron by the descending acidic fluid. Beneath this is a transition zone of pink bauxite moving into the more familiar red bauxite, with a thickness of 2 metres. The pink zone represents the diffuse edge of the bleaching alteration front. Within the lower red bauxite there are zones of high iron with a distinctive red/brown colour. It is suggested that these represent re-precipitated iron within the bauxite.
Fig. 5.25 shows a more complex bleached bauxite section where the zones of red, yellow and bleached bauxites are less easily distinguished. This may be due to focusing of the bleaching fluid flow along and within proximity of fracture planes. However the same processes have occurred, resulting in precipitation of the goethite rich ferric iron precipitate along the fractures.

**Bleaching alteration at the sample scale**

At the hand specimen scale, the bleaching process can be easily recognised. Fig. 5.25 is an image of pisolithic third horizon bauxite showing a visible bleaching front. On the right of the image is a preserved section of red bauxite with pyrite veinlets and inter-pisoid pyrites. The matrix of this section has a distinct red colour and is clearly rich in iron. Moving left from this a bleached zone has developed where the original pyrite rich veinlets have been oxidised to goethite, and both the
groundmass and the pisoids have become noticeably whiter, indicating a loss of iron. The bauxite has clearly retained its texture throughout the bleaching process. The area around the oxidised veinlet has retained its red colour suggesting iron removal was less effective here. This indicates that the formation of the pyrite veinlets may have decreased the permeability of the wall-rock surrounding the vein, via some form of alteration (e.g. the addition of silica and iron), thereby reducing the penetration of the acidic bleaching fluids. On the left hand side of the image is a band of layered yellow and brown, goethitic ferric iron precipitate. The goethite precipitation is also seen in between the white pisoliths close to the edge of the sample. Therefore this hand specimen illustrates on a micro scale the same processes that have affected the bauxite on a metric (ore body) scale.

5.5.6. **Re-precipitation of the leached iron**

It has been shown in this investigation that the iron lost during bleaching, has been reprecipitated as thick goethitic deposits within fractures and at the base of the ore bodies. This
precipitate typically has a banded structure reminiscent of liesegang banding, and can be interlayered with calcite derived from dissolution of the underlying limestones.

The REE patterns of the ferric iron precipitates show that they have a distinct negative Ce anomaly compared to the original red bauxites from which they were derived. Conversely the bleached bauxite has a distinct positive Ce anomaly which is evidence that these two lithologies are genetically linked. The fact that Ce remained within the bleached bauxite as opposed to being leached at the same rate as other REE suggests that it was within its more stable, oxidised form (Ce$^{4+}$). The Ce oxides found within the bauxites (Chapter 4, section 4.3.3, Fig. 4.13D), may represent re-precipitation of this element after bleaching, however more work is needed to identify the REE mineralogy within the bauxite before and after bleaching.

The similarity in REE pattern between the ferric iron precipitate and the green chloritised bauxite suggests that epigenetic chloritization may also occur through the re-distribution of iron from the bauxites, as they have similar REE anomalies. It may be that where the mobilized iron was re-precipitated under more reducing conditions, chlorite minerals were stable as opposed to goethite. The silica for the chamosite probably came from dissolved amorphous silica from silicate minerals.

Fig. 5.26: A reflected light photo of pisolitic third horizon bauxite showing the overall bleaching process at a hand sample scale. The oxidation of pyrite in the sample near the left hand side had caused the leaching and re-precipitation of iron as goethite on the sample edge on the far left hand-side. The sample in the image is 5cm across.
The mechanism of re precipitation

The mechanism of precipitation was one that encouraged the formation of goethite over any other iron oxide mineral, and the dissolution and re precipitation of calcite rather than any iron carbonate or calcium sulphate.

With dissolved calcium carbonate and sulphate removed from the oxidised pyrite within the bleaching fluids, it may be assumed that gypsum would form at the base where the acidic fluid reacted with the footwall carbonates. However no gypsum was identified within any of the lithologies analysed using XRD analysis. This reveals, according to the Ca-C-O-S-H pourbaix
diagram in Fig. 5.27, is that the pH at this point must have evolved from below pH 4, to above 6.5-7 (i.e. fully neutralised to alkaline.) This change also allows the precipitation of the mobile Fe$^{2+}$ as goethite as shown on Fig. 4.30 in chapter 4.

Iron carbonates such as siderite are also absent from the iron precipitates. This suggests that the conditions of precipitation were oxidising as iron carbonates would only be stable at reducing conditions (Klein & Hurlbut 1993.)

Assuming these pH-Eh conditions to be correct, the following model is proposed for the formation of these Ferric iron precipitates, and is shown schematically in Fig. 5.28.

Fig. 5.28: A schematic model of the stages of the ferric iron precipitate interlayered with dissolved and re-precipitated calcite

When the Fe$^{3+}$ laden, acidic descending fluids (Fig. 5.28A) eventually reached the footwall limestone, dissolution of the carbonates would have neutralized the acidic fluids (Fig. 5.28B), forcing precipitation of the iron under oxidising conditions and a high overall water activity. The Fe$^{2+}$ would have been oxidised into Fe$^{3+}$ and precipitated as ferrihydrite, eventually forming goethite under the high water activity conditions, interlayered with calcite layers. Each paired goethite and calcite layer may represent a fresh wave of acidic bleaching water being neutralised and deposition of the calcium carbonate followed by the iron oxides (or vice versa), or they formed from a single depositional event in which geochemical self-organisational via the Ostwald-liesegang supersaturation-nucleation-depletion cycle thought to be responsible for liesegang band formation (Ortoleva et al., 1987.) This produced a layered goethic-calcitic deposit (Fig. 5.28C). Where bleaching occurs along fractures and faults, neutralisation of the acidic fluids is
achieved through mixture and dilution with fresh, pH neutral meteoric water flowing along the fractures, encouraging goethitic fracture fills, without calcite (see Fig. 5.25.)

5.5.7. Implications for exploration

The results of this investigation have important implications for bauxite exploration within the Parnassos-Ghiona zone and similar karst-associated bauxite worldwide. These are summarised below:

1. Sulphide-bearing bauxites are only found within the late Cretaceous third horizon bauxites of Mount Iti of the Parnassos-Ghiona zone, primarily towards the top of the bauxite ore bodies. The main sulphide is pyrite, and can occur in concentrations of up to 20-30% of the bauxite.
2. Coal overlying the ore bodies is an indication that sulphide minerals will be present in the underlying bauxite. Coal deposits found at the footwall-hangingwall limestone contact is an indication of proximity to a bauxite ore body. Sulphide minerals may be present in bauxite without an overlying coal layer.
3. Sulphide minerals were at one time present within Mount Ghiona. Deeper, less exposed bauxites may still contain sulphide minerals. These will again be found towards the top of the ore bodies.
4. Oxidation of the sulphide minerals has caused iron mobilization and removal from the bauxite. This leaves a bleached bauxite significantly enriched in hydrous aluminium oxides.
5. Bleaching is more extensive within Mount Ghiona than Mount Iti, and is intensified by faulting, particularly normal faulting, in both regions.
6. The re-mobilized iron that has been re-precipitated as goethite rich deposits at the base of the ore body can be avoided during mining with careful planning. The goethite found within faults and fractures is harder to avoid, being within the ore body itself, however, its easily identifiable appearance should make separation during processing possible by hand.
7. Green chloritised bauxite within the third horizon is also evidence of epigenetic remobilization of iron, and may be in close proximity to bleached bauxite.
5.6 Conclusions

This chapter sought to understand the formation history of the sulphide minerals within the Parnassos-Ghiona bauxites and their relative paragenesis of the various sulphide occurrences, and their role in epigenetic processes affecting the bauxite ore.

The sulphide minerals are found within the third horizon ore deposits of Mount Iti. The sulphides formed within swampy conditions developed above the ore bodies after their deposition. Sulphides initially grew as disseminated, euhedral pyrite minerals within the soft bauxite, through bacterial reduction of seawater sulphate within a primarily open system. Once all of the freely available iron within the bauxite matrix was consumed, pyrite formation continued as a replacement process, utilizing the hematite rich cortices of pisoliths and bauxite clasts, which continued through closure of the sulphate system. Finally, either diagenetic fracturing or tectonic activity produced fractures in the bauxite, which allowed pore fluids, enriched in heavy sulphur isotopes, to be utilized either by bacterial reduction or possibly by thermochemical reduction to form iron sulphide veinlets.

Epigenetic oxidation of the bauxites by meteoric waters percolating along faults and fractures promoted destruction of these sulphides creating sulphuric acid. This acid leached through the bauxite, mobilizing the iron as Fe$^{2+}$, leaving white bleached bauxites, enriched in hydrous aluminium oxides. The mobilized iron was then deposited as goethite in fractures within the bauxite, and at the base of the ore bodies through neutralisation of the acidic fluids via interaction with fresh meteoric waters, or by reaction with the alkaline carbonate footwall rocks. Re-oxidation of Fe$^{2+}$ to Fe$^{3+}$ in a neutral, oxygen rich environment with a high water activity encouraged the precipitation of goethite, interlayered with calcite from the dissolved carbonates. Re-precipitation of the mobilized Fe$^{2+}$ within reducing environments within the bauxites is the likely cause of epigenetic chlorite mineral formation also seen within the third horizon bauxite.

References


Chapter 6 – The relationship between the bauxite ore bodies and the carbonate units of the Parnassos-Ghiona Zone

6.1. Introduction

For the purposes of bauxite exploration, it could be assumed that the ore bodies represent local anomalies, in terms of their mineralogical, geochemical and geophysical properties, along the three bauxite-bearing horizons within the Jurassic-Late Cretaceous limestone sequences of the Parnassos-Ghiona zone. It was clear during field investigations that there is a distinct zone of interaction and alteration between the bauxites and the adjacent limestone bodies, of varying degree and extent. This chapter aims to investigate and model the overall geological and geochemical ‘fingerprints’ of the bauxite, by examining the interaction between the bauxites and limestone host rocks at various stages in the ore genetic process, and systematically examining the lithogeochemistry of the limestone host rocks with distance from the bauxite ore bodies. Through this, the work aims to aid exploration by providing a model of potential “pathfinder” elements and geological features.

6.2. Literature Review

6.2.1. Karstified limestone and bauxites

Karstified limestone plays host to around 20% of the world’s bauxite deposits. Bardossy (1982) states that karst structures have four roles in bauxite deposit formation:

1. They act as traps to collect bauxite, clay or other parent material.
2. They provide good drainage conditions, and can concentrate water flow, which benefits alumina enrichment.
3. The associated weakly alkaline conditions are favourable for bauxite formation and preservation.
4. The depressions protect the bauxite material from subsequent erosion.

The karstification of the limestones within karst bauxite deposits was originally thought to occur before bauxite deposition, however some studies have indicated that post-bauxitisation subsurface corrosion could play a much more important role in karst development under bauxite deposits. Petrascheck (1989) identifies the necessity for this process within the bauxites of southern Europe, including Greece, suggesting that the original degree of karstification was much less than observed at present, and that post bauxite karstification will have extended and
deepened the karst features, many of which will contain bauxite. Valeton (1972) (and references there in) identify four separate karstification episodes in karst bauxites in France:

1. Main, pre-bauxite karstification.
2. Continued karstification during sedimentation of the bauxite.
3. Local karstification immediately following diagenesis.
4. Youngest karstification, controlled by modern day topography.

Economoupoulos et al. (1993) described in the Parnassos-Ghiona bauxites, at a local mine scale, the non-bauxite bearing karstic structures (possibly formed after bauxite formation), as ‘horizontal and sub-horizontal channels, irregularly branching and interconnected by narrow passages, widening out into great voids passing into narrow pipes. They are characterised by recurrent zigzags and bizarre shapes due to the complex system of joints and faults dissecting the limestones.’

6.2.2. The Hangingwall and Footwall

Some attention has already been given to the features of the hangingwall and footwall limestones surrounding the bauxites in Chapter 2. Key features are re-summarised here:

**Hangingwall limestones**
- The hangingwall of the second horizon bauxites is medium grey, well bedded and can be interbedded with clay layers. The hangingwall immediately above the bauxite is typically a pink coloured bauxitic marl. Evidence for debris flows with carbonate rip up clasts in the first few layers above the bauxites have also been found (See chapter 2).
- The hangingwall of the third horizon around Mount Iti is typically dark grey in colour with a distinctive petroleum smell caused by a high content of organic matter. This becomes more medium grey further up the stratigraphic column. Within Mount Ghiona the hangingwall is typically medium grey in colour, with a lack of significant organic matter. The limestones of both Mountains contain abundant rudist bivalve fossils.
- The hangingwall-bauxite contact of both horizons can often be sheared, sometimes with thick layers of limestone-bauxite breccia (up to 1 metre), growth of new calcite, and bauxite alteration due to circulating fluids.

**Footwall limestones**
- The footwall limestones of the second horizon are pale grey to near white in colour, massively bedded, and overall weakly karstified.
The footwall limestones of the third horizon are also pale grey-white and massively bedded. Karstification is more intensive with sinkhole and channel karst structures identified. In both Mount Iti and Mount Ghiona, alteration of the footwall has been identified that produces a yellow, red, brown discolouration, silicification, and pseudo-brecciation of the footwall.

Laskou and Economou-Eliopoulos (2013) determined that the footwall limestones of the Greek bauxites have $\delta^{13}\text{C}_{\text{PDB}}$ isotopic values of between -0.8 to -4.8‰ and $\delta^{18}\text{O}_{\text{PDB}}$ isotopic values of between -5.9 to +3.8‰. More specifically, their analysis of second and third horizon bauxite footwall limestones from the Mount Parnassos deposits produced values of -0.8 to +0.4‰ $\delta^{13}\text{C}_{\text{PDB}}$ and -0.8 to -0.9‰ $\delta^{18}\text{O}_{\text{PDB}}$ for the second horizon; and -5.9 to -3.9‰ $\delta^{13}\text{C}_{\text{PDB}}$ and -3.0 to -1.7‰ $\delta^{18}\text{O}_{\text{PDB}}$ in the third horizon. The more negative carbon isotopic values in the third horizon were attributed to the increased deposition of organic matter and subsequent oxidation, encouraging fractionation of $^{12}\text{C}$ in $\text{CO}_2$.

**Alteration zones in Mineral Exploration**

Many mineral deposits, particularly those formed either partially or wholly through epigenetic processes, often have around them a zone or zones of host rock alteration, marked by a combination of changes in colour, mineralogy, geochemistry and texture. These zones can be of considerable lateral extent, and can be of great value to exploration (Moon et al. 2006.) Part of this method of exploration is the delineation of ‘pathfinder’ elements, elements that occur in higher concentrations close to areas of mineralization in comparison to normal background concentrations.

As karst bauxites are residual mineral deposits, they are not typically associated with the epigenetic processes required to produce alteration zones in the host rocks. However, the bleaching process described in chapter 5 is an example of an epigenetic process that generates element mobility and re-distribution beneath the ore bodies and within the adjacent footwall limestones of the third horizon. The alteration of the underlying limestone may be detectable in a similar way to other alteration haloes around non-residual ore deposit types. Geochemical differences between the hangingwall and footwall limestones may also prove useful in:

(a) Identifying the bauxite horizons, as geochemical signatures may change around the ore bodies, and

(b) Identifying stratigraphic locations as the hangingwall and footwall limestones may show clear geochemical differences, even away from the bauxites.
6.3. Results

6.3.1. Field Observations

The limestones surrounding the bauxites vary lithologically with proximity to the bauxites. These observable variations are summarised here.

Figure 6.1: The distinctive features of the hangingwall and footwall limestones surrounding the second horizon ore bodies. A. A typical example of the karstified footwall surface with in-fills of red bauxite. B. A bauxite-filled karst fissure penetrating for 2 metres beneath the main ore body (hammer for scale). C. Distinctive dendritic manganese oxide minerals on footwall surfaces and fractures beneath the bauxite ore bodies. D. The distinctive well bedded and often discoloured hangingwall limestone above a second horizon ore body. E. Small lenses of gypsum within the footwall immediately beneath the hangingwall-footwall contact away from a bauxite ore body. Leaching of this gypsum has left distinctive voids in the rock. F. Clayey and iron rich limestones at the hangingwall-footwall contact away from a known bauxite ore body.
**Second horizon bauxites**

The second horizon footwall limestone is generally pale grey, although it can have a red/pink colour when close to the bauxites, creating a visibly altered zone of up to 10cm in thickness. The footwall is only gently karstified overall; however the karst surface is jagged at the metre scale (shown in Fig. 6.1 A), often penetrated by fissures filled with bauxite material that extend down for several metres beneath the main bauxite body, an example of which is shown in Fig. 6.1 B. The second horizon footwall also contains clay filled fractures and dendritic growths of black/brown manganese oxide minerals (Fig. 6.1 C.)

The hangingwall directly above the second horizon is typically well bedded, medium grey limestone. Close to the ore bodies it can contain layers of bauxite marl and higher clay content (shown in Fig. 6.1 D) and in Mount Iti it is inter-beded with thin clay units for 10 to 20 metres vertically above the contact. In Mount Ghiona thin clay seams (<1cm) were found at the hangingwall-footwall contact when traced away from the bauxites for 20-30 metres. In Mount Iti, small gypsum lenses were found just beneath the second horizon contact around 30 metres away from a known bauxite deposit. These gypsum lenses have often been dissolved and leached out leaving distinctive voids in some of the limestones (shown in Fig. 6.1 E.) In some places in Mount Iti, at a similar distance, the second horizon contact was also marked by red stained limestone and clayey lenses (shown in Fig. 6.1 F); however this clay was irregular and non-continuous.

**Third horizon bauxites**

As previously described in chapter 2, the third horizon hangingwall above the ore deposits in Mount Iti is dark grey/black with a strong petroleum smell when broken (shown in Fig. 6.2 A and B.). In Mount Ghiona it is a medium grey colour without the high organic content. Therefore the bituminous limestones in Iti may be linked to the coal deposits found above the bauxites. Higher in the stratigraphy the hangingwall loses its organic content and becomes medium grey, similar to that of Mount Ghiona.

The coal deposits found in Iti and clay deposits found in both Iti and Ghiona represent the end of bauxite deposition during the late Cretaceous and mark the boundary between the bauxite horizon and hangingwall. These clays and coals have been seen to extend outside of the ore bodies for several metres, however it is unknown if the clay or coal exists in solid deposits without an underlying bauxite body. The root fossils found in Iti (see Chapter 2) suggest that the organic material accumulation was at least partially in-situ or from nearby sources. Sufficient plant growth for this accumulation is unlikely to have been possible on the bare karstified limestone and would have required the soft, water retaining, bauxitic clay and soil for root stabilization and organic
matter preservation. With this in mind it is likely that the coal deposits will be found in association with the bauxites in the Parnassos-Ghiona zone.

Figure 6.2: A selection of photographs showing the distinctive features of the third horizon hangingwall and footwall limestones. A. Layers of clay and black organic rich limestone directly above a third horizon ore body in Mount Iti. B. Black limestone with red iron rich fractures above a heavily faulted ore body. C. Footwall limestone with an in-situ surface breccia of tan/yellow coloured altered limestone clasts and red/pink bauxite. D. Hangingwall limestone from Iti with distinctive black patches for up to 15-20 metres from an ore body. E. Heavily altered red limestone showing mottled colour and banding from beneath an ore body in Iti. F. Heavily altered brecciated footwall limestone with distinctive parallel banding indicating that the alteration occurred after tectonic activity.
The third horizon footwall karst contact is smooth, and heavily undulating, often with a pseudo breccia/conglomerate of bauxite and limestone forming at the footwall’s surface (sees Fig. 6.2 C.) Like the second horizon karst surface, the third horizon footwall is also penetrated by bauxite filled fissures for several metres.

Typically the footwall limestone surrounding the third horizon bauxite ore bodies exhibits different degrees of alteration depending on the distance from the ore body. The normally pale grey micritic limestone develops dark patches and a mottled appearance with proximity to an ore body, observed to be up to 30 metres away from a known ore body (shown in Fig. 6.2 D) Closer to and beneath the bauxites the limestone typically take on a tan-yellow colour and, in areas of intense alteration, red/brown colours. All of the altered limestone appears mottled. The alteration can often display layered patterns, shown in Fig. 6.2 E and F. This suggests a pervasive, repetitive alteration process. As the banding within the breccia clasts in Fig. 6.2 F are all parallel, it is can be assumed that the alteration phase occurred after brecciation and faulting. This alteration is seen intensively in both Mount Iti and Mount Ghiona third horizon ore bodies.

Silicification was also observed near the footwall contact in heavily altered zones, creating a harder limestone with conchoidal fracture, found in limestone directly beneath the bauxites. Dendritic manganese oxide and iron oxide growths are common in fractures and on exposed surfaces in both the bauxite and the footwall limestones.

The heavily altered yellow/red limestone is seen beneath the ore bodies to a vertical distance of 2 to 3 metres and either side of the ore bodies for an equal distance. It is also most intense around bauxites that have undergone extensive bleaching as described in chapter 5.

The ‘Geological Fingerprint’ of the Parnassos-Ghiona bauxites

Based on these observations and previous research on these deposits three summary models are presented here to show the distinctive features of the second and third horizon ore bodies and their host rocks, and the extent and characteristics of the alteration zone around the ore bodies, for both Mount Iti and Mount Ghiona, to aid understanding of ore genetic processes and bauxite exploration. These are presented in Figs. 6.3 to 6.5.
Figure 6.3: Summary model for second horizon ore bodies in both Mount Iti and Mount Ghiona, showing the features in the hangingwall and footwall limestones that are present close to the bauxites, and the extent and characteristics of the alteration zone around the ore bodies.
Figure 6.4: A geological model for third horizon ore bodies in Mount Iti, showing the features in the hangingwall and footwall limestones that are present close to the bauxites.
Figure 6.5: A geological model for third horizon ore bodies in Mount Ghiona, showing the features in the hangingwall and footwall limestones that are present close to the bauxites.
6.3.2. Geochemical variations in the limestones surrounding the bauxites

A series of geochemical transects of the hangingwall and footwall limestones for both the second and third horizon bauxites are presented here to show element variability and enrichment associated with the bauxite ore bodies. The data were collected using PXRF methods along vertical and horizontal transects.

**Vertical Variability in Trace Elements**

**Second Horizon**

The second horizon ore bodies are represented in this investigation by an ore body in Mount Ghiona exposed at the surface, with over 40 metres of footwall exposed beneath, and around 4.5 metres of accessible exposed hangingwall above. Transect V1 shown in Fig. 5.6 represents a 4.5 metre vertical transect above the Makrilakoma, second horizon ore body, in Makrilakoma Valley, Mount Ghiona. Each point represents the average of at least 2 analyses. The purple shaded area represents the location of the bauxite ore body in relation to the transect.
metre transect in the hangingwall directly above the second horizon bauxite, the data for this graph are presented in Table 5.1. The data show some moderate variability in concentration of each element analysed in the units above the second horizon bauxite, however the only distinctive change occurs within 30cm of the top of the ore body. Fe, K, Ti, Mn, Ni, Zn, As and Zr all show an increase in concentration within 30cm of the top of the bauxite ore body. The most distinctive changes are in Fe which increases from around 10,000ppm to 75,000ppm at its maximum, Mn which increases from <600ppm up to 35,000ppm and Ni from <100ppm up to 1500ppm in the first 20cm above the ore body. Sr is the only element to show a decrease in proximity to the bauxite, dropping from 180-120ppm to 46ppm above the ore body.

The geochemical analysis of the footwall of the second horizon is presented in transect V2 in Fig. 6.7. This transect represents a section of 40 metres beneath the bauxite, with analyses on an 8 metre spacing, with each point on the diagram representing the average of at least 2 analyses. The data are shown in Table 6.2. This analysis detected only a few elements compared to transect 1; the omitted elements occurred below the detection limits of the PXRF used. The concentrations

![Element Concentration along transect V2 (ppm)](image)

Figure 6.7: Geochemical variation along a 40 metre vertical transect in the footwall limestone beneath the Makrilakoma, second horizon ore body, in the Makrilakoma Valley, Mount Ghiona. Each point represents the average of at least 2 analyses. The purple shaded area represents the location of the bauxite ore body in relation to the transect.
of the three elements detected are much lower within the footwall when compared to the hangingwall. The variation seen in Fe is the greatest in the transect, however it only represents a change of around 300ppm in total, which is insignificant when compared to the variation observed in the hangingwall. Sr concentrations are between 40-90ppm, and Ni is between 33 and 45ppm.

**Third Horizon**

The third horizon is represented here by a single transect that incorporates the hangingwall-footwall contact immediately next to a third horizon ore body in Mount Iti (Fig. 6.8). Each point represents an average of at least 2 analyses, and the data are shown in table 6.3.

Compared to the second horizon footwall limestone, the third horizon footwall has a higher detectable trace element concentration and element range overall. Within the hangingwall, most trace elements analysed show an increase in concentration within 50cm of the bauxite. As within the second horizon, elements notably enriched include Fe, Mn and Ni, as well as Cr. Within the first metre of footwall beneath the bauxites, Fe was recorded in concentrations greater than 63,000ppm (6.3%), which declined to around 20,000ppm a metre beneath the contact. Mn was...
measured at 873ppm close to the contact, but decreased to between 300-350ppm within 0.5m of the contact. This is still considerably higher however than the 17-24ppm Mn concentrations found in the hangingwall. Ni concentrations are highest at the contact and within the footwall, reaching 355ppm, compared to 47-54ppm in the hangingwall. Cr showed an interesting variation with detectable concentrations of 200-390ppm at the bauxite contact and within the first 0.5 metres of hangingwall, dropping to <33ppm outside of this zone. Arsenic (As) is also higher in the footwall, reaching maximum recorded values of 37ppm. Sr again shows a difference in concentration between the hangingwall and footwall with values between 141-210ppm in the hangingwall, decreasing to between 45-60ppm in the footwall.

All of the Sr values measured in the vertical transects show a similar pattern of variation between the hangingwall and footwall in each horizon. In the third horizon hangingwall, Sr averaged around 175ppm and in the footwall 56ppm, which is very similar to those of the second horizon at 136ppm and 67ppm in the hangingwall and footwall respectively.
**Table 1**: The data and statistical analysis of the element concentrations across transect V1 presented in figure 6.

<table>
<thead>
<tr>
<th>Transect Distance Metres</th>
<th>K (ppm)</th>
<th>Ti (ppm)</th>
<th>Mn (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>Zn (ppm)</th>
<th>As (ppm)</th>
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**Table 2**: The data and statistical analysis of the element concentrations across transect V2 presented in figure 6.

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<th>Fe (ppm)</th>
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**Table 3**: The data and statistical analysis of the element concentrations across transect V3 presented in figure 6.

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Horizontal Variation

Due to issues of accessibility, and the apparently greater intensity and extent of alteration beneath the third horizon ore bodies, horizontal transects were focused on third horizon ore bodies. Two horizontal transects were analysed, beginning beneath two separate bauxite ore bodies in Mount Iti and extending away from the ore bodies. Of the elements analysed using the portable X-ray fluorescence technique, only some occurred in concentrations that could be accurately measured and showed quantifiable variations. Of these, Iron was by far the most reliable element, with nickel and strontium also showing some variations close to ore bodies.

The results from transect H1, presented in Fig. 5.9, show the concentrations of iron, nickel and strontium within the third horizon footwall limestone in Mount Iti. This transect is 50 metres long, at a distance of 2 metres from base of the ore body and 3 metres from the third horizon hangingwall-footwall contact. The measurements were made on a 2 metre spacing. The results are shown in table 5.4 and each data point is the average of at least 2 readings at each location.

The footwall limestone directly beneath the bauxite contains Fe concentrations between 1465 ppm and 10628 ppm, averaging 5181ppm. The graph suggests that the ‘high iron’ footwall zone extends for around 10 metres away from the edge of the ore body, where the Fe concentration sharply drops to an average of 660ppm, ranging between 316ppm and 1542 ppm, and remains at that concentration for at least a further 22 metres until the end of the transect.

Ni concentrations shows a similar pattern to Fe along the transect, though at a greatly reduced intensity, dropping from an average of 35ppm, with range 24ppm to 54 ppm, down to an average of 23ppm with range 12ppm to 35ppm at around the same 10 metre distance from the ore body edge. Fe and Ni concentrations along this transect show a positive correlation with an $r^2$ value of 0.53. Sr concentrations along the transect show a different pattern, having a lower concentration beneath the ore body compared to the more distant limestones, increasing from 57ppm average, with range 35 ppm to 91ppm, to a zone of 84ppm average with a range of 49ppm to 134 ppm at around 18 metres from the ore body. Sr does not show any correlation with either Fe or Ni.

Most other elements analysed were at concentrations below the PXRF detection limit, however individual analyses did identify detectable concentrations of some elements. Several analyses beneath the ore body identified up to 51ppm Cr and 64ppm As, both of which were not detected outside the limits of the ore body. Ti was identified at concentrations of up to 5896ppm beneath the ore body, whereas away from the ore the maximum concentration recorded was 374ppm. Mn was found at concentrations of up to 68ppm, declining to 38ppm outside the ore also.
In transect H2, presented in Fig. 5.10, both the hangingwall and footwall were analysed. The transect is 100 metres long. The hangingwall data were taken at a distance of 2 metres above the third horizon contact and the footwall data were taken at 3 metres below the contact and 2 metres from the base of the ore body, where present. The measurements were made on 5 metre spacing. The results are shown in tables 5.5 and 5.6, each data point is the average of at least 2 readings at each location.

The footwall shows a similar elemental distribution to transect 1. Beneath the ore body and within 10 metres of the ore body, the footwall Fe concentration averages 2383ppm, with a range from 923ppm to 4124ppm. At a distance of around 35 metres from the edge of the ore body the Fe concentration declines to an average of 672ppm, and then drops again at 50 metres distance to an average of 310ppm. Fe in the hangingwall remains relatively constant along the whole transect, averaging 689ppm. Between 35 and 50 metres distance along the transect H2 (15 to 30 metres from the edge of the ore body), Fe was undetected. It is unknown whether this is a true geological feature of the footwall, an issue with the sampling, or an equipment malfunction, however at the same distance on transect H1 iron is detected in reliable concentrations.

Sr increased in concentration beneath the bauxite ore body, from 62ppm up to 185ppm, which is the opposite to the pattern in transect H1 which showed higher Sr at distance from the ore body. Ni concentration did not show any significant variation along this transect, remaining at an average of 26ppm, with a range of between 15 to 35ppm.

Where Mn was detected, it occurred at values of between 46-69ppm in the footwall and 48-90ppm in the hangingwall, Zr was detected at concentrations of between 10-20ppm in both the hangingwall and footwall and Ti occurred at concentrations of between 283-416ppm in the footwall (and was not detected in the hangingwall). No major variation with proximity to the ore body was seen in any of these elements.

Together these transect show that the footwall limestone shows a greater variation in element concentration than the hangingwall with increasing proximity to an ore body. Within the footwall, iron shows the greatest variation and has the best potential as a pathfinder element with several distinctive and abrupt changes in average concentration identified up to 60 metres from the ore bodies. Within 3 metres of the ore bodies, elements such as manganese, titanium, nickel and strontium show significant increases that can be used in conjunction with iron to locate an ore body.
Figure 6.9: Variation of Fe, Ni and Sr along a 50 metre, horizontal transect in the footwall limestone beneath and away from a third horizon bauxite ore body in Mount Iti. Each analysis is the average of at least 2 analyses. The purple shaded area represents the area beneath the bauxite ore body. Note logarithmic y-axis scale for iron.
Figure 6.10: The variation of Fe, Ni and Sr along a 100 metre, horizontal transect in the hangingwall and footwall limestones beneath and away from a third horizon bauxite ore body in Mount Iti. Each analysis is the average of at least 2 analyses. The purple shaded area represents the area beneath the bauxite ore body. Note logarithmic y-axis scale for iron and strontium.
Table 6: The data and statistical analysis of the element concentrations across transect H2 (footwall), presented in figure 6.10.

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<th>Transect H2 Hangingwall analysis data</th>
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<td><strong>Distance Metres</strong></td>
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Table 6.4: The data and statistical analysis of the element concentrations across transect H1 presented in figure 6.9.

Table 6.5: The data and statistical analysis of the element concentrations across transect H2 (footwall), presented in figure 6.10.

Table 6.6: The data and statistical analysis of the element concentrations across transect H2 (hangingwall), presented in figure 6.10.
6.3.3. Trace element concentrations

The trace element concentrations of three samples of third horizon footwall limestones were analysed via ICP-MS. The three samples were taken from Mount Iti and represent the unaltered pale grey footwall typical of the Parnassos-Ghiona zone, the black mottled footwall found in association with many of the ore bodies, particularly within Mount Iti, and the intensely altered red/yellow limestone found beneath ore bodies that have undergone ore bleaching. The trace element concentrations of these three samples are compared in Fig. 5.11, and the REE concentrations of the samples are presented in section 5.4.3.

There is little difference between the un-altered limestones and the limestone with mottled black patches. The altered limestone however has been greatly enriched in V, Ni, Zn, with minor enrichment in Sc, Cr, As, Sr, Ba and Pb. There has been no significant change in Th, U, Mo, Nb, Cu or Zr during this process.

The variability in trace element concentrations between non-altered and altered limestones

Figure 6.11: The trace element concentrations of three third horizon footwall limestone samples representing non-altered limestone, black mottled limestone and red/orange altered limestone to investigate the geochemical changes associated with footwall alteration. Each trace element pattern is representative of 1 sample.
6.3.4. The Rare-Earth Geochemistry of the altered footwall limestone

The REE contents for the three third horizon footwall limestones are presented in Fig. 5.12 below. The REE total concentration is low for all three samples; however it is clearly increased through alteration.

The REE pattern for the un-altered and altered limestones shows a clear increase in the total REE concentration through footwall limestone alteration. The ratios of LREE/HREE and LREE/MREE

![Comparison of REE concentrations of unaltered and altered footwall limestones](image)

<table>
<thead>
<tr>
<th></th>
<th>Unaltered</th>
<th>Limestone with black patches</th>
<th>Altered red/orange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total REE (excluding Y) concentration (ppm)</td>
<td>11</td>
<td>33</td>
<td>243</td>
</tr>
<tr>
<td>LREE/HREE (excluding Y)</td>
<td>3.96</td>
<td>2.86</td>
<td>1.87</td>
</tr>
<tr>
<td>LREE/MREE (excluding Y)</td>
<td>2.12</td>
<td>1.50</td>
<td>1.00</td>
</tr>
<tr>
<td>MREE/HREE (excluding Y)</td>
<td>1.87</td>
<td>1.90</td>
<td>1.88</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>REE pattern anomaly</th>
<th>Unaltered</th>
<th>Limestone with black patches</th>
<th>Altered red/orange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>0.97</td>
<td>0.50</td>
<td>0.57</td>
</tr>
<tr>
<td>Eu</td>
<td>0.65</td>
<td>0.69</td>
<td>0.65</td>
</tr>
<tr>
<td>Y</td>
<td>1.18</td>
<td>1.26</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Figure 6.12: A comparison of the REE concentrations of unaltered and altered third horizon footwall limestone. Each REE pattern is representative of 1 sample. The accompanying tables show the total REE concentration and the ratios of LREE, MREE and HREE to reveal fractionation across the REE group, and the intensity of the anomalies of Ce, Eu and Y.
both indicate a greater enrichment of MREE and HREE relative to LREE in the altered footwall.

There is a strong positive anomaly of Y in the altered limestone and the partially altered limestones and strong negative anomalies of Ce and Eu in the altered limestones, and to a lesser degree within the partially altered limestones. Quantifications of these three anomalies, achieved through ratioing the measured concentration against an interpolated value using the geometric mean of the two elements either side of the anomaly, are shown in Fig. 6.13. Values greater than 1.0 indicate a positive anomaly, whereas values less than 1.0 indicate a negative anomaly.

The quantified values suggest that the negative Eu anomaly is constant in the limestone, and is not affected by the alteration. The negative Ce anomaly does vary in intensity, being almost absent in the unaltered limestone, becoming intensified by alteration. This suggests that either Ce was removed from the limestone, or that the alteration fluid itself was depleted in Ce, thereby enriching the limestone in REE other than Ce. The positive Y anomaly is present in all three samples; however it clearly increases in intensity in the altered limestones, indicating an yttrium-rich alteration fluid which is typical of fractionation through fluid-rock interactions.

6.3.5. Results Summary
The results presented in this chapter have shown that the bauxite ore bodies of the second and third horizons have a distinctive geological and geochemical ‘fingerprint’, which can be linked to processes during deposition and burial, and diagenetic and epigenetic phases. The significant results have been summarised in table 6.7 below.

6.4. Discussion

6.4.1. The alteration of the footwall limestones
Significant alteration of the footwall limestones has been found, mainly within the third horizon footwall limestones, close to bauxite ore bodies, in particular those that have undergone significant iron remobilization associated with processes of ore bleaching.

The alteration of the footwall typically occurs in zones, being intense close to the ore body, and depleting with increasing distance as would be expected. The intensive alteration close to the ore bodies is characterised by increased contents of Fe, from around 300ppm in un-altered limestone, up to >60,000 ppm beneath the ore bodies and increased Ni, from 20 ppm up to >350 ppm beneath the ore bodies. Sr and Mn have also been shown to have increased beneath the ore bodies in the most intensely altered limestones.
Trace element analysis has also indicated a significant enrichment in Ni within the altered limestones, as well as increases in V and Zn, and to a lesser extent, Cr, Sr and Pb, as well as enrichments in REE. When the trace element concentrations are compared with those detected within the ferric iron precipitates from the base of the bauxite (see Fig. 6.14), there is a clear and strong similarity in the patterns of the two lithologies suggesting a close genetic relationship between bleaching, iron re-precipitation and footwall limestone alteration.

The relative differences in As concentration between the altered limestone and the ferric precipitate can be explained by the affinity for As to precipitating goethite (Pedersen et al. 2006), which scavenged the As before it was able to penetrate the footwall limestone. Similarly, the relative difference in Sr concentrations can be explained by the background concentrations of around 100ppm Sr within the footwall limestone.
<table>
<thead>
<tr>
<th>Horizon</th>
<th>Geological Unit</th>
<th>Location</th>
<th>Distinctive Features close to bauxite ore bodies</th>
<th>Geochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Third</td>
<td>Hangingwall</td>
<td>Mount Iti</td>
<td>Dark grey, bituminous limestone. Thin coal seams and clays present 1-2 metres above bauxite.</td>
<td>Increase in Fe, Mn, Ni, and Cr within 50cm of bauxite contact. Sr content of 100-200ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount Ghiona</td>
<td>Thin, sometimes organic rich, clays immediately above bauxite. Medium grey limestone.</td>
<td>Not directly studied, assumed similar to Mount Iti.</td>
</tr>
<tr>
<td></td>
<td>Footwall</td>
<td>Mount Iti</td>
<td>Dark red, orange, yellow, heavily altered limestone, detectable up to 30 metres from ore body.</td>
<td>Increase in Fe content, detectable up to 50 metres away. Higher Ni, Sr and Mn within 3 metres of the bauxite. Order of magnitude increase in total REE close to bauxite. Sr content of 0-100ppm.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount Ghiona</td>
<td>Dark red, orange, yellow, heavily altered limestone, some silicification.</td>
<td>Not directly studied, assumed similar to Mount Iti.</td>
</tr>
<tr>
<td>Second</td>
<td>Hangingwall</td>
<td>Mount Iti</td>
<td>Layers of bauxite marl within 1 metre above bauxites, gastropod fossils found.</td>
<td>Not directly studied, assumed similar to Mount Ghiona.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount Ghiona</td>
<td>Layers of bauxite marl within 1 metre above bauxites</td>
<td>Increase in Fe, K, Ti, Mn, Ni, Zn, As and Zr within 30cm of the top of the bauxite ore body. Decrease in Sr within the same distance. Fe present in 10,000ppm content for at least 5 metres above bauxite.</td>
</tr>
<tr>
<td></td>
<td>Footwall</td>
<td>Mount Iti</td>
<td>Pale grey limestone, some red staining alteration</td>
<td>Not directly studied, assumed similar to Mount Ghiona.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mount Ghiona</td>
<td>Pale grey limestone, some red staining alteration</td>
<td>Increase in Fe within 15 metres of base of ore body up to 300ppm</td>
</tr>
</tbody>
</table>

Table 6.7: A summary of the main results of this chapter
Geochemical Alteration as a tool for ore body exploration

The footwall alteration seen around the third horizon is distinct enough and pervasive enough to potentially be used as an exploration tool. Using the data from transects H1 and H2, presented in this chapter, the model for geochemical zonation of some of the most variable elements was created and is presented in Fig. 6.14. For this model average concentrations were used as an approximate guide to the expected trace element concentrations at variable distances from the ore body. The boundaries were set based on measured changes within the transects described above.

The model shows that the bauxite can influence the footwall geochemistry up to 50 metres away from the ore body margin. The hangingwall in contrast only shows variability within 50 cm of the ore body and so would not contribute to a geochemical exploration program.

The extent of the footwall alteration is strongly dependant on the degree of bleaching within the ore body and iron remobilization. It is therefore expected that the alteration zones will be larger within Mount Ghiona where the bleaching is more extensive. The extent of the alteration zone may have some connection to the size of the ore body as with a greater volume of bauxite, there

Figure 6.13: A comparison of the trace element concentrations of ferric iron precipitate and altered footwall limestones to show the genetic relationship between the two. Note the logarithmic Y-axis scale.
is more iron to leach. However the size of the ore body does not necessarily correlate with the degree of bleaching.

The increase in trace element concentration within the first 30cm of limestone above the second horizon bauxites is interpreted as being due to mixing of the carbonate material with loose bauxite particles at the ore body surface during marine transgression and limestone formation. The evidence for debris flows in the first few layers discussed in chapter 2, and in section 6.2.2 of this chapter, also suggests local, turbulent conditions suitable for bauxite-limestone mixing. This period was short lived, having swiftly developed into calmer conditions in which the purer, low trace element-hangingwall limestone, seen in the rest of the geochemical profiles, formed.

6.5. Conclusions and further work

This investigation sought to identify the characteristics of the second and third horizon hangingwall and footwall limestones in the Parnassos-Ghiona zone bauxite ore body group, with the aim of understanding the interaction between the limestones and bauxites during the bauxite ore genesis, and to identify potential tools for improved exploration efficiency.

1. Geological variability around ore bodies can be used to locate the bauxites. The well bedded limestones and interlayered clays, as well as several layers of bauxitic marls acting as a ‘transition’ zone between bauxites and hangingwall limestones are local to second horizon bauxites in Mount Iti and Ghiona. Dark-grey to black, bituminous rich limestone and interlayered coal deposits are distinctive of third horizon bauxites in Mount Iti. Third horizon bauxites of Mount Ghiona can have clay rich layers above the ore bodies. Distinctive footwall alteration, particularly beneath ‘bleached’ bauxites, is common to ore bodies in Mount Iti and Ghiona.

2. Third horizon footwall alteration is primarily related to the mobilization and redistribution of iron through ore body bleaching described in chapter 4. This has led to zonation of iron within the footwall that can be identified up to 50 metres from the ore bodies, with an overall increase from around 300ppm away from the ore body up to around 60,000ppm (6%) iron in the 2 metre zone around the bauxite.
Figure 6.14: A model for third horizon limestone geochemical alteration zones, with proximity to the bauxites. The model is based on data presented in transects H1, H2 and V3. The elemental variation shows potential for use in geochemical exploration. Concentrations presented in this model (as subscripts to each elemental symbol) are given in ppm.
The altered footwall is also enriched in Ni, V and Zn, and to a lesser intensity Cr, Sr and Pb and REE. Comparison with the ferric iron precipitate found at the base of ore bodies as a result of bauxite bleaching and iron mobilization indicates a close genetic relationship between the iron deposits and the altered footwall limestones.

3. The strontium values of the hangingwall and footwall limestones of both the second and third horizon show a similar variability. Strontium concentrations within the hangingwall are between 100-200ppm whereas in the footwall concentrations are typically between 0-100ppm. These values vary close to bauxites; however the distinction may be useful in identifying the location of the bauxite horizon by delineating between hangingwall and footwall limestones where other methods are not suitable (i.e. in drill core samples where bauxite was not found.)

4. The key path finder elements are Fe, Ni, Mn and Sr. These are readily identifiable in the field using portable XRF equipment, hence providing a feasible exploration tool, albeit spatially limited.

This chapter presents initial data and interpretations for the potential pathfinders for the bauxite ore bodies that are fossilised within the carbonate units. Due to constraints in outcrop dimensions, and underground tunnel length and orientations, data collection along set length transects at constant sampling distances was often impossible. Sampling methods were chosen to obtain data from the largest area possible, with as high frequency as time and equipment would allow. Repeating these analyses on drill core samples that represent long transects through hangingwall, bauxite and footwall lithologies, at set analysis intervals should produce a more refined host rock alteration model. Similarly, due to the constraints imposed by the bauxite outcrops, both geological and geochemical variations at distances greater than 100 metres were not analysed in depth. Drill core analysis could also help solve this.

References


Chapter 7: The application of remote sensing methods to karst-associated bauxite deposits in the Parnassos-Ghiona zone, Central Greece

7.1. Introduction
Remote sensing has become a standard tool in mineral exploration, being one of the first and ongoing stages in nearly all modern exploration programs. Using various types of satellite and airborne imagery, remote sensing can be quickly employed to rapidly assess large sections of ground for signs of ore deposits and associated features. The technique can be specifically used to identify areas of ground that are rich in particular economic minerals, it can highlight ground that has undergone alteration associated with mineralisation events, particularly those of a hydrothermal nature, and it can be used to detect prominent linear structures (lineaments) that may control ore body geometry or subsequent deformation and alteration (Sabins, 1999.)

This chapter examines the application of selected remote sensing techniques to the exploration of Mediterranean-type karst-associated bauxite deposits within the Mount Iti and Mount Ghiona regions of the Parnassus-Ghiona orogenic zone. The chapter assesses the application of remote sensing data to detecting bauxite ore bodies and discriminating bauxite-bearing lineaments, and provides the first detailed evaluation of the application of lineament and multispectral remote sensing analysis techniques to ore deposit identification and localisation in the Parnassos-Ghiona region.

7.2. Literature review

7.2.1. Remote sensing in exploration for bauxite and other mineral deposits
Remote sensing has been shown in a number of published examples to have useful applications in bauxite exploration programs (Chen, 1991; Sanjeevi, 2008; Cheng et al., 2012). Remote sensing methods in exploration geology can be split into 2 main types:

a. Multispectral analysis – the analysis of the intensities of different wavelengths of electromagnetic energy reflected by the local geology to identify different lithologies based on their composition.

b. Lineament analysis – the identification and modelling of linear features associated with potentially ore-bearing features such as thrusted contacts in the exploration area.
7.2.2. Multispectral analysis.

Various methods of multispectral signature analysis can help distinguish bauxite ore bodies from the surrounding host rocks (whether they be original parent rock, a secondary site of bauxite re-deposition or karstified carbonates.) With respect to karst-associated bauxites, the strong mineralogical differences between the alumina-iron oxide rich bauxites and calcite-rich limestones create easily identifiable spectral signatures for the two main lithologies. Relevant examples are given below.

Khairi and Izadpanah (1998) utilised mathematical algorithm and statistical processing of remotely sensed Landsat-TM images to separate bauxite bearing Permian limestones from barren Oligocene limestones in the Saqez region of Iran using ratio imaging of a combination of different ages of limestone, as well as identify areas rich in iron oxide associated with bauxites that are present within the limestones. They found that a (3/1)/5/7 image with an equalized contrast stretch identified the limestone areas as blue, and the iron oxide rich areas as red. Using difference imaging of bands 5-7 as red, 4-2 as green and 3-1 as blue, they were able to distinguish between Permian and Oligocene limestones quite clearly.

Das (2008) used spectral signatures and spectral mixture modelling to target lateritic bauxite deposits within the Eastern Ghats mobile belt in Koraput, India. Das found that a colour composite image of bands 7 (red), 4 (green) and 3 (blue) displayed the bauxites as red patches and the vegetation in green. Das also employed several methods of spectral processing, involving classifications of the spectral signatures of the bauxites, vegetation, soil and other features to highlight the best exploration targets and the results proved successful.

Sanjeevi (2008) used ASTER imagery, SRTM-DEM and field studies for the quantification of mineral content in limestone and bauxite rich areas (lateritic-type bauxite) in southern India. Sanjeevi states that ‘the intensity of spectral reflectance/absorption of limestone or carbonate minerals recorded in remotely sensed data is a function of their chemical composition and purity’. (Pure limestone will reflect the visible and near infra-red (NIR) energy, while shortwave infra-red (SWIR) in the 2.35µm will be absorbed). Therefore Sanjeevi suggests that it is possible to quantify the purity of a limestone deposit by analysing the visible and carbonate absorption SWIR bands in a satellite image. Sanjeevi utilised spectral unmixing, a process that unmixes the mixed pixel to determine the fractions of each spectral end members (which combine to produce the pixel’s spectral signature.) The results of this method were described as ‘fairly good,’ and validation of the results with chemical analysis of the limestones gave a correlation coefficient of 0.758 which
was deemed statistically significant. The results also highlighted several lateritic bauxite deposits occurring as hilltop cappings.

7.2.3. Lineament analysis
Lineament analysis has been used successfully to aid mineral deposit exploration, and support geological investigations in a range of regions and deposit types (Sabins, 1999; Watson et al., 1990, Griffths et al., 1987). Lineament analysis can be applicable to exploration for both lateritic and karstic bauxites. For example, in the case of in-situ bauxite formation, faults and fractures within a rock undergoing bauxitisation can aid fluid flow to deeper sections of the parent rock, the result being a much thicker bauxite ore body. Identification of lineaments associated with faulting can help model the thickest and therefore more economic sections of the bauxitic laterite profile or, in cases where tectonic controls on ore location dominate, identify major ore-bearing structures. Karstification of carbonate rocks would also be most prominent along faults and fractures, which could control the location, orientation and size of karst-associated ore bodies.

Some researchers have gone as far as attempting to produce methods of automatic lineament mapping of images e.g. Maged and Hashim (2010) who used LANDSAT-TM images of their research area in the Sharjah Emirates. They combined satellite image enhancement, automatic lineament detection, and 3D visualizations, created using SRTM data, to create a 3D image of lineament distribution that provides ‘excellent information about lineament and geological features’, particularly for interpreting the regional geological structure. While this method is faster than more manual methods, it removes the interpretational skills and geological knowledge of a human operator. In this investigation lineament identification was performed manually, for this reason.

7.3. Methodology
The satellite data used in this study was from the LANDSAT-7 TM data for WRS path 184, row 33, acquired on the 5th August 2002, processed and provided by the U.S. Geological Survey. The study area is located between latitudes 38°23N and 38°56N and longitudes 22°05E and 22°30E and has an area of approximately 60km by 36km. The area was carefully selected to ensure that the entire study area was included within one image along with a sufficient area of the surrounding geology for large-scale geological and structural analysis. The two main methodologies discussed above were applied to the region:

1. Lineament analysis to assess whether satellite imagery can be used to identify major geological structures that control the locations of the bauxite ore bodies.
2. **Multispectral analysis** to assess whether the use of the various spectral signature analysis methods can be used to identify the locations of bauxite ore bodies, and discriminate the limestones that host the ore bodies.

Bands 1, 2, 3, 4, 5, 7, and 8 were used to achieve the objectives of this study as these bands can provide sufficient information to interpret surface geology. Before analysis of the LANDSAT data, individual band images were subjected to various processing methods depending on their final use. The entire process is shown in Fig. 7.1 and is described in detail in the following sections. The methodology used follows recommendations in Sabins (1996), Sabins (1999), Robinove (1982), Chavez (1988), Chavez (1996), Maged and Hashim (2010) and Sanjeevi (2008.)

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**Figure 7.1:** A visual guide to the methodology used for this investigation
7.3.1. Lineament Analysis

In the geological sense, a lineament is ‘a mappable, linear or curvilinear feature of a surface’ that may represent the 2D expressions of 3D geological features. Lineaments may be created by two groups of features:

1. Geomorphic features which are the expressions of terrain relief such as straight stream valleys or aligned segments of valleys or ridges.
2. Tonal features which are created by contrast differences in the surface which are commonly the result of differences in vegetation, moisture content and soil or rock compositions.

The majority of lineaments seen in surface geology are related to faults, joints, bedding planes, lithological contacts and other planes of weakness, especially those where susceptibility to weathering has further highlighted the lineament locations (Sabins, 1996; Maged & Hashim, 2010.) According to Sabins (1996) there is no minimum length for lineaments; however significant features are typically in the order of tens or hundreds of kilometres.

Understanding these lineaments can be crucial to a geological understanding of a research area, as their orientation and frequency can reveal important information about the tectonic history of the area and the location of fault/joint hosted mineral deposits (Maged & Hashim, 2010.) Mapping of these lineaments has become easier through the use of remote sensing technology, being successfully used across the globe in various studies (e.g. Halbouty, 1976; Sabins, 1999; Papadaki et Al., 2011). Mapping in this way allows simultaneous measurement over large areas of the Earth’s surface, often as a precursor to in-situ field measurements.

Maged & Hashim 2010 (and references therein) summarize that lineament information extraction can be divided into three categories based on the methodology used:

1. Lineament enhancement and extraction for characterisation of geological structure.
2. Image classification to perform the geologic mapping or locate spectrally anomalous zones attributable to mineralisation.
3. Superposition of satellite images and multiple data such as geological, geochemical and geophysical data in a geographical information system.

This investigation will focus mainly on the first category, using atmospherically corrected images along with various lineament enhancement techniques, to identify the major lineaments within and around the Mount Iti and north Ghiona zones.
Various processing techniques can be applied to a satellite images to aid lineament identification.

1. **Contrast enhancement** highlights tonal differences, and light/shadow effects of topography.

2. **Edge enhancement** uses filters to either expand the width or increase the pixel value difference across the feature. The filters can be non-directional (Laplacian filters) or can be adapted to highlight lineaments trending in a particular orientation (N-S, E-W, NE-SW etc.)

3. **Hillshading** which is essentially treating the image as a topographical map, and artificially illuminating the image at low sun angles, from varying azimuths, to enhance the lineaments.

4. **3D Visualisation** of the research area by combining the satellite image with a digital elevation model (DEM) (Maged & Hashim, 2010.)

(Sabins 1996)

Figure 7.2: A comparison of Band 7 and Band 8 LANDSAT 7-TM bands, to show the affect that a difference in pixel resolution has on the detail of the image. Note how much more detail can be seen in the band 8 image.

Lineament analysis was carried out here using single-band LANDSAT 7–TM satellite images in its basic, grey-scale format, without using an atmospheric scattering correction (corrections are not necessary for lineament analysis as it is the difference in pixel values that highlight the lineaments, rather than the absolute values. The relative differences between pixels would remain constant within each band image before and after atmospheric scatter correction, and if any further enhancement techniques were applied, it is likely that the corrected values would be
overprinted anyway.) Most of the analysis was carried out using the band-8 panchromatic image as it has a 15 by 15 metre pixel resolution, where bands 1 to 7 have a 30 by 30 metre pixel resolution, making band 8 the more detailed and accurate for this purpose (see Fig. 7.2). Band 8 represents a wavelength of 0.52 to 0.90 μm which is a panchromatic combination of bands 2, 3 and 4. For this reason, bands 1, 2, 3, 4, 5, and 7 were also included in the analysis as they can be influenced by changes in geology, which may create visible lineaments.

### 7.3.2. Contrast Enhancement

In order to make lineament identification easier, the selected images were processed to enhance the visibility of linear structures. First the contrast of each image was enhanced using histogram stretching techniques. Maged and Hashim (2010) provides a good explanation of the method, as does (Sabins, 1999), however here it is explained with direct reference to the individual band images.

Each LANDSAT band image is composed of a series of pixels, each with a DN (digital number) value of between 0 and 255. However a typical raw image will not have pixels that span this entire range, for example, the majority of pixels within the band 8 image in Fig. 7.3A fall within a very small range as shown by the accompanying histogram. Contrast enhancement works by artificially re-distributing the pixel values so that they span the entire range of 256 grey scale values available. (It should also be noted that contrast enhancement will modify any previous calibration work, so enhancement of carefully calculated multispectral images should be done after the other processing methods are complete.) Following Sabins (1996) three different types of contrast enhancement were tested on the research area to see which method gave the optimum re-distribution. These methods were:

1. **Linear contrast stretch** which simply re-assigns the lowest pixel value in the raw image to 0, and the highest pixel value to 255, and spreads the remaining pixels out accordingly. The disadvantage of this method is that only a few pixels occupy a large space at the head and tail of the new distribution. This can be compensated for by using a ‘saturated linear contrast stretch’ where a certain percentage of the pixels (in the case of image 7.3C 2%) are forced to occupy the 0 and 255 bins, and the rest of the pixels distributed across the 1 to 254 bins.

2. **Gaussian or Normalized contrast stretch** which is also a form of linear contrast stretch, re-orders the pixel values into a Gaussian bell-curve distribution, as is often found in nature.
This can also benefit from applying a pixel saturation, in order to fully spread the bell curve.

3. **Uniform distribution or equalized contrast stretch** which is a non-linear method attempts to equalize the occurrence of all grey-levels within the image. This means that the bins within the original raw data histogram that had a high-frequency of pixels will be spread out into a wide range of neighbouring grey-level values, whereas the areas of low pixel frequency, will be re-distributed into a narrow range of grey-level bins.

Comparison of these three methods with the original image shows that they all increase the level of detail within the image, making features much easier to identify. However they have all produced slightly different images. The normalization technique favoured the central section of the pixel range, but gave a good overall distribution. The equalization technique gave a greater contrast to the image; however the extreme ends of the pixel ranges seemed to be agglomerated, creating some sections that are either too dark or too light to distinguish much detail.

It was decided that the Gaussian distribution with a 1% pixel saturation at each end was best for the regional analysis as it preserved more detail in the brighter limestone areas around Ghiona and the darker regions of Iti. It should be noted that sub-sections of the image as used in future sections of this analysis, as well as slightly different regional images would have a different pixel distribution histogram from the ones presented, and therefore may benefit from alternative enhancement methods.

### 7.3.3. Edge Enhancement

Once the images had the optimum contrast display, several methods of edge enhancement or ‘automatic edge detection,’ were used to quickly and objectively identify strong contrast boundaries between the image pixel intensities. However, as these methods are susceptible to noise in the images, they had to first be filtered.

**Removing noise from the images**

The regional image was filtered using a ‘low-pass filter’ or ‘smoothing filter’ to remove the noisy pixels and replace them with a value calculated from some variable of the surrounding pixels. These filters work by using a window (often referred to as a ‘kernel’, ‘mask’ or ‘operator’) of a few pixels in dimension over each pixel in the image, applying a mathematical calculation using the pixels under that window and replacing the central pixel with the new calculated value. The window is moved across the image one pixel at a time until the entire image has been calculated and a new image has been generated. In this way, the filter removes areas of high-spatial

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frequency (where pixel values vary greatly over a small space), leaving an image of low spatial frequency. By varying the window dimensions filters can be designed to enhance and suppress many different types of features (CCRS no date.) For this purpose a Median filter was used with a radius of 3 pixels, which replaces each pixel by the median of the surrounding 5x5 pixels. The reason this was chosen is because it is a simple and efficient filter which is very good at preserving edge detail in the image. Fig. 7.4 compares a band 7 image before and after this smoothing operation. The standard of edge preservation using this filter is clear when some of the more obvious grey-scale boundaries in the image are compared.

The smoothing filter was not applied to the local analyses of Mt. Ghiona and Mt. Iti, as it was felt that preserving as much detail as possible was crucial to the small-scale interpretation. After processing of these images, the noise created from edge detection was minimal compared to the larger images.

**Automatic edge detection**

Automatic edge detection methods operate in a similar way to low-pass filters, in fact, edge detectors are commonly known as high-pass filters. They work in the opposite way to low-pass filters, and actually emphasis areas of high-spatial frequency and reject areas of low spatial frequency, which highlights the sharp tonal boundaries associated with lineaments. Sabins (1996) states that edge enhancement works in two ways, either by expanding the width of the linear feature or increasing the DN value across the feature. Two types of filter exist; directional and non-directional. Directional selectively highlights edges that have a particular orientation, whilst non-directional highlights all edges regardless of orientation. It was decided that non-directional filters would be used for this investigation. Two edge detector filters were used: Sobel and Roberts. They both have similar principles; however the Sobel operator has been designed to preferentially highlight vertical and horizontal lineaments, whereas the Roberts operator highlights diagonal lineaments. By combining the results of both operators, all orientations of lineaments will be included in the analysis. Other methods that could be used are ‘hill-shading’ where the pixel intensities are treated as topographical data, and an image is produced that represents the light reflected off the topography from a given ‘sun’ orientation and height in the sky. The strong changes in pixel value are then highlighted as ‘shaded’ areas on the image produced. An example of this is given in Appendix 8 of band 8 with a sun orientation and height.

**Lineament identification and interpretation**

Before lineament identification, histogram equalization was used on all of the images to make visualisation of the identified edges easier. The edge enhanced images were then analysed to
identify the significant lineaments with frequent reference to the original images to differentiate between the geologically significant lineaments, and those associated with anthropogenic structures and other non-significant features. Lineaments were selected by a human operator (i.e. the author) and highlighted by hand. By doing this a regional lineament model and two local lineament models were produced which show the distribution, orientation and length of the recognised lineaments within the research area. The orientation data for each lineament within the models was also collected and plotted as several rose diagrams. Using these data it was possible to group the lineaments into several categories, and by comparing the features of each group to in-situ structural data collected from the research area (see Chapter 8), lineaments could be matched to particular geological features.

Once the lineament models were created, the start and end co-ordinates of each lineament were extracted from the modelling software, and then used to calculate the azimuth of each lineament. This orientation data was then plotted up as rose diagrams for each model to show the main lineament orientations within each model. Using these plots, the main lineament groups were distinguished and the models were re-plotted to show the spatial diversity and frequency of the different lineament groups across all three models.
Figure 7.3: A comparison between methods of contrast enhancement used in this project, with the altered digital value histograms shown beneath each image. The images are: a. Band 8 image before enhancement, b. normal contrast stretch enhancement, c. normal contrast stretch with 2% pixel saturation, d. equal area contrast stretch.
Figure 7.4: LANSAT-7 TM band 8 image of Mount Ghiona before and after smoothing with a low-pass median filter. This benefitted subsequent automatic lineament detection techniques by removing noise from the image.
Finally the lineament data were compared with in-situ structural measurements in an attempt to classify each group and link it to a particular type of structural feature.

7.3.4. Multispectral analysis

Image Calibration

‘Proper and consistent use of Landsat digital data requires that the digital numbers be converted into quantitative physical values such as radiance or reflectance’ (Robinove, 1982.) Conversion of the digital numbers requires corrections for the effects of certain solar and atmospheric conditions at the time of data collection, in order to produce digital numbers that represent physical values. Without atmospheric correction of the data, analysis will be of the earth-atmosphere system rather than the earth alone, and failure to convert the digital numbers, especially when using spectral processing techniques, will produce incorrect and misleading results (Robinove, 1982; Sabins, 1996.)

The data used in this thesis was calibrated using the COST method developed by Chavez 1996. The COST method is a radiometric calibration for remotely sensed data to compensate for the effects of atmospheric scattering, absorption and refraction of the radiated electromagnetic energy received by the satellite, and for sensor gains and offsets, solar irradiance and solar zenith angles. The objective of this calibration process is to convert the satellite-generated digital levels (DL) to absolute surface reflectance values (Chavez, 1996.) The COST calibration method is achieved by applying the following equations to each DC in each Landsat image.

\[
\rho_k = C'_k \cdot (DL_{zen,k} - DL_{p,k})
\]

*Equation 1*

Where:

\[
C'_k = \frac{a_{1,k}}{\left(\frac{1}{\pi} \cdot (\cos \theta_s)^2 \cdot \left(\frac{E_{0,k}}{D}\right)\right)}
\]

*Equation 2*

<table>
<thead>
<tr>
<th>Pk</th>
<th>Surface reflectance</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL_{zen,k}</td>
<td>Digital level at satellite sensor</td>
</tr>
<tr>
<td>DL_{p,k}</td>
<td>Effects of atmospheric scattering (see below)</td>
</tr>
<tr>
<td>(a_{i,k})</td>
<td>Gain in band k</td>
</tr>
<tr>
<td>(\theta_i)</td>
<td>Solar zenith angle in radians</td>
</tr>
<tr>
<td>(E_{0,k})</td>
<td>Mean solar irradiance in band k</td>
</tr>
<tr>
<td>(D=d^*)</td>
<td>Distance between the Earth and the Sun</td>
</tr>
</tbody>
</table>

\(P_k\) is the reflectance values that this method calculates, and \(DL_{sen,k}\) represents the digital levels recorded by the satellite.

The \(DL_{p,k}\) value was calculated using the improved dark-object subtraction technique developed by Chavez (1988 and 1989). This is designed to remove the additive effects of atmospheric scattering on the data, based on the principle that in every image there should be some pixels that are completely in shadow and therefore should be recorded as zero. Any values above zero recorded for these pixels are due to the scattering of the electromagnetic energy or ‘haze.’ The amount of haze in an image can greatly affect the results generated from multispectral ratioing (Chavez, 1989.) The user can select the haze value for each image based on the difference between the lowest pixel value in the image and 0. This value is then removed from the corresponding image to account for the haze effects. The problem with this dark-object subtraction method is that it could over compensate in some spectral bands, and so the improved method instead uses one haze value, preferably from a band in the visible spectrum, to predict the haze values for subsequent bands based on a relative atmospheric scattering model. In addition, as very few targets on earth would have a completely zero reflectance; it was suggested by Chavez 1989 to use a 1% minimum reflectance rather than a zero reflectance minimum.

Following Chavez (1988, 1989 and 1996) and based on the starting haze value calculated from the full Landsat tile for band 1 (51), a ‘very clear’ relative scattering model for the data was adopted, and relative haze values (with 1% reflectance minimum) of 50.5, 28.4, 14.7, 5.9, 3.8 and 0.1 were used for bands 1, 2, 3, 4, 5, and 7 respectively. Care was taken to verify these predicted models with each band to ensure that they did not over compensate for the haze in any of the images.

**Multispectral Imaging**

The calibrated images were used to create several colour composite, ratio and differential images in an attempt to distinguish the bauxite ore bodies from the limestone host rocks. First a true colour image was produced using bands 1 (blue), 2 (green) and 3 (red) and following Sabins (1996)
a false colour image was produced to distinguish vegetation using bands 4 (red), 3 (green) and 1 (blue.)

Ratio imaging, which involves dividing one spectral band by another to highlight certain spectral variations of the Earth’s surface was attempted. The ratio images created were 3/1, which highlights iron rich areas and 5/7 which highlights areas rich in clays (kaolinite, montmorillonite etc.) (Sabins, 1999.)

Following Khairi & Izadpanah (1998) two colour ratio composite images were constructed to see whether the hangingwall and footwall limestones of the bauxites can be distinguished from each other, and whether the bauxites themselves could be distinguished from the limestones. These are a (5/3/1)/(4/2/1)/(7/5/1) image and a (3/1)/5/7 image respectively. A difference image of bands 5-7/4-2/3-1 was also created as this was stated by Khairi & Izadpanah (1998) as being ‘the best way for separating the limestones from each other.’

Finally, principle component analysis was used on all 6 images to analyse the combined signatures of all the bands to categorise the area into spectrally different zones which were then checked against known geology to verify whether the surface exposures of the bauxites are large enough, and show sufficient spectral contrast, to be identified.

Ground truthing and geological map studies were also applied to check whether the various images can successfully and confidently aid bauxite exploration.

7.4. Results and Analysis

7.4.1. Lineament analysis models
The lineament models created using the edge detection filters are shown in Fig. 7.5 for the regional model, and the models for the Mt Iti and Mt Ghiona sub-sections are shown in Figs 7.6 and 7.7 respectively.

Comparison of the known ore body locations in relation to the major lineaments for both Mount Iti and Mount Ghiona do not show any clear relationship. This suggests that there is not a particular dominant bauxite hosting lineament set within the Parnassos-Ghiona zone. Field evidence does exist to show that bauxite outcrops follow the more N-S orientated structures, as opposed to the E-W structures in Mount Ghiona, and along E-W structures in Mount Iti. These relationships cannot be identified at the larger scale in satellite imagery.
Figure 7.5: Lineament model for the entire research area, encompassing both Mount Iti and Mount Ghiona.
Figure 7.6: Lineament model for the Northern bauxite bearing region of Mount Iti. The known outcrops of bauxite from across Mount Iti are highlighted, blue for second horizon, purple for third horizon, in order to compare ore body location and major lineaments. The ore body locations are based on a combination of field evidence and geological maps.
Figure 7.7: Lineament model for the Mount Ghiona area, focusing mainly on the exposed carbonate rocks. The known outcrops of bauxite from across Mount Ghiona are highlighted, blue for second horizon, purple for third horizon, in order to compare ore body location and lineament locations.
7.4.2. Lineament models orientation data

The orientations of the lineaments from each of the models are shown as rose plots in Fig. 7.8. The lineaments across the Mt. Ghiona model are more variable in orientation than those in the Mt. Iti model. The majority have an orientation between 340° and 090°, however, it is difficult to distinguish individual groups within these lineaments from the rose plots alone.

In-situ measurements of structural features around the northern Ghiona area identified a series of thrust fault planes that have an average strike of ~345° (discussed further in Chapter 8). Additionally, there is one known thrust fault along the northern edge of Mount Ghiona that strikes approximately 070°, which is visible on the Landsat imagery as a steep escarpment facing to the north. There are also two sets of extensional fault systems identified in the area. The first system is orientated between 320° to 340° and is thought to be associated with the Itea-Amfissa detachment, a 25-30km long extensional detachment on the eastern edge of Mount Ghiona, orientated NNW-SSE, separating it from Mt. Parnassos (Papanikolaou & Gouliotis, 2006). The second group is orientated ~000° to 020° and is possibly associated with relaxation of the compressed lithosphere after initial Hellenic arc formation during the Alpine Orogeny.

Initial analysis of the Ghiona lineament model data indicates that all four deformation structures have been identified by remote sensing. If the lineaments are split into groups based on the four structural categories, it becomes apparent that the structure types are not evenly distributed over the area.

Mount Iti

The lineament model for Iti is dominated by predominantly E-W trending lineaments with most lineaments orientated between 080° and 110°. Comparisons with in-situ structural measurements show that both data sets are concordant. The structural analysis identified two main structures:

1. Thrust faults most of which are orientated between 110° and 130°
2. Normal faulting, most of which are orientated between 070° and 100°
The lineament data suggests that the lineaments are mostly related to normal faults, and the similarity in orientation of the thrust and normal fault structures means that differentiation through remote sensing imagery is very difficult.

Figure 7.8: Rose plots of the lineament orientations from the three lineament models in Figs. 7.5, 7.6, and 7.7. A. Regional model lineaments, B. Iti model lineaments, C. Ghiona model lineaments.
7.4.3. **Multispectral Analysis**

Fig. 7.9 shows a true-colour image of the exploration area. In the far north of the image, the Sperchios valley is visible as the predominantly green area, with numerous square fields, roads and buildings. To the south of this valley is the northern slope of Mount Iti, formed predominantly of carbonate rocks and outcropping as an escarpment, representing the southern fault of the major graben system of the Sperchios Valley. The majority of the mountain is covered by the Pelagonian thrust sheet which is partially visible as the large dark area across the majority of Mount Iti. To the south, the bright white limestones of Mt Ghiona are clearly visible, and the contact between Mount Ghiona and Mount Iti being marked by the escarpment relating to the

![Figure 7.9: True colour image of the research area produced using Landsat bands 1, 2 and 3.](image-url)
north Ghiona extensional fault.

One of the major differences between the two mountains is the amount of vegetation present. Iti has significantly greater vegetation coverage than Ghiona, likely due to its flysch coverage, which is shown in Fig. 6.10, which is a false colour image of bands 4 as red, 3 as green, and 1 as blue. Vegetation is visible as red areas in this image, as bands 3 and 1 (red and blue visible light respectively) are absorbed by plants, whereas band 4 (near infra-red) is reflected by vegetation.

Figure 7.10: False colour image of the research area using bands 4, 3 and 2, designed to highlight vegetated areas as red colour pixels.
Fig. 7.11 is a false colour image made of bands 7 as red, 4 as green and 2 as blue. This was created to show variation in geology as well as vegetation. In this image vegetation appears green and the limestone appears pink. It is useful to show the outcrops of bauxite hosting limestones, particularly within the heavily vegetated Mount Iti regions. The pink area in the central western
area is part of the Vardoussia zone. The small outcrops of limestone along the northern edge of Mount Iti can be clearly discriminated in this image; however it is clear that the poor exposure in the Mount Iti area and the dense vegetation means that further multispectral analysis would not be able to discriminate the ore bodies and alteration zones from the surrounding limestones. Therefore from this point on, the multispectral analysis will be concerned with the well exposed carbonates of the north Ghiona area. Figs 7.12 and 7.13 were created to try to distinguish the Ghiona hangingwall and footwall limestones from each other, based on potentially difference spectral signatures, following Khairi & Izadpanah (1998.) Figure 7.12 is a difference image using the differences between 5 and 7 for red, 4 and 2 for green and 3 and 1 for blue. Compared with the geological map of the area, it is clear that the spectral signatures of the limestones are too similar to be differentiated in this way. However the blue/purple spots that are seen within the limestones may be linked to areas of high iron content, potentially highlighting bauxite ore bodies.

Figure 7.12: A difference image of the limestone around North Ghiona, produced to try to separate the different carbonate sequences.
Fig. 7.13 was specifically designed to highlight bauxite ore bodies based on their high iron content with respect to the limestones. It uses a ratio of bands 3 and 1 as red, band 5 as green and band 7 as blue, following the results of Khairi and Izadpanah (1998.)

This image highlights some small potential areas of high iron within the pale blue limestones. The red areas around the outer regions of the picture are likely to relate to vegetation or surficial deposits, as is clear from Fig. 7.11 (432). Of the two images, it seems to be the differential image that shows potential for identifying bauxite outcrops within the limestone sequence.

Fig. 7.14 below is a small area within image 7.12 that represents the Makrilakoma Valley, an area in northern Ghiona with known second and third horizon bauxites present. Within this image the bauxites of Makrilakoma and Arkouda, two separate second horizon bauxites, can be identified. The large purple area to the west of the Makrilakoma ore body is the Vraila mine and dumpsite. It appears that remote sensing is able to identify the bauxite orebodies based on their relative high iron content with respect to the limestones. However, the ore bodies themselves are represented
by only a few pixels. It could also be argued that the reason the Arkouda ore body is visible is because it occurs along a valley that would be in shadow during the time of measurement, rather than a difference based on spectral signature. Comparison of the other dark purple zones within image Fig. 7.12 with the known ore body locations, and with in-situ observations during surface mapping, did not identify any correlation between ore bodies and spectral signatures. They either represent spoil heaps, or areas of shadow on the image. In the case of the former, this illustrates the potential utility of multispectral analysis in identifying the areas that require post-mining rehabilitation (e.g. Paull et Al., 2006; Charou et Al., 2010.)

7.5. Discussion

7.5.1. Review of the method
The Mediterranean type karst-associated bauxites within central Greece pose a difficult problem for most remote sensing techniques, as the majority of each ore body is ‘hidden’ between thick limestone sequences, with relatively small surface outcrops, represented by no more than a few pixels (based on LANDSAT 7 data.) Therefore direct identification of bauxite ore bodies may prove difficult and the spectral signatures could also be confused with existing bauxite or clay-rich spoil heaps from past mining activity. Lineament analysis may suffer from similar draw backs, however the generally well formed fault and joint sets that occur within limestone, and the ease at which they can be exploited and accentuated by weathering, makes lineament analysis methods better suited to the research area.

The lineament analysis methodology proposed here is a simple series of image processing techniques that should work for all regions within the research area and at all scales, with only a few minor modifications. It has been applied here to LANDSAT imagery, but it should work equally well with aerial photography images and Aster data imagery. Over all, it was felt that lineament analysis worked best on the Ghiona area where continuous exposure and low vegetation meant that lineaments could be more easily recognised. Within the Iti region the vegetation cover shown by Fig. 7.10, and the flysch and ophiolitic thrust sheets cover the majority of the limestone sequences. This means that remote sensing methods applied to this region are severely inhibited.
Figure 7.14: A. Difference image of bands 5-7, 4-2 and 3-1 showing the makrilakoma valley of North Ghiona. B. Photo of the Arkouda Tripa bauxite orebody, with its location pointed out on A. C. Photo of the Makrilakoma ore body with its location pointed out on A. These two ore bodies can be identified on the remote sensing image, however they are represented by only a few pixels.
7.5.2. Implications for exploration

Remote sensing as a tool for exploration of Greek bauxites has been shown to have the following benefits and limitations.

1. Lineament analysis in combination with structural analysis can reveal the dominant structural controls across an area of interest. Lineament models created in this way can aid understanding of the geological structure of the research area, allowing for large scale observations to be made, which would otherwise require extensive fieldwork to produce. On the more local scale, the models can indicate the structures that are likely to be encountered when mining in a particular area, which will benefit ore body modelling and mine planning.

2. Spectral analysis can be used to search small areas for potential bauxite exposure. However this technique will only work in areas of low vegetation (i.e. good geological exposure), and so the results from Iti are difficult to interpret. The small size of the bauxite outcrops make identification a problem, and some ore bodies could be mistaken for noise, or not recorded by the satellite imager at all.

7.6. Conclusion

7.6.1. Detection of bauxite ore bodies

Multispectral analysis techniques were used to try to discriminate the bauxite ore bodies from the surrounding carbonate host rocks based on their different spectral signatures. The results suggested that the spectral signatures of the bauxites and limestones contrast sufficiently to be differentiated, however, the small outcrop size of the bauxites mean that the ore bodies are represented by no more than a few pixels within the Landsat imagery. It is for this reason that the multispectral techniques that have been used successfully on lateritic bauxites, do not translate with the same effectiveness to the Greek karst-associated bauxites. Higher resolution remote sensing imagery may improve discrimination however.

7.6.2. Detection of bauxite bearing lineaments

It was hoped that bauxite horizons could be identified on Landsat imagery as lineaments, and traced to identify potential bauxite bearing areas and exploration targets. Unfortunately the bauxite bearing horizons are very difficult to distinguish on the Landsat imagery, and comparison of the known ore body locations in relation to the major lineaments identified for both Mount Iti
and Mount Ghiona do not show any clear relationship. Similar spectral signatures of the footwall and hangingwall limestones of both the third and second horizon bauxites mean that the boundary between the units is difficult to identify. Put into remote sensing terms, the difference in pixel values on either side of the geological boundary are too similar to be recognised as lineaments by lineament enhancement tools or by normal observation.

Lineament analysis however has been successfully shown to correlate with in-situ structural data, making it a useful tool to investigate the larger scale geological structure. While it is difficult to identify individual ore hosting lineaments, such as bedding planes or thrust faults, it can be used to show the predominant structure orientations across the research area and aid in the development of regional and local structural models (discussed further in Chapter 8).

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Chapter 8: The Geological structure of the Iti and Ghiona mountains in Central Greece, and the implications for Karst-associated bauxite exploration

8.1. Introduction
The search for new bauxite deposits buried under the deep carbonate overburden in the Mediterranean karst bauxite deposits depends greatly on an appreciation of pre- and post-bauxite tectonics (Hose 1978). In comparison with the larger geotectonic zones of Greece, studies into the structure of the Parnassos-Ghiona zone have been limited, and none have looked in detail at the effects of the geological structure on the bauxite deposits. Initial observations of the bauxite for this project indicated that the local and regional structure is more complex than current models show. For successful bauxite exploration, particularly beneath the flysch and ophiolite deposits covering the majority of Mount Iti, a detailed structural understanding will help predict the locations and depths of bauxite deposits. This chapter aims to investigate the tectonic history and current geological structure of bauxite-bearing carbonates within the Iti and Ghiona mountains, and propose a model of the geological structure of the bauxite rich areas that can be used to further explain the geological evolution of the deposits, and provide an important tool to future exploration practice.

8.2. Current Structural Understanding

8.2.1. Regional Tectonic History
The carbonate deposits of the Parnassos-Ghiona zone developed within and around the Mesozoic Pindos Ocean, which formed from rifting of the northern margin of Gondwana during the Early-Middle Triassic, following a period of crustal extension which started during the mid-Permian. Continental break up and sea-floor spreading began during the Carnian-Norian periods of the Late Triassic (Robertson 2012). The Western side of this rift developed into the Apulian microcontinent and the Eastern side into the Pelagonian microcontinent and at some point during extension both microcontinents were offset by a series of major transform faults including the Sperchios and Corinth faults (see Fig. 8.1), which had an important influence during later extensional deformation.

Carbonate deposition began during the Late Triassic on a large isolated platform separated from the Apulian margin during oceanic crust development by a basin floored with oceanic crust and deep sea sediments. According to Robertson et al., (1990), the platform remained isolated from
tectonic deformation until the early Tertiary. To the north and south, the platform was bounded by the Sperchios and Corinth transform faults respectively (identified on Fig. 8.1.)

During the Mid Jurassic, around 165Ma, a westward dipping ocean-ocean subduction zone developed near to the Pelagonian margin, with an associated supra-subduction zone oceanic ridge where melting of rising asthenosphere from subducted oceanic crust gave rise to the ophiolites now found across Greece. From this point, the Pindos Oceanic basin entered a phase of regional convergence, with the Apulian margin moving northeastwards (Doutsos et Al., 1993.) Fig. 8.1 presents a palaeographic reconstruction of the Pindos Ocean at this time, including the locations of the Parnassos-Ghiona platform, and the westward dipping subduction zone and supra-subduction zone ridge, and the transform faults.

Figure 8.1: Palaeogeographic reconstruction of the Pindos Ocean during the Mid-Jurassic (170Ma), Adapted from Robertson et Al., (1990).
During the middle to late Jurassic the subduction zone collided with the Pelagonian passive margin to the East, forcing much of the oceanic crust, metamorphic soles and accretionary melange onto the Pelagonian zone through top-to-the-northeast thrusting, indicated by structural evidence taken from many of the ophiolitic sequences, including the Iti Ophiolite (Robertson et Al., 1990; Robertson, 2012.) It was this predominantly ultra-mafic to mafic sequence that has been proposed as the source material for the bauxite (Valeton et Al., 1987.)

The Pindos Ocean wasn’t entirely closed during the ophiolite emplacement, but remained open as a remnant basin in which carbonate deposition on the Parnassos-Ghiona platform continued relatively unabated until the Late Cretaceous (Robertson et Al., 1990.) During this time, either tectonic doming (Hose, 1978), or cyclic sea-level rise and fall exposed the carbonate platform to karstification and bauxite deposition during the Kimmeridgian, Tithonian and Cenomanian to Turonian (Valeton et Al., 1987.) What is clear from this time frame is that all three bauxite horizons were deposited during a phase of convergence.

During the Palaeocene to Eocene, activation of an eastward dipping subduction zone consumed the remnant Pindos Ocean surrounding the Parnassos-Ghiona platform, eventually impinging the platform on the margin of the Apulian micro-continent. Continued convergence created a series of westward verging thrust sheets attributed to crustal wedging along the Pindos suture (Robertson 1990, Doutsos et Al., 1993). Flexural subsidence and hinterland uplift, combined with erosion, at this time gave rise to deposition of the Flysch units. Soon after this, the Parnassos-Ghiona zone was overthrust, from the northeast, by sequences from the Pelagonian zone, still preserved in several isolated outcrops across the research area overriding the flysch deposits.

Morris (1995) has shown evidence that the Parnassos-Ghiona zone acted as a major obstacle to the southwest advancing Pelagonain nappe. This forced the southern Pelagonian zone to ‘mould’ itself around the southeast Parnassos-Ghiona zone with a clockwise rotation of 50°, and pinning, and possible anti-clockwise rotation of the NW margin of the Pelagonian zone, around the Parnassos-Ghiona zone. (Morris 1995.) Figure 8.2 shows a model for this rotation with respect to the different zones. Closure of the Pindos Ocean also marked the end of Carbonate deposition upon the Parnassos-Ghiona platform.

Considering this rotational thrust emplacement of the northern and southern edges of the Pelagonian overthrust, it is likely that the orientation of compressional deformation across the Parnassos-Ghiona zone is not uniform, meaning that differences between the overall structures of Mounts Iti and Ghiona may occur.
From around 37Ma, into the Oligocene period, east-west extensional tectonics affected most of the Hellenides, resulting in low-angle normal faulting, creating widespread emergence, thinning of previously thickened crust, and erosion and deposition of syn-tectonic molasse (Doutsos et Al., 1993.) This extensional event is likely to have produced many normal faults across the Parnassos-Ghiona area, including the Itea-Amfissa detachment, observed along the eastern slopes of Mount Ghiona, separating it from Mount Parnassus. This detachment is a 30km long normal fault zone that dips between 25° to 40° to the east (Papanikolaou et Al., 2009.)

By the Pliocene, the majority of Central Greece was incorporated in the Aegean back arc basin, resulting in widespread N-NE - S-SW extension, including the formation of the Sperchios graben to the north of the research area, and the Corinth graben to the south (Doutsos et Al., 1993.) The Sperchios fault is a WNW-ESE trending, high angle fault system that cuts through central Greece.
The geometry and kinematics of the fault system are of a NNE-SSW extensional stress regime, and along with the Kremasta and Corinth fault systems, they represent an underlapping extensional zone between the Cephalonia transform fault in the W, and the North Anatolia fault to the NE. The three fault systems together form antithetic domino-type trailing faults in respect to the SSW-wards motion of the Aegean block (Killas et al., 2008.)

8.2.2. The Structure of the Parnassos-Ghiona Zone

As Mettos et al., (2009) observed, most recent studies on the Parnassos-Ghiona zone are based on old geological and mapping data, from studies such as Renz (1940), Aubouin (1959) and Celet (1962), as no systematic geological mapping has been conducted there since. As such, many models for the region have not been checked using modern methods.

The popular model for the Parnassos-Ghiona zone stated that it is a thrust sheet with a large-scale anticline structure of NNW-SSE axial direction, with a highly inclined western limb. It was also originally thought to have been thrust to the south west, onto the Vardoussia subzone (Renz, 1940) (the model is shown in fig. 8.3A; Mettos et al., 2009 and references therein.)

Doutsos et al., (2006) proposed a new model for the Parnassus-Ghiona zone, suggesting that the Parnassus-Ghiona and Vardoussia zones acted as a back-stop to Meso-Hellenic thrusting, creating a doubly-vergent accretionary wedge formation across Hellenic mountains between the ‘pro-lithosphere’ of the Apulian micro-continent which converges onto the ‘retro-lithosphere’ of the Pelagonian micro-continent. They also adopted the west-vergent thrust model shown in Fig. 8.3B.

Mettos et al., (2009) used geological mapping, including an extensive micro-paleontological study and tectonic observations to conclude that there is no evidence, either tectonic contact or secondary structural deformation, for a west verging overthrust structure between the Parnassos-Ghiona zone and the Vardoussia sub-zone to the west. They agree that the Ghiona limestones are folded into a large-scale, NNW-SSE trending, anticlinal structure, with a sub-vertical axial plane but with a steeply inclined western limb, which passes under the Vardoussia flysch sequences. This folding occurred due to E-W shortening responsible for the Hellenic nappe stacking. Through analysis of data from the excavation of the Ghiona water tunnel, Mettos et al., (2009) also identified many highly inclined normal faults, principally striking NW-SE in the Ghiona limestones and Vardoussia flysch. Their model is shown in Fig. 8.3C
8.2.3. **Local structures within the Parnassos-Ghiona zone**

Kiskyras (1978) in studying the bauxites of Mount Helicon, southeast of the Parnassos-Ghiona zone, suggested that the Jurassic sediments were less folded and deformed than the overlying Cretaceous sediments on account of their higher consolidation. This led to folding of the third horizon bauxites and surrounding limestones which is not seen in the second horizon units. Kiskyras describes several examples of tectonic structures within the Helicon area drawing special attention to ‘Reversed synclines’ which are noted as ‘a general phenomenon’ in the Helicon area and as ‘economically significant.’ Some examples of some of the structures identified by Kiskyras are shown in Fig. 8.4.
Post emplacement deformation of the Iti ophiolite has been identified by Karipi et Al., (2008), who recognised that the latest tectonic activity in the area, which is associated with the formation of the Sperchios normal fault, resulted in the development of two normal fault sets, a NW-SE set that is almost parallel to the Sperchios fault, and a NE-SW to NNE-SSW trending set that is perpendicular to the Sperchios fault (Karipi et Al., 2008.) The perpendicular set is perhaps associated with the earlier E-W Oligocene extension.

8.2.4. The structure of the bauxite ore bodies

The structure of the Parnassos-Ghiona bauxite ore bodies has been discussed by several workers. Petraschek (1989) observed that the ore bodies within the ‘Parnasse District’ have been shown to follow a NE-SW trend, which perhaps relates to a structural control on the main orientation of the bauxites. If so, it would most likely be through exploitation of fractures and faults developed during Mesozoic compression.

Several workers have alluded to the presence of non-horizontal ore bodies and structural complexities that have been found during exploration and mining. Peppas et Al. (2002) describe the bauxite as being ‘normally of lenticular type’, with ‘typical dimensions range from 30-500 meters in length or width with a thickness between 1-30 meters.’ The inclination of the ore bodies are stated as between 10 to 30 degrees, but in ‘exceptional cases’ it may reach 70 degrees. They don’t state where these ‘exceptional case’ deposits occur or why, however they do explain that the room and pillar mining method, usually used for the more horizontal ore bodies, does not work for the steeply dipping ore bodies. Instead sub-level stoping has been used, using sublevel drives at 10 metre intervals to mass-blast and extract the ore. This was successful, however it allowed for ‘serious dilution problems’ of the ore.
8.2.5. **The gaps in knowledge**

The formation and tectonic development of the Parnassos-Ghiona platform within the Pindos Ocean is well understood, and the small but important role the Parnassos-Ghiona platform played in the convergence and tectonic stacking of the Hellenide units has been modelled by several workers.

The effects of the tectonic evolution on the development of the Parnassos-Ghiona platform has been briefly explained above, however the structures formed in response to each tectonic phase, particularly at an ore body scale are still poorly understood. Also no model to date satisfactorily explains the reason for the steeply dipping (70 degrees) ore bodies, where they may be found or what larger structures they may be associated with. There are also no models to show the structural geology of Mount Iti, both where the bauxite outcrops at the surface, and deeper beneath the flysch and Pelagonian ophiolites. The models for Mount Ghiona lack sufficient detail to properly aid underground bauxite exploration.

This investigation therefore aims to develop structural models of both Mount Iti and Mount Ghiona, with enough detail to help predict the location, inclination and depth of the bauxite bearing contacts within the carbonate platform units. It will also identify the locations and explain the potential causes of steeply dipping ore bodies within the Mount Iti and Mount Ghiona areas.

8.3. **Methodology**

This investigation required several methods of structural analysis at different scales of observation in order to show the relationship between regional, more local and ore deposit scale structures. For large scale observations, lineament analysis of Landsat TM-7 images (chapter 7) was used to help identify large lineaments and lineament trends present across the Iti and north Ghiona regions. The lineament orientation data and in-situ structural measurements from the same locations are shown to have a good correlation in chapter 7, for structural analysis it was assumed that the lineament model is a reasonably accurate depiction of the general variation in structural geology. Therefore data and models are further used in this chapter to discuss the overall structural trends across the bauxite bearing areas.

The structural data of bedding planes, faults, joints and kinematic indicators were collected via surface and underground mapping of bauxite deposits and the surrounding lithologies. Underground mapping utilized historic and operational mines within the Mount Iti and Ghiona areas, and allowed for in depth ‘3D’ exploration of ore body structures. This was an advantage in areas where inaccessible surface terrain or poor exposure prevented detailed mapping. The
structural data were plotted as pi-poles using low hemisphere equal area stereographic projections to compare and contrast major structural trends across Mounts Iti and Ghiona. Interpretation was aided by the additional plotting of average planes for bedding and fault data, indicated where appropriate in the following Figures. Where large quantities of data were plotted, e.g. normal fault data, contouring of the pi-poles, using the Fischer method, was applied to make visual interpretations easier. The data were also used to create cross-sections of important ore body groups to indicate the nature of areas of particular structural complexity. The data were combined in order to show how the structure of the Parnassos-Ghiona zone has evolved since the Triassic.

Finally, the dimensions and orientations of ore body axes were measured and plotted as a rose diagram to identify if there is an underlying tectonic control on the orientations of ore bodies within particular regions.

8.4. Structural data, observations and models

8.4.1. Regional scale

Mount Iti
Mount Iti is mostly covered by the Palaeocene flysch of the Parnassos-Ghiona zone and the Pelagonian thrust sheet. The main carbonate exposure is along the Northern edge adjacent to the Sperchios Valley. As exposure along this section was still relatively poor, the main source of data was from underground mapping, focusing on the Duo Vouna region in the east.

The structure of the Duo Vouna area
It has already been established that certain ore deposits within the research area exhibit a steep or vertical inclination, and Duo Vouna is an area that contains many of these deposits, including locally overturned ore bodies. Fig. 8.5 is a simplified geological map of the Duo Vouna area. According to the geological maps only B3 bauxite outcrops in this area, and currently, only B3 bauxite is being mined from the Duo Vouna region. The thrust sheet overlying the Parnassos-Ghiona zone sequence is a sequence of thrustsed units including ophiolites, flysch and carbonates from the Pelagonian zone.
Fig. 8.7 shows the overall structure of the Duo Vouna area, based on over 300 measurements of bedding planes, faults, joints and kinematic indicators. Lineament analysis was used to aid the development of this model. The vertical and overturned ore bodies are part of the steep limb of an inclined, isoclinal, anticline structure formed through NNE-SSW compression.

Figure 8.5: Geological map of the Northern part of Mount Iti, with the location of the cross section in figure 8.7 indicated.
Figure 8.6: Selection of photos showing structural features found within Mount Iti and Ghiona. A. Major West directed thrust fault running along the Makrilakoma Valley, Mount Ghiona. B. Major southeast directed thrust fault with bauxite ore at its base, along the northern edge of Mount Ghiona. C. Two sets of slickensides along the fault surface of the thrust fault in image B. D. Tight, overturned fold within well-bedded flysch deposits, overlying Mount Iti. E. A vertical third horizon bauxite ore body, between the dark grey hangingwall and pale grey footwall, along the northern edge of Mount Iti. F. A southwest directed thrust fault with fault breccia, cutting and significantly offsetting the third horizon contact of Mount Iti.
Figure 8.7: NE-SW cross-section across the Duo Vouna area of Mount Iti to show the overturned fold structures in the carbonate sequence, and the effects of subsequent normal faulting on the inclined third horizon bauxite contact. The stereonets on the left present the bedding plane data for the lower sub-horizontal section of the third horizon and the upper inclined section of the contact. The stereonet below presents the thrust fault data recorded in Duo Vouna. The great circles on the stereonets are representative of average planes, colour coded to indicate the data sets they represent.

Key
- Bedding plane data
- Thrust plane data set 1
- Thrust plane data set 2

THRUSS FAULTING

Av. Thrusts 298/56
Av. Thrusts 107/64
As well as folding, thrust faulting is frequent across the Duo Vouna area, an example is shown in Fig. 8.6 F. Movement has occurred in both a SW and NE direction; interpreted here as a series of SE thrusts with NE directed backthrusts as indicated in Fig. 8.7.

Elsewhere along the Northern Iti slope there is evidence for more inclinations of the B3 and B2 horizon contacts such as the vertical orebody shown in Fig. 8.6 E. Unfortunately many bauxite surface outcrops lack the accompanying underground mines for deeper cross-section development. The folded structures of Mount Iti, however, also match structures identified by Kiskyras (1978) across Mount Helicon to the southeast, which has also been overthrust by the Pelagonian thrust sheet.

Figure 8.8: Stereonet interpretation of the Duo Vouna fold axis and fold axial plane using the bedding data from the sub horizontal and inclined limbs. The orientation data for the interpreted structures has been labelled on the stereonet.
structure has an axis with a 15° plunge, trending 289°. The axial plane is striking 101°, dipping 61°
NNE. A comparison with thrust fault data in Duo Vouna, presented in Fig. 8.7, shows that
thrusting is almost parallel to the fold axial plane. This can be interpreted as thrusting coming at a
later stage to folding, utilizing the weakened fold hinges as weakness planes to accommodate the
necessary movement.

Extensional faulting in the Duo Vouna area can be divided into two broad groups; both striking E-
W, the only difference being the direction of dip. Both of these fault sets can be linked to the
recent extensional deformation being parallel to the Sperchios Valley graben.
Mount Ghiona

The northern area of Mount Ghiona is shown in Fig. 8.10. The area is sparsely vegetated, and geological exposure is excellent. The terrain is of three broadly N-S trending dry valleys that have several occurrences of second and third horizon bauxites present. These valleys have previously being suggested to represent the northern splayed end of the Itea-Amfissa detachment (Papanikolaou et Al., 2009) although no conclusive evidence has been produced.

In order to understand the structure of the Northern Ghiona area a 5km E-W transect was followed across the Ghiona mountain to capture a cross-section of the structure of the region. An east-west transect was chosen as this would cut across the major N-S trend of the identified valleys, and also include several known bauxite exposures. The results are presented as a cross-section in Fig. 8.12. The main structures across the northern Ghiona area are a series of N-S trending thrust faults with an eastward movement direction, the fault along Makrilakoma Valley is shown in Fig. 8.6 A. It is suggested that erosional exploitation of these thrust zones has been responsible for the formation of the valleys.

Figure 8.10: Geological Map of Northern Mount Ghiona showing the locations of the cross sections in figures 8.12 and 8.13.
The thrusts have a broadly N-S strike, between 010° in the west, to 350° in the east, and dipping between 40° to 60° to the west. The limestones units across this region have been inclined by this thrust stacking, and so are also dipping westward between 20° to 30° in the west, to a more shallow dip of 10° to 15° on the eastern side. The thrusting is therefore at a greater angle than bedding, however in many cases small scale movements have been observed along bedding plane contacts, in particular the bauxite-hangingwall limestone contact, which has often been utilised as a plane of weakness for thrusting. Where a thrust fault cuts across a bauxite-carbonate contact at a low angle, it can cause an imbrication of up to a metre in height.

The carbonate-bauxite sequence has subsequently been cut by extensional faulting. These normal faults do vary in orientation and dip; however, from the data presented in Fig. 8.12, three main groups emerge. These can be further grouped into two sets, those in a NW-SE orientation, and those in a NNE-SSW orientation, as shown in Table 8.1.

<table>
<thead>
<tr>
<th>Extensional Fault Groups</th>
<th>Average Strike</th>
<th>Orientation</th>
<th>Dip</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>320°</td>
<td>NW-SE</td>
<td>SW</td>
</tr>
<tr>
<td>2</td>
<td>200°</td>
<td>NNE-SSW</td>
<td>ESE</td>
</tr>
<tr>
<td>3</td>
<td>150°</td>
<td>NW-SE</td>
<td>NE</td>
</tr>
</tbody>
</table>

Table 8.1: The average strike, orientation and dip directions of the three main extensional fault groups recorded across Mount Ghiona.

**The Northern Edge of Mount Ghiona**

Surface and underground mapping also revealed a change in thrusting direction along the northern edge of Mount Ghiona, which is shown in figure 8.6 B, and the cross-section in Fig. 8.13. Thrusting of this sheet is in a SE orientation, with the measured thrust planes having an average strike of 067°, and an average dip of 53° to the NW. Bedding planes and the ore horizon are also inclined to around 33° towards the NW.

Thrust structures in this sheet include: the steeply dipping nature of the bauxite and limestone beds; small scale shears along the bauxite-hangingwall contact (vertical offset of ~0.5m) which strike sub-parallel to the main thrust contact; several back thrusts also striking sub-parallel to the main thrust contact, but dipping to the south; a small nappe structure within the limestone beds; and there are larger scale kink bands within the limestone beds and back folding resulting in the overturning of a small section of the bauxite ore body.
Striations along measured thrust planes, shown in figure 8.6C, indicated at least two directions of movement and data of these are presented in figure 8.11. The first set conforms well to near dip-slip movement during the initial thrusting at a trend of around $320^\circ$, plunging around $50^\circ$. The second set suggests more oblique movement having a trend of $051^\circ$ and a plunge of $30^\circ$ to the NE which suggests re-activated strike-slip movement, initiated by recent extension and normal faulting. The normal faults identified all have a broadly NW-SE orientation, with dips to the SW and NE.

Figure 8. 11: A stereographic projection showing thrust plane data from the northern edge of Mount Ghiona, and striation lineation data, suggesting at least 2 directions of movement along this fault zone.
Figure 8.12: West-East trending cross section across the Northern region of Mount Ghiona, accompanied by structural data collected from the region, presented as stereonets. There is no vertical exaggeration. The colours of the cross-section are as in the key of Figure 8.10.
Figure 8.13: NNW-SSE Cross-section across the Northern slopes of Mount Ghiona to show the second thrusting orientation. Structural data has also been presented as stereonets. The colours of the cross-section are as in the key of Figure 8.10.
8.4.2. Ore deposit scale

Ore body structure
The shape and size of each ore body is partially controlled by the karstic structure it is filling; however in many deposits the bauxite does not fill the entire karst hollow, i.e. the karstic void was not full to the brim with bauxite material. The bauxite only represents the lower section of the karst, the upper section is often filled with coal and clay, where present, and limestone.

Tectonic controls on ore body location
In modern day karstic terrains, the karstification process is strongly influenced by joints and faults within the limestone which promote and focus carbonate dissolving fluids. It has already been established that the bauxites across the ‘Parnasse district’ have a NE-SW trend, but it is important to understand if this trend is true for Mount Iti and Mount Ghiona, and whether variations exist on a smaller scale.

Figure 8.14: Comparison of the long axes of bauxite ore bodies within Mount Iti and Mount Ghiona.

The orientation of the long axis of known bauxite ore bodies within the Mount Iti and Mount Ghiona regions was acquired and plotted in the two rose plots below. It was assumed that the orientation of the exploited structural feature (if present) would match that of the long axis of the developed karst structure.
The rose plots show that the orientations in Iti do conform to the NE-SW dominant trend stated by Petraschek (1989). Those in Ghiona however do not follow the same trend, and appear to be more variable. This may be due to several reasons; the deeper karst structures of Mount Iti may emphasise the structural controls better, there may be a difference in structural orientation between Mount Iti and Mount Ghiona or perhaps there is an additional/alternative control on karst development within the region (hydrology, elevation etc.) It is also likely that a larger data set is needed to identify the dominant trends.

8.4.3. The effects of the tectonic activity at the ore body scale

Compressional Tectonic structures

The cross-section in figure 8.15 shows the structural features observed within a near horizontal, third horizon, ore deposit in NE Mount Iti. Several faults cut across the ore body. In the centre of the cross section are 3 normal faults, each with a downthrow of 1-2 metres, striking NW-SE / W-E, and are associated with the recent N-S extensional activity. Towards the NE of the section, as the orebody approaches the vertical limb of the overturned Iti fold, several thrust and back-thrust faults have been developed as a result of compressional deformation. Most of the thrust structures have a 1-2 metre offset Al., so, however some may be considerably larger.

Figure 8.15: Cross-section of the Kato-Kopresies ore body within the North Iti Mountain. The thrust faults formed during the Eocene compressional deformation, followed by normal faulting associated with the current extensional deformation. Structures associated with both faulting events can dissect and offset bauxite ore bodies.
Towards the NE end of the cross section, the orebody becomes noticeably thicker, changing from around 5-8 metres in the south east, to up to 19 metres in the Northeast. While this thickening may be mainly controlled by the original palaeogeography of the karst landform, there is evidence that the thrust structures can produce local thickening of the orebody, through small scale thrust stacking and repetition, which can affect mine design, hangingwall stability and ore recovery and dilution.

Figure 8.16: Small scale shearing of the bauxite bodies can produce local thickening, hangingwall stability, recovery and dilution.

**8.5. Discussion of structural models**

The geological structure of Mount Iti and Mount Ghiona has been greatly affected by orogenic activity since the end of the Palaeocene. Differences in structure orientation between Mount Iti and Ghiona indicate variations in stress direction between Iti and Ghiona, which are a function of regional structural development. The structure of Mount Iti and Mount Ghiona can be explained by the following model:

1. Deposition of the Parnassos-Ghiona Limestones and intercalated bauxite horizons on an isolated platform, during the Late Triassic to Late Cretaceous, in the middle of the Pindos Ocean. Orogenic activity and the major deformation was within the Pelagonian and Inner Isopic zones to the east; the Parnassos-Ghiona zone remained relatively undeformed during this time. The dimensions of the bauxite ore bodies in this investigation fail to confirm or deny the previous structural controls identified for the bauxites (Robertson, 2012.)

2. During the Palaeocene, uplift and erosion lead to the deposition of the Flysch layer as a concordant layer, directly above the limestones.

3. Eastward dipping subduction beneath the Parnassos-Ghiona zone eventually led to the closure of the Pindos Ocean, east-west compression, and the over-thrusting and rotation of the Pelagonian zone onto and around the Parnassos-Ghiona zone from the east. Data from this investigation show that in Mount Iti, syncline and anticline features indicate a
dominently southwest thrusting direction, which affected both the limestone sequence and the overlying flysch. Further south, the dominant direction is east-west orientated compression, creating the eastward dipping thrusts across North Ghiona (Karipi et al., 2009, Robertson, 2012.)

4. Clockwise rotation of the Pelagonian sheet around the southern edge of the Parnassos-Ghiona zone was estimated at around 50° by Morris (1995.) Applying this to the direction of deformation in Ghiona, it would change the orientation from 090°-270°, to around 140°-320°, which would match the direction of compression required for the formation of the thrust sheet along the Northern edge of Ghiona. Therefore, in this model, it is proposed that the SSE directed thrust sheet along the north of Mount Ghiona represents a back-thrust in response to the clockwise rotation of compression direction. The thrust direction in Mount Iti would also require anti-clockwise rotation of about 45° from the east-west direction in Ghiona.

5. The first extensional phase in a broadly east-west direction, following the Eocene compression gave rise to the Itea-Amfissa detachment, along with many of the normal fault structures seen across North Ghiona; a fault set which is significantly less pronounced within Mount Iti (Papnikolaou, 2009.)

6. Finally, north-south directed extension associated with the development of the Sperchios and Corinth half-grabens, created many east-west trending normal faults within Iti, and several around North Ghiona, in particular, extensional reactivation of the northern-Ghiona thrust sheet, with high angle displacement (Mariolakos et al., 2009; Robertson, 2012.)

8.5.1. Implications for exploration and extraction

Mount Iti

Between the two studied regions, Mount Iti is the more structurally complex. The folding and thrust faults identified in Duo Vouna are likely to be part of a larger, repetitive complex that will continue further south and west, beneath the Sub-Pelagonian thrust sheet. Bauxite ore bodies found within this complex will be subject to the same structural deformation as those in Duo Vouna, including more inclined, vertical and overturned ore bodies. The intensity of deformation is also likely to decrease further south towards the front of the thrust sheet.

Further normal faulting is likely to be present further south; however the frequency may again diminish with increased distance from the edge of the Sperchios Valley.
**Mount Ghiona**

The parallel thrust valley structures of Mount Ghiona have inclined the bauxite horizons by around 15-30° to the west. Surface drilling, angled to intersect the inclined horizons at 90°, will help reveal whether bauxite bodies exist within the thrust sheets at depth.

Thrusting along the northern edge of Mount Ghiona has caused inclination and thrusting of the ore horizon, which may be repeated further south, outside the extent of this investigation.

Normal faulting combined with the good exposure of the carbonate platform across Mount Ghiona also allowed extensive bleaching of the bauxite, in particular where two perpendicular faults intersect (see chapter 4 for more information on bleaching.)

**8.5.2. Further work**

One aspect that was unable to be properly studied in this investigation is a hypothesis that as the flysch deposits and the underlying carbonates of Mount Iti have shared a similar deformation history they will show the same orientation and degree of deformation (in a relative sense, as the flysch deforms and fold much more readily than the carbonates.) In locations of highly deformed flysch at the surface, shown in figure 8.6 D, it is possible that the underlying carbonates have also

![Figure 8.17: Stereonet to show the comparison between Fold axial planes within the Parnassos-Ghiona limestones and the overlying flysch. The similar strike of the fold structures suggests a similar mode of formation.](image-url)
been folded creating vertical ore bodies and associated deformations. Further south, flysch deformation is less prominent, the underlying carbonates may too be flatter and less folded. A preliminary comparison of fold axial plane orientations in the flysch deposits and in the carbonates is shown in figure 8.17.

Although it is only a small data set, the structures in the carbonates and the flysch do appear to have a similar orientation. This may provide a simple yet highly effective tool in predicting the structure of the carbonates and bauxite horizons beneath the flysch deposits.

The structural models proposed by this investigation are also based on all the data currently available, and as new discoveries are made, and mining continues deeper within both Mount Iti and Mount Ghiona, the models should be adjusted, adapted and revised in light of new evidence.

8.6. Conclusions
The Karst-associated bauxite deposits of Mount Iti and Mount Ghiona, Parnassos-Ghiona zone, Central Greece, are hosted within a carbonate platform sequence that has undergone regional scale deformation during the Orogenic events responsible for the formation of the Hellenides Mountain range. To aid bauxite exploration, the structural evolution of Mount Iti and Mount Ghiona has been investigated and interpreted.

Within Mount Iti, compression during the Eocene led to overthrusting of the adjacent Sub-Pelagonian zone from the northeast onto the majority of Mount Iti. This caused south-westward verging anticlinal folding, that has produced inclined, vertical and locally overturned bauxite ore bodies. Southwest directed thrust faulting (and associated back-thrusting), also associated with the Sub-Pelagonian overthrust, is frequent across Mount Iti, and is sub-parallel to the fold axial planes.

Extensional deformation, associated with the Sperchios graben, across Mount Iti produced two broad groups of normal faults, both striking E-W.

In the northern area of Mount Ghiona, compression caused eastward directed thrusting. Rotation of the compression direction to a SSE-NNW orientation towards the end of the compression event caused thrusting along the northern edge of Mount Ghiona in a SSE orientation.

Extensional faulting across Ghiona has produced two main fault sets; one striking NW-SE, and the other NNE-SSW, both of which are likely to be related to post-compression relaxation and broadly E-W extension of the orogenic zone.
At an ore body scale faulting can dissect and offset individual ore lenses, can cause imbrication of the ore body contacts, can produce instabilities in mine structures and can affect recovery and dilution rates. Faulting also provides conduits for fluid flow encouraging bleaching and passive Al-enrichment of the bauxite as explained in Chapter 5.

References


Chapter 9: The ore genetic history of the Parnassos-Ghiona bauxites

9.1. Introduction
This Chapter is a discussion of the data and interpretations presented within this thesis and its integration with previous research to develop an ore genetic model for the Parnassos-Ghiona bauxites, in particular, those of Mount Iti and Mount Ghiona.

The bauxites have formed through a combination of processes primarily associated with sedimentary rock formation. They should therefore be treated as sedimentary ore deposits, and this Chapter is structured to address the main stages in sedimentary rock formation. The ore genetic process is summarised in Fig.9.1.

9.2. Source
Firstly, there is no doubt that these bauxites are allochthonous in origin as described by previous workers (Ozlu, 1983; Valeton et al., 1987; Nia 1971; Laskou & Economou-Eliopoulos 2007; Laskou & Economou-Eliopoulos 2012). Aside from the fact that the ‘terra rossa’ theory of bauxite formation in which the bauxite material is sourced from non-carbonate material within the underlying limestone has largely been disregarded by bauxite researchers, the high purity of the non-altered footwall limestone of the bauxites in the Parnassos-Ghiona zone presented in Chapter 5, suggests that it is a very unlikely source material.

The source of the bauxite material has been interpreted previously using concentrations of certain indicator elements within the bauxites. For example, Ozlu (1983) used Zr, Ga and Cr concentrations of bauxites across the Mediterranean karst-associated bauxite belt to determine their respective source lithology. Ozlu’s analysis of the second and third horizons determined a basic rock source for the second horizon, and an ultramafic source for the third horizon. This was followed by a comprehensive study of the bauxites and other laterite derived deposits across central Greece by Valeton et al., (1987), who agreed with a predominantly ultramafic source for the bauxites, and identified the ophiolites of the Pelagonian zone as the probable source.

This investigation analysed the trace element concentrations of the second and third horizon bauxites of Mount Iti and Mount Ghiona (see Chapter 4), and revealed significant differences that reflect on the original source material of the bauxite. The second horizon has higher concentrations of Zn and Cu, whilst still having significant concentrations of Ni and Cr. The third horizon has higher concentrations of Cr and Ni (which supports a comparatively more ultra-mafic source) but with significantly lower Cu and Zn. It should be noted however that Cu and Zn are not
Figure 9.1: A summary diagram of the overall ore genetic process and the main processes occurring during each stage in the development of the Parnassos-Ghiona bauxite.
as reliable indicator elements as Cr due to their potential mobility during bauxitisation. The differences in Cu and Zn may be influenced by variability in leaching of the primary source material. Data presented by Valeton et al., (1987) partially after Reche (1983), on the chemical compositions of the ophiolitic lithologies (harzburgites, amphibolites, and gabbros), also show differences in these elements.

While the harzburgites are highly enriched in Ni and Cr and low in Cu and Zn compared to the other lithologies, their Al\(_2\)O\(_3\) contents of only around 2wt% make them a problematic source, however, serpentinization may contribute to aluminium enrichment before bauxite formation. The gabbro lithologies also have high Ni and Cr, and a much higher Al\(_2\)O\(_3\) content of 15% wt which indicates that these are a more likely source for the third horizon bauxites. The second horizon bauxites, with their enrichment in Cu and Zn are closer to the volcanic rocks associated with the ophiolites, which again have an Al\(_2\)O\(_3\) concentration of around 15 wt%.

The detrital mineral components of the bauxites suggest contributions from varying sources. The chromite grains found within the second and third horizon bauxites agree with a mafic or ultramafic source, whereas zircon grains and xenotime grains suggest a more felsic lithology (see Chapter 4).

The REE have been used within this investigation to highlight processes and genetic relationships between different lithologies. Within every sample analysed for REE concentrations (i.e. red, silicified and sulphide bauxites (Chapter 4), yellow, white, green bauxites and re-precipitated iron deposits (Chapter 5) and altered limestone beneath the bauxite (Chapter 5), there has been a consistent negative anomaly of Eu identified, with an intensity value of between 0.63 and 0.79 (Eu/(0.5*(Sm+Gd))). This suggests that Eu has remained in its trivalent state and has not been significantly fractionated during any process since deposition of the bauxite source material. The anomaly may be a feature of the original source material, which has been retained during low temperature, near surface weathering conditions. Negative fractionation of Eu can be the product of high temperature magma chamber processes, where Eu is removed from magma via plagioclase crystallisation and separation. As such, mafic and ultra-mafic rocks typically have negative Eu anomalies (Bau, 1991.) Fractionation may also occur through high temperature hydrothermal alteration processes, such as those occurring at mid-ocean ridge systems (Sverjensky 1983.) The negative Eu anomaly is therefore consistent with a mafic-ultramafic ophiolitic source (for both horizons.) It should be noted that weathering of more felsic lithologies
can also produce negative Eu anomalies in the weathering products through loss during feldspar breakdown (Condie et al., 1995). However, a predominantly felsic source is considered unlikely due to the high Ni and Cr concentrations of the bauxites.

In summary, the data presented in this investigation supports an ophiolitic source for the second and third horizon bauxites within the Parnassos-Ghiona zone, and the differences between the second and third horizon bauxites could be explained by the geochemical differences between the more ultramafic and the more mafic compositions of the ophiolite suite.

Considering the average Al$_2$O$_3$ concentrations within the ophiolitic lithologies of around 15 wt% (Valeton et al., 1987, Reche 1983) there would need to be significant laterisation and enrichment of the source material in order to produce the bauxite ore bodies that have an average wt% Al$_2$O$_3$ of 55% (Valeton et al., 1987, Laskou & Economou-Eliopoulos 2007, data from this investigation.) In Chapter 1, several estimations of the resource tonnage were presented, and spanned from 100MT of proven reserves (Newman 2012) up to 600MT reserves (USGS 2013.) The respective tonnage of ophiolite, at 15wt% Al$_2$O$_3$, required to produce these estimated reserve tonnages, at 55wt% Al$_2$O$_3$, are presented in Fig. 9.2. The proven reserves of 100MT of bauxite alone would require around 400MT of ophiolitic source material. The estimations of 600MT of bauxite would

![The amount of weathered ophiolitic material required to produce the Parnassos-Ghiona bauxites](image)

**Figure 9.2:** The tonnage of ophiolitic source material at 15wt% Al$_2$O$_3$ to produce bauxite at 55wt% Al$_2$O$_3$ at various reserve tonnage estimations for the Parnassos-Ghiona zone.
require over 2000MT of ophiolitic source to produce. While these calculations are rather basic, it
gives an indication of the size of the original ophiolite and the scale of weathering required
assuming that it is the only source for the bauxite.

While the interpretations here assume a single source for the bauxite, it is possible that the
bauxite material may have been derived from multiple sources. Sediments within modern day
transport systems, such as rivers, are rarely, if at all composed of material from a single rock type,
or rock formation, owing to catchment areas spanning over several rock types. It is also highly
unlikely that the second horizon and third horizon (and the first horizon) have identical source
lithology/lithologies. After marine transgression over a bauxite horizon, submergence by marine
conditions, basin deepening, basin uplift, sea-level fall and re-exposure, it would be highly unlikely
that the same drainage conditions would be established, with the same land surface topography.

What is clear is that during bauxite formation, ophiolites were exposed within the surrounding
regions, and trace element concentrations of the bauxites suggest that material from these
ophiolites was transported and incorporated into the bauxite material. The differences between
horizons may reflect the relative contributions of different lithologies within the ophiolite
sequence, caused by continued erosion and/or tectonic uplift and exposure of underlying more
ultra-mafic lithologies during the time period between the submergence of the second horizon,
and the exposure of the third horizon footwall, and/or the contributions of other non-ophiolitic
lithologies.

9.3. Transportation

This investigation supports the review presented in Valeton et al., 1987 that suggests the transport
of bauxitic material was from the NE towards the SW via widely ramified river systems. The
textural investigations presented in Chapter 4 indicate fluvial transport, with high enough energy
to transport and rework the coarse pisolites and bauxite clasts. Channel-like karst structures
observed within the third horizon of Mount Iti and Mount Ghiona have formed through these
sub-aerial river systems, cutting through the exposed limestone surface.

The transport phase must have included several successive phases of re-deposition of the bauxite
material to allow time for pisolith formation, partial consolidation and bauxite clast formation.
The bauxite was therefore transported in discrete stages rather than a continuous slow flow of
the bauxite material, perhaps initiated by periods of heavy rainfall and high energy flow
conditions. During transport the bauxites clasts and pisoliths were abraded and rounded, before deposition and continued concretion growth.

The coarseness of the bauxite of both horizons would have made it too heavy for any significant transport by aeolian processes. Similarly, mass movement under gravity is also unlikely as this would not explain the well-rounded shapes of the majority of the bauxite clasts and abraded and broken pisoliths.

The Parnassos-Ghiona zone has been described as forming as an isolated platform within the Pindos Ocean (Mettos et al., 2006). Assuming the mode of transport to be inferred correctly, eustatic sea-level fall during periods of emergence and bauxite deposition must have been sufficient for direct sub aerial contact with the sub-Pelagonian zone source rocks.

9.4. Deposition and burial
Deposition of the bauxite onto the karstic voids would have occurred due to a final loss in transport energy and perhaps the meeting of these river systems with the open sea in lagoonal/estuarine settings. The nature of the karstic terrain to trap sediments and protect them from further erosion (Bardossy, 1982) may have also play a role in the deposition and accumulation of the ore bodies.

The second horizon bauxites are Kimmeridgian to Tithonian (156 to 145.5mya) in age and were deposited in, or were very quickly transgressed by, a shallow marine environment (Fig 9.3). Evidence of this is the sequence of bauxite layers of predominantly fine grained bauxite gel material. As deposition slowed towards the end of the depositional phase, shallow marine gastropods flourished in the soft muddy bauxite, and their shells were eventually fossilised into the upper bauxite layers. The re-establishment of limestone-forming conditions allowed the mixing of biogenic calcareous material and bauxite at the top of the ore bodies to create layers of bauxitic marl. Periodic influxes of bauxite material into this carbonate depositional environment created red-coloured layers above the main ore bodies. A break in the deposition of the main bauxite ore body, or a temporary rise in sea level, allowed development of an inter-layered limestone unit identified by Valeton et al., (1987.)

The third horizon bauxites are Cenomanian to Turonian (99.6 to 89.3 mya), and were deposited as a layered sequence of predominantly coarse pisolitic bauxites and bauxite clasts within a bauxite gel-like matrix, after a long period of transport and continued re-working, suggested by the complex textures presented in Chapter 4. As described by Petraschek (1989), the karst structures
were deeper towards the NE of the platform due to earlier exposure, possibly reflected by the more pronounced karst structures of Mount Iti compared to Mount Ghiona. The bauxites were deposited in a more terrestrial environment compared to the second horizon, infilling channels and sink-holes in an exposed karstified terrain, as suggested by the shapes of many karst structures across Iti and Ghiona.

After deposition of the third horizon bauxites of Mount Iti, a swampy environment developed above the bauxite, perhaps due to sedimentary infilling of the incised fluvial channels. This swamp environment was colonised by abundant plants rooted in the soft bauxite (indicated by root fossils within the bauxites.) Accumulation of the dead plant material in this swampy environment would have allowed the build-up of peat, which was the precursor to the coal deposits found above the bauxites of Mount Iti (Kalaitzidis et al., 2010).

As the coal deposits were not found in the area of Ghiona studied, it is unlikely that the Mount Ghiona third horizon bauxites formed within the same swampy palaeoenvironment as those of Mount Iti. It is suggested here, following previous suggestions by Bardossy (1982), Valeton et al., (1987) and other workers, that the third horizon bauxites in the Ghiona area represent a shallow marine/lagoon environment that was adjacent to the swampy, perhaps delta-like environment represented in the Mount Iti area (Fig 9.3).

It is proposed in this investigation that some of the organic matter from the swamps, as well as clay material, was transported SW into the shallow marine environment that would eventually be the northern section of Mount Ghiona. Oxygen depleting bacterial processes fuelled by the organic matter developed anoxic conditions within the bauxite sediment column of both Iti and Ghiona.

The rate of organic matter decomposition within the Ghiona bauxite was roughly equal to the rate at which it was being deposited, leaving only small amounts to be preserved as thin (<1cm) organic layers above the ore bodies. Within the swampy Mount Iti area, the rate of accumulation was far greater than the rate of decomposition, which allowed for preservation of the organic matter above the bauxites.
Figure 9.3: Two schematic models for the source, transportation and deposition of the second horizon bauxites (A) and the third horizon bauxites (B) of Mount Iti and Mount Ghiona, highlighting the main differences in their formation.
Burial of the third horizon bauxites occurred due to marine transgression and re-establishment of limestone producing conditions. The high quantities of organic matter above the bauxites of Mount Iti mixed with the forming hangingwall limestones giving them their distinctive dark-grey colour and high organic content. Further influxes of organic matter from swamp environments further inland, created discrete thin organic horizons within these limestones in the layers above the bauxites. This suggests that as marine transgression progressed, the swampy conditions migrated further inland. The lack of organic matter in the Mount Ghiona area meant that the overlying limestones have a more typical medium grey colour. Within this re-established marine environment, rudist bivalves flourished and now serve as a marker horizon for the third horizon hangingwall limestones.

9.5. Diagenetic processes

In this section, diagenesis is defined as the processes that occur within the bauxite after deposition that are the result of organic matter breakdown and associated mineralogical changes, compaction and dewatering and conversion of the original sediment into lithified rock. Diagenesis of bauxite deposits commonly results in changes to the texture, mineralogy and geochemistry of the ore. Valeton (1972) distinguishes the following diagenetic processes in karst bauxite deposits:

1. Changes in chemical and mineralogical composition
   a. Desilicification transformation of clay minerals into Al-hydroxide hydrates
   b. Dehydration transformation of Al-hydroxides into hydrated Al-oxides and Al-hydroxides
   c. Partial removal of iron
   d. Basal enrichments of certain trace elements.

2. Changes in textures
   a. Development of vesicular textures, pisolitic textures or breccia-like textures
   b. Lithification

Not all of these diagenetic changes have been recognised within the Parnassos-Ghiona bauxites. De-silicification of the clay minerals is suggested here to have occurred within the original bauxite source material as opposed to bauxitisation in-situ on the karst surface. While minor amounts of de-silicification may have occurred, the lack of a typical weathering profile vertically through the ore bodies, as indicated in Chapter 4, suggests that the material deposited onto the karst platform had already been de-silicified. In some of the vertical transects, the upper levels of the bauxite are the richest in SiO₂ which is unlikely for an in-situ bauxite profile.
Dehydration transformation of the deposited Al-hydroxides happened within both horizons. In agreement with Valeton (1965), Coombes (1969), Bardossy (1967) it is suggested that the redox conditions under which dehydration occurred controlled the resulting mineralogy of the hydrous Al-oxide phases. The hydrous Al-oxides crystallised out of a gel-like phase, as indicated by the micro-crystalline, equigranular and randomly orientated texture of the Al minerals throughout the second and third horizons. The more oxygenated second horizon environment that produced abundant hematite throughout the bauxite also encouraged boehmite formation. The more reduced environment that produced abundant iron sulphides (pyrite) throughout the third horizon bauxite encouraged diaspore formation, and the close association of these iron and aluminium phase types is seen throughout Mount Iti and Mount Ghiona. This has resulted in a boehmitic second horizon, and a predominantly diasporic third horizon, with some boehmite where reducing conditions were not established.

The partial removal of iron and basal enrichment of certain elements (REE, Ni, Zn, V, Pb, As) has occurred within the Parnassos-Ghiona bauxites, many examples of which have been presented in this investigation. However they are considered in this investigation to be predominantly epigenetic in occurrence, and will therefore be discussed in section 9.7.

Aside from these changes, within the second horizon, localised anoxic conditions promoted the development of chlorite minerals as pisolith layers and diagenetic coatings around bauxite pebbles.

Diagenetic textural changes proposed by Valeton (1972) particularly the growth of pisolitic and breccia textures are not consistent with the data presented here. The textures of the bauxites, particularly the third horizon show evidence of multiple stages of pisolithic growth and destruction, as well as bauxite clast (breccia) formation and subsequent rounding through transport. These pisolith structures are formed during bauxitisation above the original source rock, and during deposition and re-working during transport. The bauxite clasts are formed through the erosion and re-mobilization of semi-consolidated bauxite during transport also. Pisolith formation is likely to have continued after final deposition on the karstified platform and during diagenesis; however textural features of the bauxite indicate at least some transport and re-working. A complete model for the formation of bauxite textures within the Parnassos-Ghiona zone (earthy, pisolitic and clastic) has been presented in Chapter 4, and it is suggested that this model could apply to other allochthonous bauxites of similar texture (e.g. karst-associated bauxites in Italy, Montenegro, Hungary etc.)
*Diagenetic pyrite formation*

Within the third horizon where anoxic conditions were more widespread, pyrite was formed aided by bacterial reduction of (presumably) seawater sulphate. This probably started soon after the establishment of swampy conditions above the third horizon bauxites, and continued during marine transgression.

The first pyrites formed were within the soft bauxite gel, before significant lithification and hydrous Al-oxide crystallisation. These pyrites are often euhedral in form, can be zoned with thin layers of hydrous Al-oxides, (indicating synchronous crystallisation of both phases), and can often be inter-grown with goethite, indicating fluctuating redox conditions during their development. They utilized the easily accessible iron from within the bauxitic gel, and also acted as trace element scavengers for As and Ni from within the bauxite. Cr is low within these pyrites as in the bauxite Cr occurs mainly as stable detrital chromite minerals. Sulphur isotope compositions have indicated that pyrite formation was predominantly in an open system utilising bacterially reduced sulphur (further details in Chapter 5).

Once the freely accessible iron was consumed, further pyrite growth utilised the iron rich zones in pisolith structures and within bauxite clasts through direct replacement of hematite by pyrite. Sulphur isotope compositions of these sulphides have again indicated bacterial reduction of sulphate as the source of the sulphur, but within a steadily closing or closed system. Again these pyrites show evidence of fluctuating redox conditions during their formation, with many examples of goethite and pyrite pseudomorphs after each other.

These processes have created the typical red bauxites of the second and third horizon and the sulphide rich bauxites of the third horizon. Further alterations of the bauxites are considered to be epigenetic and are discussed in section 9.7.

Finally, burial within the thick carbonate sequences and overlying flysch together with sequences elsewhere has caused lithification of the bauxite deposits, creating a significantly harder ore in comparison, to the softer, often friable lateritic bauxites found in sequences elsewhere (e.g., Australia, Brazil, Africa).

**9.6. Tectonic deformation**

During the formation of the Parnassos-Ghiona zone and interlayered bauxites, the carbonate platform was isolated from any major deformation (Robertson et al., 1990.) It was during the Eocene that the regional scale orogenic activity associated with the second main phase of the formation of the Hellenide mountain chain deformed the Parnassos-Ghiona bauxites.
Deformation began with a compressional phase where the Parnassos-Ghiona zone was sandwiched between the Sub-Pelagonian zone to the east and the Pindos zone to the west as a result of the closure of the Pindos Ocean. During this event, the Sub-Pelagonian zone was overthrust onto the Parnassos-Ghiona zone in a south-west directed movement that primarily affected the north-eastern edges of Mount Iti and Mount Parnassos. This created anticlinal-synclinal folding along the north-eastern edge of the Parnassos-Ghiona zone, including Mount Iti, as the carbonate units were compressed under the pressure of the advancing thrust sheet. Consequently, the bauxite horizons within this area are no longer horizontal, and there are many examples where the bauxite ore bodies are steeply inclined, vertical and even overturned by up to 10 degrees.

Within Mount Ghiona, the compressional effects are also seen, however due to rotation of the Pelagonian zone around the Parnassos-Ghiona zone during thrusting, the compressional direction was closer to E-W in orientation, and has led to the formation of several westward dipping thrust faults across the northern Ghiona area, which have offset and imbricated (on a large scale) the bauxite horizons (See structural models in Chapter 8).

The compression had also lead to shearing of the bauxite-hangingwall contacts within several ore bodies, which created layers of limestone-bauxite breccia and small-scale (1 metre) imbrications of the bauxite-hangingwall contacts.

Following this was a period of extensional deformation as the thrusted units relaxed and rebounded (Papanikolaou, 2009) which produced significant N-S striking faulting across Mount Ghiona and less significant NE-SW faulting across Mount Iti.

Finally a second phase of extensional faulting associated with the formation of the Sperchios Graben in the north and the Corinth Graben in the south produced significant normal faulting across both Mount Ghiona and Mount Iti, particularly focused in the areas close to the Sperchios Graben (i.e. North Iti), and near the North Ghiona fault which separates Mount Iti from Mount Ghiona.

These brittle deformation events created fractures, faults and offsets within the bauxite ore bodies that have acted as conduits that encouraged epigenetic alteration of the bauxite (see Chapters 5 and 8).

9.7. Epigenetic processes
Several epigenetic processes have been recognised within the Parnassos-Ghiona bauxites, all of which have been intensified by brittle deformation.
One of the earliest epigenetic stages was the formation of pyritic veinlets, whilst the bauxite was still largely under reduced conditions. The sulphur isotope composition of these veinlets is distinctly different to the authigenic pyrites and replacement pyrites found elsewhere. It is suggested that these pyritic veinlets have formed from the residual $^{34}S$ rich fluid after intensive bacterially driven fractionation, giving a distinctively heavier isotopic signature than the other sulphide occurrences, although thermally-reduced sulphate could also create sulphides of this isotopic composition (see Chapter 5.)

Within the second horizon bauxites of Mount Iti and Mount Ghiona, silicification of the fine grained bauxites has been identified by the development of secondary kaolinite. Where the hangingwall-bauxite contact sheared, fluid flow along this contact has depleted the top layer of the bauxite in Si, Ca and some Fe.

Epigenetic alteration is most extensive in the third horizon. Oxidation of pyrite within the coal and the bauxite, by oxygen rich meteoric fluids flowing along faults and fractures, created acidic, $H_2SO_4$ bearing, fluids. Percolation of this fluid through the bauxite mobilized $Fe^{2+}$ from the decomposed pyrites and destabilised hematite minerals, removing Fe from the bauxite, producing an $Al_2O_3$ enriched, ‘bleached’ bauxite. As well as Fe, this fluid mobilized some Si and Al, probably from the breakdown of residual silicate minerals such as kaolinite. Other elements mobilized by the acidic fluids were V, Ni, Zn, As, Pb, Sc and REE, particularly LREE, excluding Ce and Y (see Chapter 5).

These mobilized elements are re-precipitated in zones where the acidic fluids were neutralized. These include within fractures and faults within the bauxite where fresh oxygen-rich meteoric water would neutralise the acidic waters, and at the base of the ore bodies, where interaction with and partial dissolution of the footwall limestone would cause acid neutralisation. In both of these locations the Fe was precipitated as goethite, often showing liesegang banding structures. At the footwall, dissolution and re-precipitation of the limestone created an interlayered goethite-calcite deposit (see Chapter 5, section 5.6.6). In this situation Al was precipitated as gibbsite, the only point where gibbsite has been found within the bauxites. Si was re-precipitated as quartz.

Whilst the chemical boundary imposed by the footwall contact caused precipitation of much of the Fe and associated mobilized elements, a fraction of the mobilized elements (with the exception of As, which was preferentially included in the goethite) penetrated into the footwall limestone creating a distinctive red/orange alteration that can be detected for up to 50 metres from the edge of an ore body. This footwall limestone alteration probably propagated along
fractures and faults, and dissolution of the limestone by the acidic fluid may have further facilitated fluid ingress (see Chapter 6).

Where this mobilized iron was re-precipitated under more reduced conditions within the bauxite itself, away from the influence of oxygenated meteoric waters, epigenetic chlorite developed, replacing mainly the bauxite matrix (see Chapters 4 and 5).

9.8. The varying redox conditions during ore genesis

Redox conditions and reactions are fundamental to the formation of the Parnassos-Ghiona bauxites (Laskou & Economou-Eliopoulos, 2007.) Evidence presented within this investigation suggests that:

1. Redox conditions control the mineral assemblages within the bauxites, in particular the Fe phases, and possibly the Al phases.
2. Redox conditions can vary between ore deposits due to differences in depositional setting.
3. Local redox conditions fluctuated over time giving rise to intergrown Fe$^{2+}$ and Fe$^{3+}$ minerals (pyrite and goethite) as well as pseudomorphic replacements of goethite after pyrite and vice-versa.

![Diagram](image)

Figure 9.4: A basic schematic model for the evolution of redox conditions within a third horizon bauxite of Mount Ghiona over time, with the major stages in ore genesis highlighted.
The historic variability in redox conditions for an ore body of the third horizon in Ghiona is sketched in Fig. 9.4. It shows how development of a reducing environment shortly after deposition will create predominantly reducing conditions in which the growth of authigenic pyrites, with some goethite can occur. The conditions would have been predominantly reducing until tectonism, uplift and faulting exposed the bauxite to oxidising conditions, gradually changing the overall conditions to a more oxidising environment where epigenetic bleaching of the bauxite was (and still is) the dominant process.

9.9. Conclusions
The karst-associated bauxites of the Parnassos-Ghiona zone, Central Greece are examples of allochthonous bauxite deposits that have formed through a complex series of processes where Eh-pH conditions varied considerably and strongly controlled the mineralogy and geochemistry of the resulting ore deposit. The ore genetic history of bauxite deposits within the Parnassos-Ghiona zone is complex, where the source, transport, deposition environment, diagenetic, epigenetic and tectonic processes combined to create lithologically and economically differing bauxite ores. These characteristics highlight the importance of a thorough understanding of the geology of karst-associated bauxites to guide exploration for these deposits.

References


Figure 8.1: West-East trending cross section across the Northern region of Mount Ghiona, accompanied by structural data collected from the region, presented as stereonets. There is no vertical exaggeration. The colours of the cross-section are as in the key of Figure 8.10.
Figure 8.2: NNW-SSE Cross-section across the Northern slopes of Mount Ghiona to show the second thrusting orientation. Structural data has also been presented as stereonets. The colours of the cross-section are as in the key of Figure 8.10