

# ANDRADITE AND MAGNETITE IN CONTACT-METAMORPHOSED CHALK NEAR PORTMUCK, ISLANDMAGEE, COUNTY ANTRIM

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**Skarn mineralisation was first reported 70 years ago by the mineralogist G. P. L. Walker at several coastal localities near Portmuck on the Islandmagee peninsula in eastern County Antrim. Described here is mineralisation associated with a 4 m wide Palaeogene dolerite dyke intruded through Cretaceous chalk. Along the dyke margin is a decimetre-thick, dull-grey band of massive magnetite-calcite rock which, in thin section, has a clustered granular texture.**

**In nearby marble, 2–3 mm diameter brown euhedral crystals of andradite garnet occur in close association with nodules of flint that have been metamorphosed to micro-crystalline quartz. Analyses by EDX indicate that the andradite is close to the ideal end-member,  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ , with minor substitution of Mg and Al. Flint is likely to be the source of silica for the crystallisation of andradite, whereas iron was probably introduced by hydrothermal fluids derived from the basaltic magma that formed the nearby sill-dyke complex.**

## INTRODUCTION

‘Skarn’ is a generic term for mineralisation formed by the metasomatic alteration of carbonate-rich rocks by the infiltration of hydrothermal fluids, or by diffusion of constituents from adjacent compositionally distinct rock bodies. Skarns are commonly formed by intrusion of magma into carbonate-rich sedimentary rocks, but can also be associated with regional metamorphism.

In the previous volume of this journal, Brian Young described hitherto unreported occurrences of magnetite mineralisation in contact metamorphosed sedimentary rocks adjoining the Whin Sill swarm in Teesdale in the northern Pennines (Young, 2017). He speculated that this mineralisation formed during sill intrusion in a process of ‘iron metasomatism’ involving the expulsion from the magma of iron-rich magmatic fluids which interacted with the country rocks. Young *et al.* (1985) had earlier described nickeline-magnetite mineralisation from former mines in the region, and attributed this to reactions between the mineralising brines and the still-hot contact metamorphosed rocks soon after sill emplacement.

The current article describes similar iron metasomatism associated with the intrusion of Palaeogene dolerite sills and dykes into Cretaceous chalk near Larne in County Antrim. Previous reports of magnetite occurrences in this area are summarised by Tindle (2008: p. 327) who refers to skarn mineralisation at Scawt Hill and Carneal, and to magnetite-bearing metasomatised basalt at various localities including Islandmagee and the nearby Isle of Muck (not to be confused with the Scottish island of the same name). Tindle (2008) also reports some occurrences of skarn andradite, including a xenolithic chalk block within the Central Ring Complex of Arran. He does not mention the Islandmagee localities, as hitherto the garnet has not been characterised to species level. This also applies to garnet from Scawt Hill, as noted by Tindle, who mentions that the garnet-like species at Carneal (in a similar geological context to Scawt Hill) is hibschite. Hibschite, which is commonly also described as ‘hydrogrossular’, is a variety of grossular garnet in which some of the silicate is replaced by hydroxide. Hydrogrossular (hibschite) is also reported

by Young *et al.* (1985) from garnet-rich selvages between magnetite- and calcite-rocks at Harwood Beck, Teesdale.

In the period from the end of the Second World War until the mid-1960s, the Ulster geologist George P. L. Walker published his mineralogical investigations of the Antrim basalts, dyke intrusions and associated zeolites. One of his first publications, in 1948, was a ‘preliminary note’ on the contact metamorphic rocks and minerals of the Portmuck area, near the northern end of the Islandmagee peninsula (Fig. 1). Walker mapped in detail the igneous features along this rocky coastline, including vents, composite lava flows and various dykes intruding the lava flows and the underlying chalk (currently designated the Ulster White Limestone). In the note, Walker describes skarn-like minerals developed in the contact metamorphosed margins of dykes. These minerals include andradite garnet, magnetite, ilmenite, apatite, ‘soda diopside’ and ‘sphene’ (now titanite). Walker’s geological map of the coastal region is reproduced as Figure 2.

Walker provides a detailed account of a specific dolerite dyke intruded through chalk “about a quarter of a mile southeast of Portmuck harbour”, a locality labelled on his map as ‘Garnetiferous chalk’. His excellent description (Walker, 1948: p. 166) is repeated here:

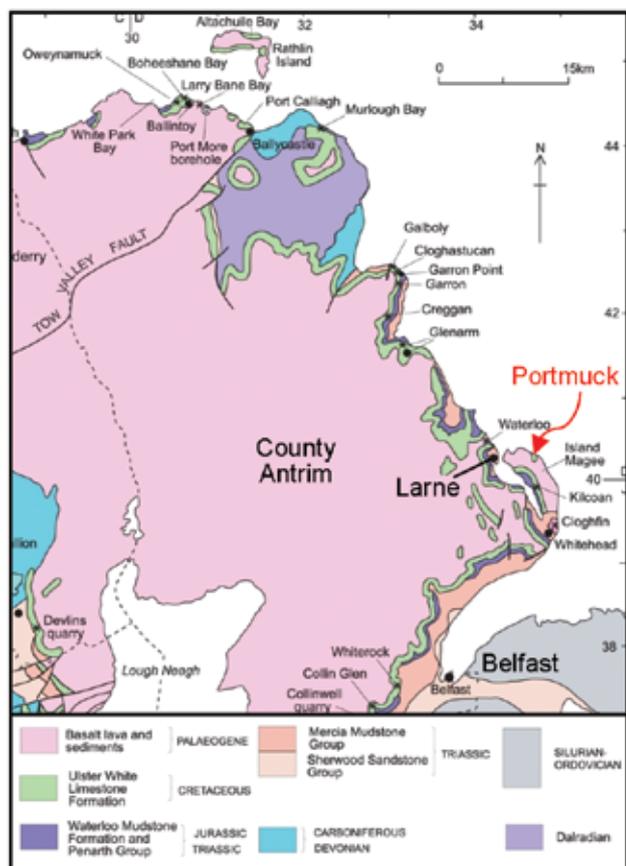
The northern margin of the dyke is vertical and very regular, and the chalk along some fifty feet of the exposed contact and for a distance of several inches from the margin of the dyke has been partially replaced by magnetite. The typical black rock that has been produced consists of approximately equal proportions of calcite and magnetite. Flint nodules occurring in this band are unaffected by this alteration. The remarkably sharp junction, simulating an intrusive junction, between the rock rich in magnetite and the altered chalk, free from magnetite is worthy of note. The black magnetite rock is easily distinguished from the brown weathered dolerite of the dyke. The southern margin of the dyke is extremely irregular, with numerous offshoots and enclosed masses of chalk. The chalk has been recrystallised to a coarse-grained calcite rock, calcite

grains up to three inches in diameter being observed. Locally the chalk contains chalcedony, garnet, magnetite and other minerals, in varying amount.

Pebbles and boulders of a variety of skarn rocks found on the bar (tombolo) are described including “Garnet-diopside rocks of various types” and “flinty rocks, usually packed with garnet, or sometimes rich in sulphides (pyrite and pyrrhotite)” (Walker, 1948: pp. 166 and 167). Walker also records abundant magnetite on joint planes in dolerite along the northern shore of the Isle of Muck, and large pink apatite crystals and well-formed ilmenite in veins in basalt adjacent to a dyke exposed at the southeast end of the island (Fig. 2). The author has not examined these occurrences due to the very considerable hazard of crossing the tombolo, which consists of rounded boulders coated in slippery seaweed and is only exposed at low tide, and because the Isle of Muck is a nature reserve and important bird nesting site with access requiring permission from the Ulster Wildlife Trust. Along the Islandmagee coast south from the tombolo is Two Mouthed Cave where zeolites (especially gmelinite-Na) are particularly well developed in vesicular basalt, however potential visitors are warned that access is challenging as this coastline is dangerously tidal.

## LOCATION

The specimens described here are from Walker’s ‘Garnetiferous chalk’ locality which is adjacent to a 4 m wide



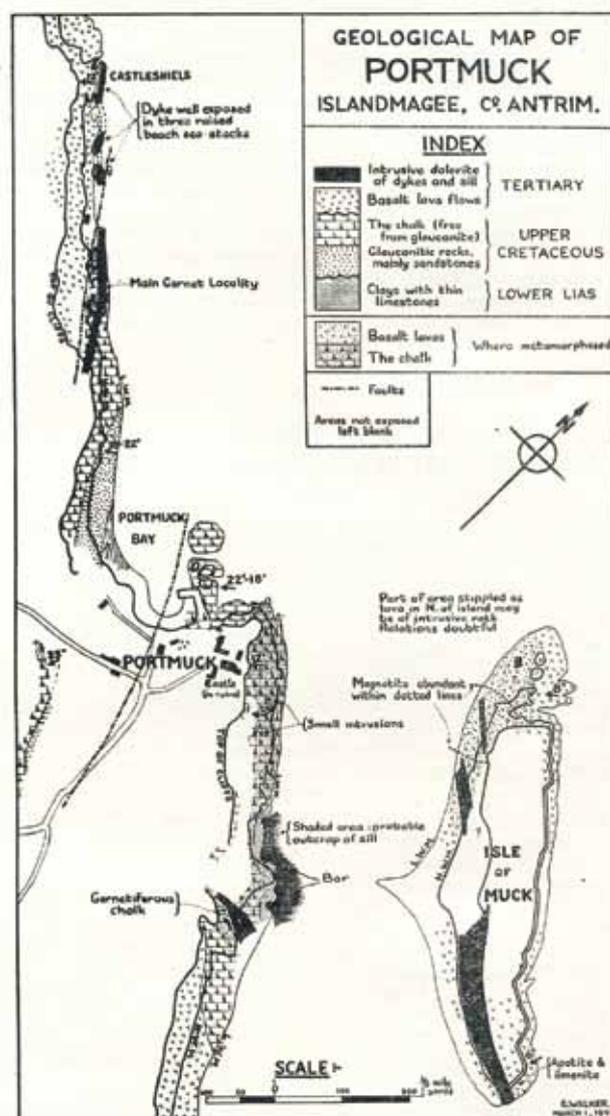
**Figure 1.** Simplified geological map of County Antrim, highlighting the outcrop of the Ulster White Limestone (from Mitchell, 2004), and indicating the location of Portmuck. Copyright of the Geological Survey of Northern Ireland, image reference number P947855, reproduced with permission.

dolerite dyke on the mainland opposite the Isle of Muck. The dyke is exposed on the rocky shore in the intertidal zone at the southern margin of a storm beach just south of the tombolo which connects the Isle of Muck to the Islandmagee peninsula (Fig. 3). The locality is at Ulster Grid reference D 3463 4021. Access to the site is not easy and requires low tide; it involves following a hazardous path around the rocky shore from Portmuck harbour leading on to the storm beach. No attempt should be made to access the site by crossing fields from Portmuck car park (Fig. 2).

## SKARN MINERALISATION

### Magnetite-Calcite Rock and Metamorphosed Flint

The magnetite-rich rock occurs principally at the contact between marble and dolerite, forming a distinctive grey band up to 30 cm wide (Fig. 4). The margins are sharply defined. The magnetite rock – marble contact runs



**Figure 2.** Walker’s 1948 geological map of the Portmuck coastline and the Isle of Muck, reprinted with the permission of the Irish Naturalists’ Journal Ltd. The locality described here, labelled ‘Garnetiferous chalk’, is southwest of the bar joining the Isle of Muck to the mainland (Islandmagee).



**Figure 3.** View northwards of the Islandmagee coastline opposite the Isle of Muck with the bar visible at top right. Rock exposures are of chalk (Ulster White Limestone) with the dark grey–brown dolerite dyke trending east–west in the centre of the view. Magnetite occurs along the northern margin of the dyke.



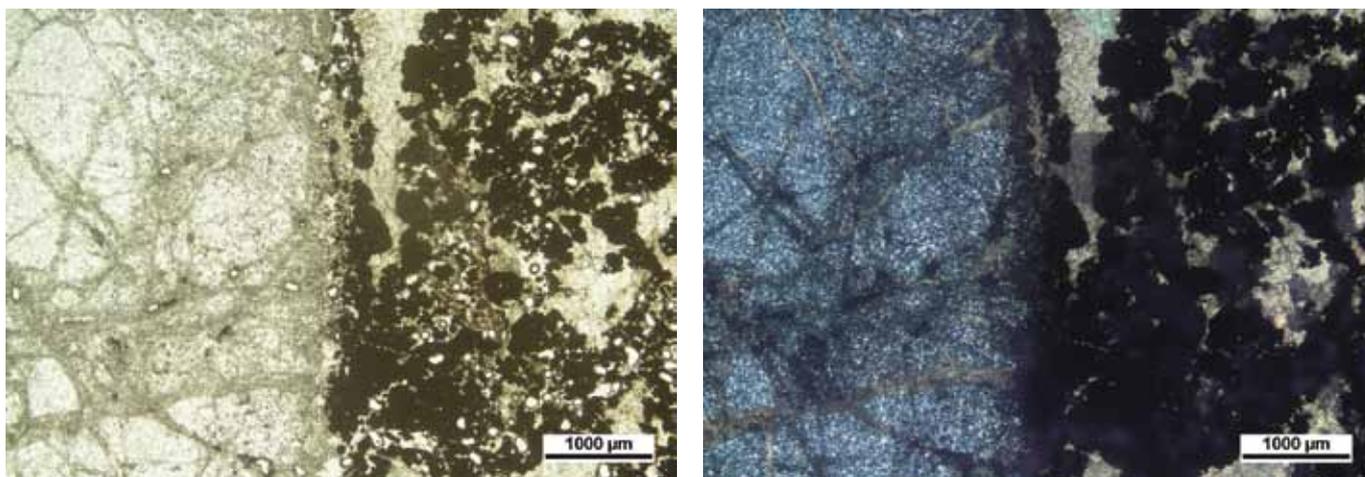
**Figure 4.** The northern margin of the dyke showing the dark grey, fine-grained magnetite rock in sharp contact with dolerite (top, south) and marble (bottom, north). Width of view approximately 0.8 m.

parallel to the edge of the dyke. Patches and stringers of magnetite–calcite rock also occur within the proximal marble. The contact between magnetite rock and dolerite is more irregular (Fig. 4). It is not clear whether this irregularity is due to disruption during mineralisation or to faulting post-dating dyke emplacement, or possibly both. In comparison to dolerite from the interior of the dyke, the marginal dolerite is fine-grained and paler in colour. The colour difference may be due to iron depletion, though this was not ascertained.

Hand specimens of the magnetite rock appear finely crystalline in comparison with the nearby marble. At the former Geology Department at Queen’s University of Belfast, a thin section was cut from a sample showing the contact between magnetite rock and a metamorphosed flint nodule within the marble. Examination using a polarising microscope (Fig. 5) reveals that the magnetite forms clusters of small crystals that are embedded in a matrix of relatively coarsely crystalline calcite. The clusters are 0.2–0.4 mm in diameter, and consist of individual crystals that are about one tenth of this size. The adjoining metamorphosed flint consists of micro-crystalline quartz that is criss-crossed with numerous veinlets of calcite resulting in a brecciated texture (Fig. 5). Some tiny crystals of magnetite occur within the calcite veinlets.

### Garnetiferous Marble

Garnet occurs occasionally within the magnetite–calcite rock, and more prominently surrounding some metamorphosed flint nodules within recrystallised limestone near the dyke. Boulders and pebbles can be found nearby, similar to those described by Walker, of flint nodules encased in magnetite–calcite rock which have a rim of garnet crystals surrounding the metamorphosed nodule (Fig. 6). The garnets are transparent honey-brown (yellow-brown if shattered) and occur as crystals which are typically a combination of trapezohedral and dodecahedral forms (Figs 7–9), usually 1–3 mm across and occasionally up to



**Figure 5.** Transmitted light images (left: plane polarised light; right: between crossed polars) of the contact between calcite-veined chalcedony (left) and magnetite rock. Scalebar width 1 mm.



**Figure 6.** Abundant euhedral brown andradite in recrystallised limestone showing the contact with an altered flint nodule in the lower part of the image. Concentric rims are visible around the crystals at top left. Field width 16.2 mm. Photo John Chapman.

5 mm. If enclosed in marble the associated calcite has a similar crystal size, and can show concentric zonation in transparency similar in appearance to ‘fortification’ banding in agate (Fig. 6). The flint has been baked to form pale grey and cream-coloured micro-crystalline quartz similar to that described above. The association of garnet with flint nodules, but rarely elsewhere within the marble, suggests that the garnet crystallised only where silica was available during formation of the skarn.

Ten garnet crystals from one sample were glued to an 8 mm diameter plate to obtain semi-quantitative energy-dispersive X-ray analyses using an EVO-SEM in the School of Pharmacy and Biomolecular Sciences, University of Brighton. The analyses confirm that they are rich in calcium and iron with traces of aluminium and magnesium. This indicates compositions close to the andradite end-member,  $\text{Ca}_3\text{Fe}^{3+}_2(\text{SiO}_4)_3$ , with minor solid solution with grossular and pyrope, respectively. Trace amounts of

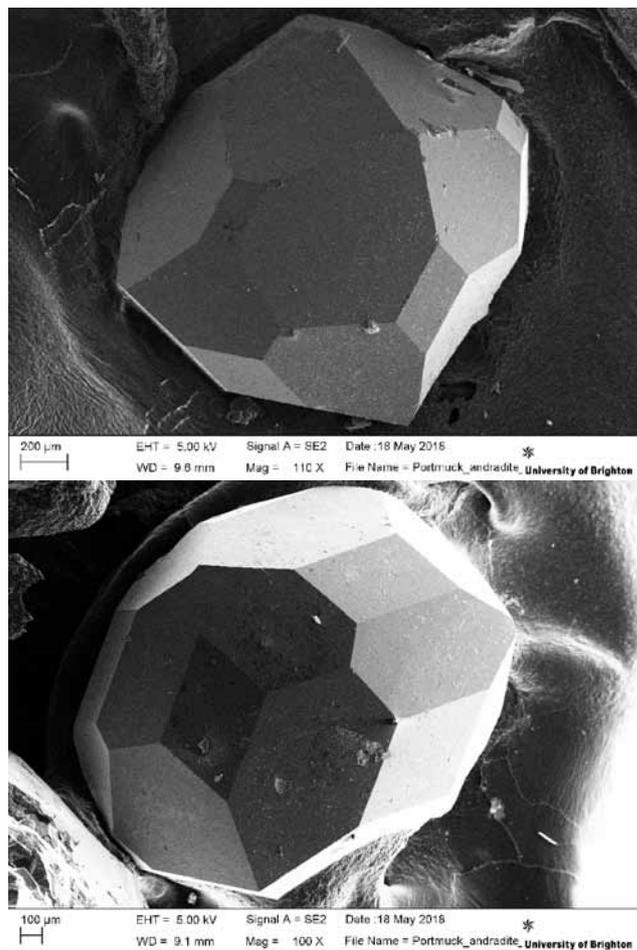


**Figure 7.** Euhedral brown andradite up to 2.5 mm across in recrystallised limestone. Photo John Chapman.



**Figure 8.** Dark brown andradite, 2 mm across, showing about equal development of two prominent crystal forms. Four-sided diamond-shaped faces of the dodecahedron {110} alternate with six (or seven) sided faces of the trapezohedron {211}. Photo John Chapman.

manganese were detected in some analyses, but no titanium (which occurs in melanite, a Ti-rich variety of andradite). Conversion of the analysed weight% oxide proportions to formula units (mole fractions) based on 12 oxygen atoms shows deficiencies in Ca+Mg of 0.42–0.56 formula units, and excesses in Fe+Al of 0.18–0.31 units and in Si of 0.29–0.39 units, in comparison to the ideal formula  $(\text{Ca,Mg})_3(\text{Fe}^{3+},\text{Al})_2(\text{SiO}_4)_3$ . These discrepancies are most probably systematic analytical errors due to non-ideal geometry during analysis [faces not exactly perpendicular to the incident X-ray beam, and other geometric and surface factors (Newbury and Ritchie, 2013)]. They might also possibly be due to cation-site vacancies or the presence of hydroxyl molecules within the andradite similar to the relationship between grossular and ‘hydrogrossular’ (hibschite).



**Figure 9.** Scanning electron microscope images of two andradite crystals showing typical crystal habits. The prominent six-sided faces, best shown in the upper image, belong to the trapezohedron {211}; they are modified by four-sided diamond-shaped faces of the dodecahedron {110}, which are prominent in the lower image.

Analyses by XRD of three samples confirm the identification of andradite, magnetite and the associated minerals calcite and quartz. Wollastonite and diopside were sought but not detected in the small number of samples examined.

## DISCUSSION

The extensive outcrop of metamorphosed chalk along the coastal section southeast of Portmuck, as noted by Walker (1948) and indicated by the shaded brick symbol on his map (Fig. 2), and of metamorphosed basalt on the Isle of Muck, suggests the presence of one or more concealed dolerite sills in addition to the exposed dykes. At the ‘Garnetiferous chalk’ dolerite dyke locality, the magnetite-rich selvage suggests a prolonged metasomatic process rather than a ‘flash’ injection of magma into a fissure. Both features support the idea that the sill-dyke complex may have been a magma reservoir feeding overlying lava flows that have since been removed by erosion.

The presence of the assemblage andradite+quartz+ calcite+magnetite, and absence (at least within the samples studied) of wollastonite and other calc-silicate

minerals, places some constraints on the physico-chemical conditions during skarn formation. The reaction of calcite and quartz to form wollastonite requires temperatures of more than 535°C, and low partial pressures of CO<sub>2</sub> (expressed as  $p\text{CO}_2$ ); larnite formation requires even higher temperatures, some researchers have suggested in the order of ~750°C, and/or extremely low  $p\text{CO}_2$  (Bowman, 1998). The generation of such low  $p\text{CO}_2$  in carbonate-rich rocks requires the infiltration of large amounts of water-rich fluids to dilute the CO<sub>2</sub> generated by the breakdown of calcite and formation of calc-silicate minerals. Bowman (1998) explains that andradite is stable over a wider range of  $p\text{CO}_2$  than grossular, shifting the wollastonite-forming reaction to higher temperatures. Andradite is also stable over a wider range of oxidation states (represented by the oxygen fugacity,  $f\text{O}_2$ ). Unless the  $f\text{O}_2$  is extremely low, wollastonite formation requires temperatures considerably in excess of 500°C. The assemblage andradite+quartz+magnetite is restricted to relatively oxidising environments, whereas lower  $f\text{O}_2$  (and higher temperature) is needed to stabilise pyroxene-bearing skarn assemblages (diopside, hedenbergite). At high pressures (50 MPa), the coexistence of andradite with quartz+calcite+magnetite constrains log  $f\text{O}_2$  values to >-25 at temperatures around 400°C (Gustafson, 1974). However the sub-volcanic system envisaged at Portmuck would involve lower pressures and probably a hydrostatic regime.

Development of the magnetite and skarn mineralisation was probably promoted by an abundance of watery fluid available in the chalk aquifer. Intrusions of basaltic magma supplied the heat for the hydrothermal system as well as for contact metamorphism. The hydrothermal fluids circulated through the chilled margins of the dykes (and probably sills) causing metasomatic alteration and extracting iron into solution. This iron then precipitated as magnetite under oxidising conditions at the dyke margin, and iron-rich watery fluids interacted with silica in flint nodules to form andradite. The marginal dyke rock and adjoining marble and altered flints were fragmented and veined, a process that can be attributed to hydraulic brecciation as the superheated watery fluid boiled in the low pressure regime. Porosity reduction and compaction as chalk was converted to marble may have helped to generate space for further injections of magma.

Walker's reports of 'soda diopside' and of pyrite and pyrrhotite in skarn rocks found in pebbles and boulders in the nearby tombolo, indicate that more reducing conditions prevailed elsewhere in the hydrothermal system. Reducing conditions were probably associated with basaltic magma intrusions into the Jurassic Waterloo Mudstone Formation that underlies the Ulster White Limestone. The mudstones are typically rich in organic matter and iron sulphides.

Further studies of the mineralogy and mineral chemistry of skarn mineralisation in the Portmuck area are warranted, particularly to ascertain if hibschite or similar hydrated garnets are present. Also of interest in the vicinity are the contact metamorphosed basalts which have not been considered here. The author hopes that this short article may inspire others to undertake considerate sampling and more detailed analysis, and to report findings in a subsequent publication: preferably less than 70 years hence.

## ACKNOWLEDGEMENTS

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