

CORKITE FROM GLANDORE MINE, COUNTY CORK, AND THE DISCOVERY OF FIVE MINERAL SPECIES NEW TO IRELAND: CHALCOSIDERITE, CHURCHITE-Y, DELAFOSSITE, KIDWELLITE, AND KINTOREITE

RICHARD P. UNITT, STEPHEN MORETON, SIMON KOCHER and
ROBERT LAWSON

(Received 19 November 2023. Accepted 29 December 2024)

Abstract

Glandore Mine, County Cork is the type locality for the uncommon lead–iron sulfate phosphate mineral corkite, the only mineral named after an Irish county. Electron microprobe analyses of thirteen ‘corkite’ samples revealed the closely related mineral kintoreite. One single spot analysis had molar Ba > Pb, which would make this a new mineral species: the barium analogue of corkite. This study also mineralogically characterises the Mn ores from Glandore Mine to species level, finding that they belong mostly to the cryptomelane–hollandite series. Other rare secondary minerals include cacoxenite and strengite, plus five minerals new to Ireland: chalcosiderite, churchite-Y, delafossite, kidwellite, and the aforementioned kintoreite. The Glandore Mn deposit results from a series of mineralising events that lasted from the early Upper Devonian until possibly as late as the Palaeogene.

Introduction

Although manganese ores are widespread across Ireland, Glandore Mine (also called Aghatubrid Mine) is one of only a few places in the country where such ores have been found in sufficient quantity to merit mining. The other localities are the nearby Roury Glen Mine, County Cork, and a mine at Howth, County Dublin. Of these, Glandore is by far the most significant (Cole 1922).

The history of Glandore Mine has been described by O’Sullivan (2002), and the summary herein is largely taken from that account. The initial discovery was in 1810 by a Colonel Robert Hall, and was of copper, not manganese. Hall was a Cornishman who had been recently discharged from military service, and who was prospecting for, and opening, copper mines throughout Counties Waterford and Cork. His attention was drawn to ash derived from burning the peat from a bog at Maulagow, County

Cork. This ash was found to be rich in copper, and Hall spent the years 1811–19 burning peat from the bog and selling the ash at profit. Exploration of the hillside above Maulagow failed to locate the source of the copper, and Hall left when the bog deposit became exhausted.

During these explorations, manganese was found, along with iron ore and baryte, loose in the drift (Weaver 1837), but mining did not start until 1833 when some local landowners began exporting manganese ore for bleach manufacture. In 1840, a rich vein of manganese ore was found when sinking a shaft in the northern part of Aghatubrid Beg townland (Glandore village, from which the mine acquired its name, is located in the southern part of this townland), evidently in search of copper, and mining scaled up, with 1,000 tons raised and ready for export by 1843. Mining continued until 1861, by which time some 20,000 tons of ore had been raised.

A revival occurred in the 1870s, under new ownership, but with a recorded output of only 580 tons between 1876 and closure in 1881 (Cole 1922). From about 1860, small tonnages of iron ore were also raised: 60 tons in 1860, more in the 1870s. A final period of mining from 1907 to 1911 raised another 326 tons of manganese ore, but from a smaller lode parallel to the main one. Thereafter, Glandore Mine received only occasional visits from geologists and mineralogists, although a brief drilling program was conducted by Irish Metal Mining Ltd. in 1968. Despite encouraging results, the program was abruptly terminated for unspecified reasons. Over time, the levels, shafts, and much of the opencast collapsed or were filled, and the dumps removed.

Nineteenth century descriptions of the manganese ore are vague, and authors were unable to fully characterise it due to the lack of modern analytical techniques. Apjohn (1844) refers to 'psilomelane', a generic term for undifferentiated hard manganese oxides. His sample was evidently impure, because it also contained appreciable silica, baryte and copper. Kane (1844) said the ore was mostly 'the true peroxide' but also present were 'the hydrated sesquioxide' and 'the earthy hydrated peroxide'. The first of these might be interpreted as pyrolusite (MnO_2), but without more details any assignment is tentative only.

The *Memoirs of the Geological Survey of Ireland* (Jukes and Kinahan 1861) quote a Mr Wyley thus: 'Very solid and massive beds of binoxide of manganese, seldom less than six feet in thickness, occurring solid and in stalactitic and botryoidal masses like hematite.' Accompanying it were baryte, hematite and quartz, but, in contrast to other accounts, no copper. The manganese gives way to iron with depth.

Daly (1918, Appendix 4) discusses an analysis of the ore which, he said, corresponded to a compound of one part of manganite and three of pyrolusite. It also contained a little copper, but less barium than other examples of 'psilomelane.'

Grennan (1969) lists pyrolusite, psilomelane, manganite and the manganese silicate mineral braunite. Although this account is within the modern era of instrumental analyses, there are no details of how the identifications were made.

Iron and copper ores are easier to identify than the notoriously tricky manganese oxides, and identifications of these may be considered more reliable. Thus, Grennan (1969) records hematite, ankerite and limonite as the main iron ores, and bornite, chalcocite, malachite and native copper as the copper ores. The copper minerals were in association with manganese ore, and mostly around an area known as the

'Copper Shaft.' Chalcopyrite was observed in quartz boulders along field margins to the north. An oddity reported by Grennan (1969) was native sulphur coating some manganese ore.

Recent attention from amateur mineralogists has added more minerals to the Glandore list. The mineralogical website mindat.org records minor amounts of brochantite, connellite, cuprite, rhodochrosite, and lepidocrocite. Goethite is common, occasionally as fine botryoidal and stalactitic masses.

The copper ore was rich. A glowing newspaper report described it thus: '[Its] character is the red oxide, with blue azurite and green carbonate layers interspersed with native copper. Many of the samples are most beautiful in appearance and have been assayed up to 57 $\frac{3}{4}$ per cent. of copper' (Anon. 1870).

This report alone would pique the interest of mineralogists, but it was another mineral that was to put the mine on the mineralogical map. Dauber (1857) referred to 'beautiful crystals' of beudantite, found by Dr Krantz (probably Dr August Krantz, 1808–72, a prominent mineral collector and dealer) at Glandore the previous summer, and provided some crystallographic data. Rammelsberg (1857) contrasted analyses of beudantite from Horhausen, Germany, with analyses from Glandore. The German material contained arsenic but very little phosphorus; the Glandore material the converse. Otherwise, they were similar in chemistry and appearance. Rammelsberg's data for the Glandore material are reproduced in Table 1. He averaged his values for analyses 3 and 4 to obtain the numbers in column 'R 5'. These averaged figures are the ones cited by later authors (Greg and Lettsom 1858, p. 272–3; Adam 1869; Hartley 1900; Anthony *et al.* 2000).

Adam (1869, p. 552) listed beudantite and corkite separately in his section on iron sulfates. This appears to be the first time the name 'corkite' was given to the mineral, thereby explicitly distinguishing it from beudantite, but Adam (1869) gives no further details other than a few physical properties and the analysis by Rammelsberg.

A further chemical analysis was carried out by Hartley (1900) using material originally collected by Dr Krantz and then in the University of Oxford, England, collection. The results from Hartley (1900) are reproduced in Table 1 (column 'H'). Doubts were raised, however, about the authenticity of the sample that Hartley had used. Miers (1900) pointed out that the specimen purporting to have been collected by Dr Krantz himself at Glandore looked more like material from Dernbach, Germany, than other samples from Glandore, something Hartley himself

Table 1—Published analyses of corkite from Glandore, and a similar mineral from Dernbach, Germany (Column S) as analysed by different authors. R = Rammelsberg (1857). H = Hartley (1900). S = Sandberger (1857). 'P/(P + S)' is the molar ratio of these elements. 'Ideal' is the ideal composition of corkite based on its formula: $\text{PbFe}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$.

% Oxide	R 1	R 2	R 3	R 4	R 5*	H	S	Ideal
SO ₃	12.40	12.32	13.55	13.96	13.76	12.72	4.61	12.0
P ₂ O ₅		8.00	9.73	8.21	8.97	9.35	13.22	10.6
As ₂ O ₅		0.21	0.37	0.10	0.24		trace	0
PbO		20.35	22.98	25.57**	24.05	32.33	26.92	33.4
CuO			2.45		2.45	1.35	trace	0
Fe ₂ O ₃		31.11	40.42	40.96	40.69	34.61	44.11	35.9
H ₂ O	9.77			(9.30)	9.77	8.45	11.44	8.1
Total				100	99.93	98.81	100.30	100
P/(P+S)		0.42	0.43	0.40	0.42	0.45	0.76	0.5

*average of 3 & 4

**combined with CuO

had also noted. Both men referred to the material as 'beudantite,' suggesting that the name 'corkite' was still not in common usage.

In 1852, a mineral thought to be beudantite had been found at Dernbach but upon analysis was found to contain phosphorus in place of arsenic (Sandberger 1857). Like Rammelsberg, Sandberger regarded both as varieties of beudantite, rather than as separate minerals. The analysis in Sandberger (1857) of the Dernbach material is also included in Table 1 (column 'S'), but the molar ratio P/(P + S) is markedly higher than in the other analyses, including Hartley's. Hartley and Rammelsberg were both using material found by Dr Krantz and the results are similar, thereby allaying fears that Hartley's sample was from Dernbach.

No other analyses of Glandore corkite have since been published, although the mineral has been well characterised from many other localities around the world. It is now understood to be the phosphate analogue of beudantite, a member of the beudantite group within the alunite supergroup (Scott 2000, Fig. 1). But given that Glandore is the type locality there are disappointingly few analyses of corkite from there, and they are all the same material collected by Dr Krantz on one visit. It is, therefore, unknown if his samples were representative, how much the type material varies, and whether other members of the beudantite group are present. This latter point is of importance to museum curators and collectors because specimens labelled 'corkite' from Glandore could, conceivably, be other members of the beudantite group, many of which are similar in appearance.

The manganese ore at Glandore has also not been well characterised, and discoveries by amateur collectors indicate that the deposit is home to more

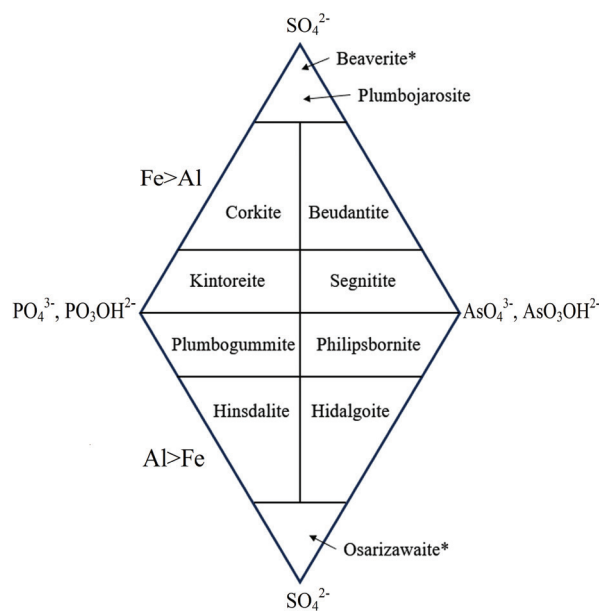


Fig. 1—Composition diagram of the lead-bearing members of the alunite supergroup; *contains copper. After Scott (2000).

minerals than are presently reported in the literature. A full description, with proper characterisation of the minerals present is, therefore, needed and given herein.

Geology of the Glandore Mine Area

Early authors refer to an east–west 'channel of manganese' extending for about three miles (Jukes and Kinahan 1861), or five miles (8km) according to Hallissy (1923) and Rundall (1939). It is not a continuous vein, but a series of occurrences along strike,

some of which have been tested by trial shafts (now all filled up) and mined in two places: Roury Glen, and Glandore (Rundall 1939). Roury Glen Mine consisted of a shaft and intersecting level. Good ore was found but mining ceased owing to a disagreement between the landowner and the mining company (Daly 1918). The site has now been cleared. Only Glandore Mine, towards the western end of the ‘channel,’ met with success and was developed as a viable mine.

Reilly and Graham (1972) described the mineralisation as being associated with a major dextral tear fault, which changes to a near-strike fault in the vicinity of Glandore Mine. The country rocks consist of sandstones and slates of Devonian to Lower Carboniferous age. The faulting occurred after regional folding, and likely was late in the Variscan (Hercynian) Orogeny. No attempt was made to date the mineralisation.

Recent studies by one of the authors (RU) suggest that the mineralisation at Glandore and Roury Glen is associated with fault intersections along a major east–west trending early basin-forming structure (unpublished observations). The stratigraphy is dominated

by sandstone, siltstone, and mudstone, comprising the transition sequence from the mud-dominant Castlehaven Formation to the sand-dominant Toe Head Sandstone Formation (Fig. 2). Throughout southwest County Cork this transition is marked by the appearance of stratiform sediment-hosted copper (SSC) deposits (Reilly 1986; Wen *et al.* 1996). Additionally, studies in the region have noted east–west-trending quartz and baryte lodes (Hallissy 1923; Reilly 1986) that were thought to post-date Variscan compression. Lang *et al.* (2020) identifies the east–west-trending structures and contemporaneous mineralisation as being associated with basin formation and yielding Re–Os dates of 367 Ma for the copper mineralisation at Mountain Mine, Allihies, on the Beara Peninsula. The SSC deposits are often located close to these major east–west structures which may have acted as conduits for the metal-bearing fluids. One of these east–west trending structures can be identified between Glandore Mine and Rossscarbery, the so-called ‘channel of manganese’ noted by previous authors.

Figure 2 clearly demonstrates the trend of the east–west structure from Glandore Mine to



Fig. 2—Geological map using data compiled from Geological Survey Ireland digital map data, Rundall (1939), and from unpublished field observations by Richard Unitt.

Rosscarbery and the association of massive quartz veins with showings of Cu in the adjacent transitional sediments.

Iron oxide/oxy-hydroxide mineralisation predominantly occurs where the east–west structure is transected by later NNW–SSE-trending faults. Many of these faults are associated with the end-Variscan tectonics of the late Carboniferous (Quinn *et al.* 2005), although some faults may have been active during sedimentation and in post-orogenic times. The fault intersections have generated localised shear zones that brecciate massive quartz and baryte and that have cemented these breccias with iron oxide/oxy-hydroxides. At Glandore Mine, early mineralisation appears to have consisted of quartz–carbonate–sulfide and baryte–hematite veins. The copper sulfides were concentrated in the eastern part where the subsequent oxidation event generated both iron and copper oxides.

Manganese mineralisation is concentrated in the western part of the Glandore Mine deposit. Manganese oxides replace iron oxide/oxy-hydroxides and partially or completely infill earlier formed cavities. This is consistent with the original oxidation event not involving Mn but generating goethite and

cuprite. The manganese and the assemblage of phosphates described in this paper, including the corkite, appear to have formed during later supergene events, with circulating Mn-rich groundwater completely replacing goethite at higher levels.

Interestingly, there are thin layers of later goethite on some of the Mn minerals. We have been unable to confirm Grennan's report (1969) of copper occurring with manganese. It is possible he mistook goethite for manganese ore, as goethite is common around the Copper Shaft.

Glandore Mine Site Description

Figure 3 shows the general layout of the Glandore Mine site. The 'Big Pit' currently provides limited underground access via vertical descent by rope, of roughly 35 metres into a stope, the bottom of which is a muddy area with fetid water on either side. An ore pile here was reported by O'Sullivan (2002) and confirmed by some of the authors (SM and RL). On the other side of the water, in the direction of the Engine Shaft and Copper Shaft, O'Sullivan (2002)

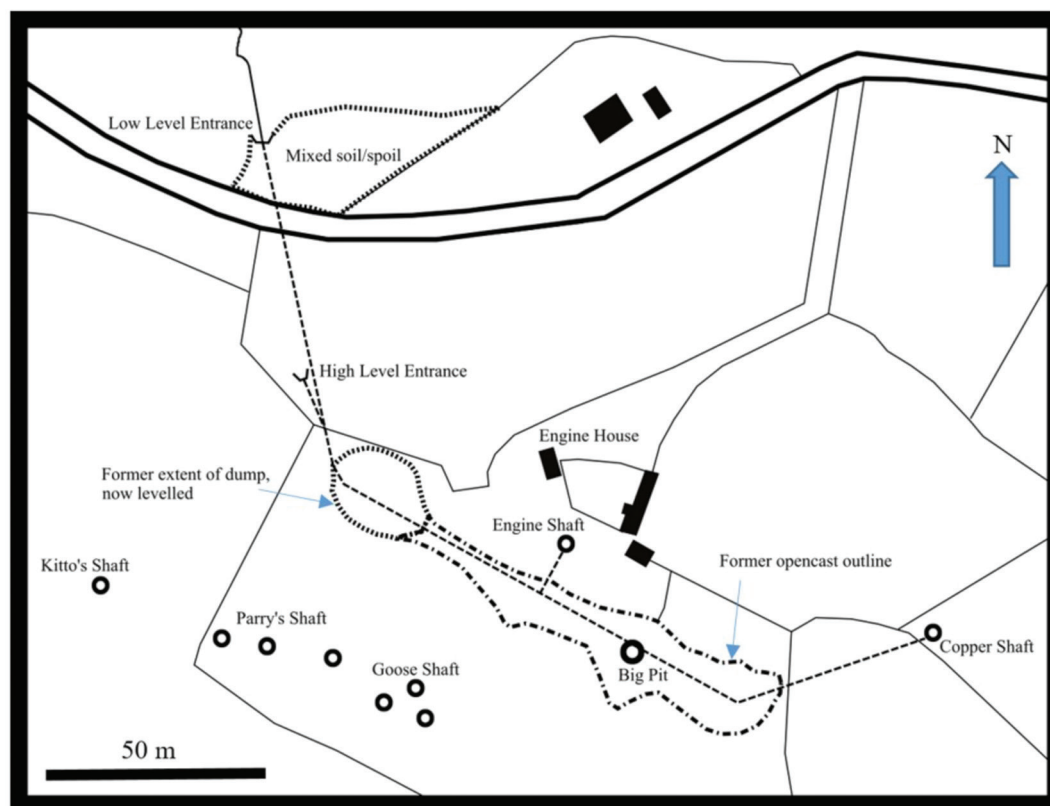


Fig. 3—Plan view of the Glandore Mine site, based on Rundall (1939), O'Sullivan (2002), Ordnance Survey of Ireland maps, aerial photography and unpublished site observations by the authors.

recorded a flooded shaft, a wooden chute with ore, and a level with copper-stained walls. We can confirm these features except that the chute with ore is merely timbers with waste rock stacked behind them. The copper-staining is post-mining malachite.

The water level in this section fluctuates greatly. O'Sullivan (2002) found it to be six feet (two metres) deep. On our first underground visit it was as described, but on our second visit it was only knee deep; however, marks on the wall indicated it had previously been near to the roof of the copper-stained level. The floor of this wet section is littered with obstacles that make it hazardous to traverse when the water is deeper than knee-depth. In the roof at this point is a vein about 15cm thick of manganese ore, but no iron mineralisation. Because the ore pile, just a few cubic metres in volume, contains a mix of Fe and Mn ores, it likely came from a deeper level and was raised up the (now flooded) internal shaft.

On the surface, a fine engine house remains but is much overgrown. The Copper Shaft is identifiable as an overgrown depression in the corner of a field. A little mine waste remains here, covered in dense vegetation on both sides of the hedgerow. The current landowner, agreed to plough the area close to the shaft on the request of one of the authors (RU) to reveal mineralised material. The remaining mine waste, which used to be locally productive in copper ores, has been well picked through and a diligent search is now required to locate specimens.

A depression just to the south of the local road (L-8325-0) marks the site of the run-in High Level. The Low Level, north of the road, is still open for 64 feet (19.5m) to a blockage, according to O'Sullivan (2002), albeit flooded nearly to the roof.

The area below the road is marked on the Ordnance Survey map (6" sheet 142, section 2) as 'Manganese Works'. It is now densely vegetated, although pieces of iron-rich mine waste, rarely with corkite, have been found here by one of the authors (RU), together with more abundant manganese-rich mine waste (samples up to 40cm), occasionally containing rhodochrosite. Extensive dumps visible in a photograph from 1939 (Rundall 1939) sadly were cleared, probably in the 1950s, when O'Sullivan (2002) reports that the opencast was filled and levelled. Some of the local walls and many of the local roads utilised the mine waste material prior to William H. Rundall's visit in 1939. The opencast is now a densely vegetated depression behind the engine house, with the Big Pit still open at one end.

Methods of Mineral Analysis

The mine site has been visited on multiple occasions by the authors (except SK) from 1986 through 2024. Mostly, this has been surface only, but underground access was achieved via the 'Big Pit' (RL and SM). The ore pile therein provided much of the manganese ore and all but one of the corkite samples geochemically analysed in this study. Sample Mn6, was collected *in situ* from the 15cm vein in the roof. All other samples were collected from the surrounding fields and former spoil heaps.

Analyses were carried out by X-ray diffraction (XRD) on a Rigaku Miniflex 600 X-Ray Powder Diffractometer using a Cu source; X-ray fluorescence (XRF) on a Bruker Tiger S8 spectrometer; scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) on a Tescan Vega 3, using a program by Oxford Instruments; and SEM using wavelength dispersive spectrometry (WDS) on a JEOL JXA-8530F electron microprobe fitted with a field emission gun. The beam current was 20nA and the acceleration voltage 20kV. Raman analyses were conducted on a Renishaw inVia Qontor confocal Raman microscope at the Mary Ward Laboratory in the School of Biological, Earth and Environmental Sciences at University College Cork (UCC), using a 532nm laser and a silica standard at 520.5cm⁻¹.

X-ray diffraction can only assign species-level identities to minerals when their crystal structure is unique. Some of the minerals described herein belong to groups with similar structure, but different chemistry. Hence, XRD can only identify the group in these instances.

X-ray fluorescence provides quantitative chemical analyses with precisions of around 0.1% to 0.2%. Thus, a reported value of, say, 35.8% may be 35.6% to 36.0%. For sample preparation, 1.0000 +/- 0.0002g of sample is fused with 10.0000 +/- 0.0002g of lithium tetraborate flux in a platinum crucible. This is poured into a mould to form a disc, or 'bead', which is then analysed by the instrument and compared against calibration lines obtained using standards. Because this method requires a full gram of pure material it is unsuited for small samples, such as corkite, but is ideal for the manganese ores which are plentiful as large masses. X-ray fluorescence gives an overall composition, but will not detect zoning, or small-scale variations in a sample.

Energy dispersive spectroscopy (EDS) allows for the analysis of tiny (even microscopic) samples, giving a quick indication of the principal elements present and their approximate proportions. It is, however,

only semi-quantitative. It was useful for sorting the ‘corkite’ samples into phosphate-rich (likely kintoreite) and less phosphate-rich (likely corkite) whilst eliminating other members of the beudantite group. But EDS lacks the precision needed for assigning species-level identifications with confidence, and for this WDS is needed.

Wavelength dispersive analysis (or electron microprobe analysis) is a technique related to EDS. It uses samples that are polished optically flat, and it compares the wavelengths of emitted X-rays to standards, thereby enabling precisions much greater than can be achieved by EDS. This makes WDS ideal for very small samples, such as corkite crystals a few hundred microns across. It can also detect zoning within such crystals, but, unlike XRF, will not give an overall composition for a bulk sample. Detection limits ranged from about 70ppm (Al) to 200ppm (Pb). Precisions for WDS estimates are difficult to estimate; results are often quoted to two decimal places and are so here, but with the caution that the last decimal place may not be justified.

A total of 387 WDS spot analyses on thirteen ‘corkite’ crystals from twelve specimens were carried out. These comprised a series of spot analyses traversing a region of interest (ROI) on the sample. An additional ten WDS spot analyses on each of two crystals from a specimen collected on surface by one of the authors (RU) are included. These were unpublished work carried out in 2012 by Dr Andrew Tindle (Open University), which he kindly made available to us. This brings the total number of spot analyses to 407. This is too large a data set to present

here, so it has been simplified by reporting the averages for each ROI.

Raman spectroscopy is a non-destructive technique that does not require any sample preparation. It can identify the structure, phase, and crystallinity of a material and can be used on very small crystals utilising a spot size of 1.2µm. The data is presented as a spectrum that can be compared to previously recorded spectra. Peaks on the spectra record wavelength and intensity and correspond to a specific molecular bond or group of bonds.

Results

Manganese ore

Determinations by XRD for the manganese ores, and for some of their associated rock matrix, are summarised in Table 2. The XRF analyses for the same ores are given in Table 3. Quartz was present in all samples except Mn 7, 8 and 9a, and is confirmed by the presence of relatively high SiO₂ in the XRF analyses. Goethite was detected by XRD in samples Mn 1, 2, 5 and 8. These also had the highest Fe contents. Neither quartz nor goethite will affect the analyses of the tunnel cations (K, Na, Ba) present in the manganese oxides (see Discussion). Sample Mn 7 contained some pyrolusite, but three peaks could not be assigned. More concerning is the presence of muscovite (XRD detection) in seven samples (Mn 1, 2, 4, 5, 6, 9b, 10), which is supported by the presence of Al in the XRF data.

Table 2—Minerals identified by XRD of Mn ores, and their rock matrix, from the ‘Big Pit’. 9a and 9b were visually distinct phases in Mn ore sample number 9.

<i>Sample/UCC</i>	<i>Coronadite group</i>	<i>Quartz</i>	<i>Muscovite</i>	<i>Other minerals</i>
Mn 1	Yes	Yes	Yes	Goethite
Mn 2	Yes	Yes	Yes	Goethite
Mn 3	Yes	Yes	No	None
Mn 4	Yes	Yes	Yes	None
Mn 5	Yes	Yes	Yes	Goethite
Mn 6	Yes	Yes	Yes	None
Mn 7	Yes	No	No	Pyrolusite & unknown
Mn 8	Yes	No	No	Goethite
Mn 9a	Yes	No	No	None
Mn 9b	Yes	Yes	Yes	None
Mn 10	Yes	Yes	Yes	None
Matrix of Mn 6	No	Yes	Yes	None
Matrix of Mn 9	No	Yes	Yes	None
Matrix of Mn 10	No	Yes	Yes	None

Table 3—X-ray fluorescence analyses of the samples in Table 2. Symbol 'A' = total Na + K + Pb + Ba + Sr (moles). 'Corrected A' is 'A minus contribution from muscovite.' 'Mineral' is the species, dependant on which cation in 'A' is dominant. Other abbreviations: Cry = cryptomelane, Hol = hollandite. Mn 9a and 9b were visibly different phases in the same sample.

Oxide	Mn 1	Mn 2	Mn 3	Mn 4	Mn 5	Mn 6	Mn 7	Mn 8	Mn 9a	Mn 9b	Mn 10	Matrix Mn 6
Na ₂ O	0.1	0	0.2	0.2	0	0.1	0.1	0.1	0.3	0.1	0.2	0.1
SiO ₂	35.8	34.1	42.3	50.6	44.7	41.8	0.1	0.6	1.2	37.7	38.6	80.4
Al ₂ O ₃	1.8	1.9	0.4	3.3	2.4	7.1	2.2	0.5	0.9	3.8	2.1	12
Fe ₂ O ₃	26.3	10.1	4.3	1.5	30.5	0.8	0.8	38.4	1.2	2.7	3.8	0.6
CaO	0	0	0	0	0	0	0	0	0	0	0.1	0
MgO	0	0	0	0	0	0	0	0	0	0	0	0.2
TiO ₂	0.4	0.1	0	0.2	0.1	0.3	0	0	0	0.3	0.1	0.6
ZnO	0	0	0	0	0	0	0	0	0	0	0	0
K ₂ O	1.1	0.6	1.3	1.8	1	2.2	1.4	0.9	2.3	1.8	1.7	3
PbO	0.3	0.1	0	0.1	0.1	0	0.1	0.4	0	0.1	0.1	0
BaO	0.2	5.2	0.7	0.5	0.4	2.6	0.5	1.7	2.3	2	0.6	1.2
SrO	0	0	0	0.1	0	0	0.1	0	0.1	0.1	0.1	0
Mn ₃ O ₄	26.6	37.6	41.4	32.8	17.1	36.2	76.7	31.1	74.1	38.6	40.3	0.1
Balance	7.4	10.3	9.3	8.8	3.5	8.7	18.1	26.3	17.7	12.7	12.2	1.8
Total A	0.029	0.047	0.039	0.049	0.024	0.067	0.038	0.035	0.074	0.056	0.048	0.029
Mn:A	11.9	10.5	14.1	8.7	9.2	7.1	26.7	11.6	13.0	9.1	11.0	11.9
Mineral	Cry	Hol	Cry	Cry	Cry	Cry	Cry	Cry	Cry	Cry	Cry	Cry
Corrected A	0.017	0.035	0.036	0.028	0.009	0.020	0.023	0.033	0.069	0.031	0.034	0.017
Corrected Mn:A	20.0	14.2	15.1	15.5	26.1	23.2	43.3	12.5	14.2	16.3	15.5	20.0
Mineral	Cry	Hol	Cry	Cry	Cry	Hol	Cry	Cry	Cry	Cry	Cry	Cry

Although care was taken to avoid contamination, samples tended to be intimately mixed with quartz, and sometimes wall-rock. Suspecting that the latter was the source of the Al (as muscovite), samples of the rock matrix from samples Mn 6, 9 and 10 (which had enough clean rock still attached for easy removal for analysis) were examined by XRD, which found only quartz and muscovite. The rock matrix of sample Mn 6 had by far the greatest amount of muscovite (by XRD) so was also analysed by XRF (Table 3).

Muscovite has the formula $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ with substitution of K by Na possible, forming a series with paragonite, the Na analogue. Consequently, it can act as a source of K and Na, thereby interfering with the results. As the molar ratio $\text{Al}:(\text{K} + \text{Na}) = 3$, it is possible to calculate the contribution of K and Na from muscovite if the Al content is known.

In matrix sample Mn 6, Na is negligible, the molar ratio K:Na being 20:1. If this is typical, then any contribution to Na, in the analyses of the Mn ores, from muscovite is insignificant and can be ignored. The contribution to the K values, however, may be significant. Looking at the analyses in Table 3, those with the lowest Al contents (Mn 3, 8, 9a)

also had no muscovite by XRD. For each analysis, assuming the Al is due to muscovite, the possible contribution of K from this source was calculated and deducted from the measured concentration of K to obtain a corrected value.

The bottom three rows of Table 3 give the XRF data for the Mn ore samples, with a correction for muscovite as explained above. These XRF data can be compared to the uncorrected rows above. According to the uncorrected data, sample Mn 2 is hollandite, the rest are all cryptomelane. After correction, only Mn 6 is affected, meaning it can be classified as hollandite. The rest are unaffected, giving confidence in their identifications.

As a check, the molar ratio Mn:A, where $A = (\text{Na} + \text{K} + \text{Pb} + \text{Ba} + \text{Sr})$, is given before and after correcting for muscovite, with the ideal ratio being 8.0. Before correction, most are quite close to this, except Mn 7, which contains pyrolusite. After correction, the ratios deviate further from the ideal, indicating that K is being over-corrected. This would happen if muscovite was not the only source of Al. That this is the case is confirmed by the analysis of the rock matrix, which has a molar excess of Al relative to K on the assumption that muscovite is the only Al

mineral present. Also, sample Mn 7 has appreciable Al (by XRF), but no muscovite (by XRD), and there is no clear correlation between silica content and Al across the analyses. Such a correlation would be expected if the wall rock was the source of the Al as muscovite. A clay mineral, possibly amorphous, would account for the discrepancies. Another possibility is that the hydronium ion, H_3O^+ , may substitute for metal cations in the tunnels. Undetectable by XRF, if present it would bring the Mn:A ratio closer to the theoretical 8.0. Mn oxide with the cryptomelane structure, but containing hydronium in place of metal cations, has been prepared synthetically (Poyraz *et al.* 2017), raising the possibility that such substitution might also occur in nature.

Because only one identification is rendered uncertain by the uncertainty in the K values (sample Mn 6), we can confidently state that the manganese ore is mostly cryptomelane with minor hollandite. These are common members of the coronadite group (see discussion).

In our analyses high Fe contents were consistently noted in samples in which goethite was found (by XRD). When goethite was absent (by XRD) Fe was much lower (0.8 %–4.3 % Fe_2O_3) so, whilst our data indicate that most of the Fe in the Mn ore is present as goethite, we cannot preclude a small presence in the framework.

Only one manganese mineral was not a member of the coronadite group. A single boulder contained pyrolusite, confirming the report by Grennan (1969). Also present in the boulder was a coronadite group mineral (sample Mn 7) identified here as cryptomelane.

Raman analysis of both massive manganese ore and individual acicular crystals in cavities in

massive ore indicate that the majority have spectra matching those published by Post *et al.* (2020) for cryptomelane.

Corkite

The matrix of twelve corkite specimens was analysed by EDS and found to be mostly iron oxide/oxy-hydroxide. Manganese, if present, was never more than a few percent. This confirms visual observations that corkite is only present in iron-rich material. The authors have not observed corkite in material dominated by manganese oxides. The corkite must, therefore, have come from the lower levels of the mine where manganese gives way to iron. The matrixes of two particularly rich corkite samples were analysed quantitatively by XRF. This confirmed the EDS findings, and found significant P, but insufficient Pb or S for this to be present as disseminated corkite (Table 4). Cu was also higher in the matrix than in the corkite. Fe and Cu phosphate species may account for these observations, but these data do not permit identification of such phases. Discrete Fe and Cu phosphate minerals have been identified in other specimens which are described in the ‘Description of the minerals’ section. It may be noteworthy that the same boulder that yielded sample ‘A’ also yielded the only churchite-Y specimen, and also one of kidwellite with trace chalcociderite. Visually, only iron oxide/oxy-hydroxides and quartz could be observed in the matrix samples that were used in the analyses.

Table 4 gives the XRF results for this group of analyses, together with the ideal composition of mid-range corkite. X-ray diffraction of the corkite matrix, and of four samples of similar material that lacks visible corkite, only identified quartz and goethite. Preparing samples of corkite for XRF

Table 4—X-ray fluorescence analyses of corkite samples, A and B, and their matrix. Collected from the ‘Big Pit’, Glandore Mine.

Oxide	A	Matrix of A	B	Matrix of B	Ideal
PbO	27.3	0.8	14.6	0.8	33.4
Al_2O_3	1.6	0.6	1.2	0.7	0
Fe_2O_3	46.9	62.8	49.1	68.7	35.9
CuO	0.4	1.2	0.6	1.3	0
P_2O_5	11.7	2.2	9.1	2.6	10.6
SO_3	5.7	0.1	3.2	0.1	12.0
SiO_2	0.1	8.1	0.6	5.1	0
BaO	0.8	0.3	2.3	0.2	0
Mn_3O_4	0.1	4.0	0.2	0.4	0
Balance	5.4	19.9	19.1	20.1	8.1
P/(P+S)	0.70	0.96	0.76	0.97	0.5

proved difficult. Only one example, 'A', contained sufficiently large crystals and patches (up to several millimetres) to allow for the preparation of a reasonably pure analyte. Even then, some goethite contamination was found in the XRD (which was otherwise an excellent match for corkite) and as high values of Fe in the XRF analysis. The molar P/(P + S) ratio was within the corkite range (0.25–0.75, see below) but towards the phosphorus-rich end. X-ray fluorescence was attempted on two other samples. One proved impossible to gather enough pure material from, so was rejected. The other ('B' in Table 4) had a higher proportion of the mineral of interest but still could not be fully separated from goethite. The molar ratio P/(P + S) was in the kintoreite range, albeit only just.

One can roughly estimate the contribution of P and S from the matrix by deducting the theoretical Fe_2O_3 value (35.9%) from the measured value. Dividing this difference by the Fe_2O_3 content of the matrix will give an approximate indication of the proportion of matrix contaminating the sample, and, hence, the amount of P and S due to this contamination. Correcting for this in samples A and B, the effect on the P/(P + S) ratio is only to reduce it by 0.1 in each case, bringing B to exactly the corkite–kintoreite boundary of 0.75.

Areas of crushed material several hundred microns across were analysed with EDS to average out orientation effects. Twenty-three samples were analysed in this way. Arsenic (<2%) was detected in two samples. In two others, about 5% Al was detected but in most it was <2%. Higher levels of Al were observed in spot analyses on individual crystal faces and edges of broken surfaces where it was found to be concentrated at the outer edges of the crystals, indicating a final Al-rich growth phase. The low levels, and often absence, of As and Al rules out most members of the beudantite group (Fig. 1). Small amounts of Cu (<2%) found in 21 of the 23 analyses (and noted also in the XRF and in the historical analyses), are too low for beaverite $\text{Pb}(\text{Fe}^{3+}_2\text{Cu})(\text{SO}_4)_2(\text{OH})_6$. By elimination, plumbojarosite, corkite and kintoreite are the remaining beudantite group minerals. These can only be resolved by careful measurement of their P/(P + S) ratios: < 0.25 is plumbojarosite, 0.25–0.75 is corkite, and > 0.75 is kintoreite. The EDS results suggest that all are within the corkite–kintoreite range. By analysing large (a few hundred microns across) areas of finely ground material, EDS gave results close to the XRF values, but for precise measurements WDS was used (Table 5).

Table 6 interprets the WDS data and assigns identities to the minerals present. Table 7 gives three individual spot analyses that were particularly interesting on account of the unusually high levels of Al, As and Ba.

Individual spot analyses have been converted to atoms per formula unit (apfu) and plotted on graphs (Fig. 4). These visually illustrate the compositional ranges found and the correlations between the key elements.

The observation by EDS that some crystals had an Al-rich, Fe-depleted rim was confirmed by WDS and illustrated in Figure 5, an element map showing the distribution of Fe, which is inversely proportional to Al (Fig. 4).

Raman analysis of the corkite from both the surface finds and the underground sample have yielded similar spectra, independent of colour or morphology. A typical spectrum is displayed in Figure 6, together with a spectrum of corkite from Iron Crag, Caldbeck Fells, Cumbria, UK (taken from the RRUFF database #R070491 (Lafuente 2015)). Minor variations observed in Raman peak intensity are the result of polarisation effects generated through differences in crystallographic orientation to the laser incidence beam.

Description of the minerals

During this work, several minerals not previously reported from the locality were found. These, and some others found by collectors but not published in the literature, as well as the already-recorded species, are described below and unless otherwise stated, all the following identifications were confirmed by the authors using the techniques listed above. Mineral names written in lower case were not found during the course of this work and require confirmation.

Ankerite $\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$

Reported by Grennan (1969). No details given.

Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Reported by Anon. (1870) and possibly represents a misidentification of connellite, which is relatively common in copper-rich samples.

BARYTE BaSO_4

Baryte seems to have been readily found in the 19th century: several contemporary authors record it (Weaver 1837; Kane 1844; Apjohn 1844; Jukes and Kinahan 1861), though not Grennan (1969). More

Table 5—Electron-probe analyses of ‘corkite’ from Glandore mine: raw data. Values are average weight percent across all analyses. Individual samples are identified by Roman numerals. Up to three regions of interest per sample denoted by Arabic numerals.

<i>Sample</i>	<i>PbO</i>	<i>SO₃</i>	<i>BaO</i>	<i>P₂O₅</i>	<i>Fe₂O₃</i>	<i>CuO</i>	<i>ZnO</i>	<i>As₂O₅</i>	<i>Al₂O₃</i>	<i>Balance</i>
i-1	32.31	8.27	0.43	12.27	34.08	0.84	0.03	0.31	0.48	10.97
i-2	32.64	8.74	0.37	12.18	33.79	0.87	0.03	0.31	0.57	10.49
i-3	33.01	7.45	0.20	13.85	33.68	0.71	0.03	0.26	0.79	10.01
ii-1	32.54	6.43	0.20	15.87	31.89	0.12	0.03	0.29	2.97	9.65
ii-2	32.90	6.45	0.07	15.87	33.06	0.07	0.04	0.26	1.99	9.28
ii-3	32.65	6.54	0.10	15.61	33.75	0.14	0.04	0.30	1.42	9.45
iii-1	31.75	5.18	0.23	14.24	34.05	0.78	0.03	4.45	0.23	9.06
iii-2	31.66	5.63	0.34	12.97	33.86	1.16	0.03	5.34	0.16	8.84
iv-1	32.78	7.98	0.14	12.84	32.71	0.83	0.03	0.25	1.44	10.98
iv-2	33.33	7.29	0.07	13.74	31.99	0.83	0.03	0.28	2.04	10.40
v-1	33.09	6.10	0.03	15.50	31.31	2.06	0.04	0.24	1.60	10.02
vi-1	32.92	5.69	0.03	15.25	31.41	2.52	0.03	0.27	1.20	10.69
vii-1	30.29	5.39	1.61	16.76	33.76	0.10	0.04	0.46	1.50	10.09
vii-2	30.87	6.20	1.20	16.08	34.08	0.05	0.03	0.37	1.49	9.62
vii-3	30.24	4.85	1.59	17.40	34.33	0.05	0.03	0.42	1.31	9.77
viii-1	32.56	8.17	0.14	14.01	33.17	0.07	0.04	0.26	1.88	9.70
viii-2	32.22	8.02	0.23	14.18	32.52	0.06	0.03	0.26	2.40	10.07
ix-1	27.71	6.53	2.45	12.85	35.03	0.67	0.03	4.23	0.16	10.33
ix-2	28.80	6.63	2.03	12.46	34.90	0.71	0.03	4.42	0.16	9.87
x-1	31.29	7.91	0.54	12.36	34.11	1.40	0.03	0.29	0.20	11.87
x-2	32.02	7.43	0.27	12.80	33.66	1.67	0.04	0.29	0.19	11.65
xi-1	31.96	7.89	0.13	13.89	35.05	0.07	0.03	0.31	1.53	9.13
xii-1	27.99	4.92	2.77	16.85	35.02	0.05	0.03	0.41	0.91	11.04
xii-2	26.82	4.11	3.12	17.64	35.72	0.08	0.03	0.51	0.63	11.33
xiii-1	32.57	7.05	0.11	14.63	33.17	0.21	0.03	0.27	1.86	10.09
xiii-2	32.74	7.23	0.11	14.22	33.01	0.42	0.04	0.28	1.86	10.09
AT1	29.32	9.50	2.26	12.30	32.89	0.01	0.00	0.69	0.86	12.18
AT2	26.25	9.53	4.76	12.46	34.18	0.01	0.00	0.86	0.26	11.69

recently, iron-stained, brecciated and sometimes cleaved, massive baryte was found near the main mine (RU). Colourless crystals, some doubly terminated up to 5mm, occur on goethite, associated with corkite. Small (sub-millimetre) bladed crystals of baryte were identified as occurring with botryoidal yellow-grey rhodochrosite. Visual and Raman identification.

Bornite Cu_5FeS_4

Reported by Grennan (1969) from the Copper Shaft. No details given.

Braunite $Mn^{2+}Mn^{3+}_6(SiO_4)_8O_8$

Reported by Grennan (1969). No details given.

BROCHANTITE $Cu_4(SO_4)(OH)_6$

A specimen of *c.* 2mm crystals of green brochantite on limonite from Glandore is pictured on the mineralogical website mindat.org. It was collected on surface in 1972 by Richard Tayler and identified using infrared spectroscopy by George Ryback.

Brochantite has also been identified in samples from the Copper Shaft, in the collection of RU, and confirmed by Raman.

CACOXENITE $Fe^{3+}_{24}AlO_6(PO_4)_{17}(OH)_{12} \cdot 75H_2O$

Observed on several specimens as radiating sprays of distinctive golden yellow needles up to several millimetres long, often much altered to yellow-brown iron oxide/oxy-hydroxide and sometimes nucleating on earlier corkite (Fig. 7a). Confirmation was by Raman spectroscopy and EDS, which gave O:Fe and Fe:P molar ratios close to the expected values, plus minor Al. Cacozenite is already well-known from the phosphate deposit at Ballycormick, south of Shanagolden, Co. Limerick, where it occurs in gossan with pyrolusite (Ryback *et al.* 1988). It has also been found at Grouse Lodge Quarry, a few kilometres south of Ballycormick (Richard Bell, personal communication, confirmed by Stephen Moreton from EDS analysis). This is, therefore, the second published

Table 6—Interpretation of electron-probe data in Table 5. ROI = region of interest; Tot. no. = total number of analyses for that ROI; P/(P + S) = molar ratio for P and S using the averaged results in Table 5. ‘Mineral’ is the overall composition, based on the average of all analyses for that ROI. C & K is the number of individual analyses for a ROI that gave a corkite (C) or kintoreite (K) composition, respectively. Samples iii and iv were different habits on the same specimen. AT1 and AT2 were two crystals from the same specimen analysed by Andy Tindle (then of the Open University).

<i>Sample</i>	<i>ROI</i>	<i>Tot. no.</i>	<i>P/(P+S)</i>	<i>Mineral</i>	<i>C & K</i>
i	1	17	0.63	Corkite	All C
i	2	21	0.61	Corkite	All C
i	3	8	0.68	Corkite	All C
ii	1	19	0.74	Corkite	16 & 3
ii	2	6	0.74	Corkite	All C
ii	3	7	0.73	Corkite	6 & 1
iii	1	7	0.76	Kintoreite	2 & 5
iii	2	9	0.72	Corkite	5 & 4
iv	1	16	0.64	Corkite	13 & 3
iv	2	9	0.68	Corkite	7 & 2
v	1	9	0.74	Corkite	6 & 3
vi	1	12	0.75	Kintoreite/ Corkite	4 & 8
vii	1	9	0.78	Kintoreite	1 & 8
vii	2	13	0.75	Kintoreite/ Corkite	6 & 7
vii	3	16	0.80	Kintoreite	4 & 12
viii	1	31	0.66	Corkite	All C
viii	2	15	0.67	Corkite	All C
ix	1	18	0.69	Corkite	All C
ix	2	18	0.68	Corkite	All C
x	1	13	0.64	Corkite	All C
x	2	10	0.66	Corkite	All C
xi	1	7	0.67	Corkite	All C
xii	1	35	0.79	Kintoreite	6 & 29
xii	2	16	0.83	Kintoreite	All K
xiii	1	18	0.70	Corkite	15 & 3
xiii	2	28	0.69	Corkite	26 & 2
AT1	1	10	0.59	Corkite	All C
AT2	1	10	0.60	Corkite	All C

Total number of analyses = 407; 90 of them kintoreite.

and third known Irish occurrence of this uncommon mineral.

CHALCOCITE Cu_2S

Reported by Grennan (1969) from the Copper Shaft. Raman analysis of remnant fractured sulfide material in goethite has identified chalcocite, associated with pyrite. The chalcocite consists of small aggregates (a few microns) of metallic blue crystals that appear to be of secondary origin, replacing former primary sulfide, possibly chalcopyrite.

CHALCOPYRITE CuFeS_2

Found by Grennan (1969) in boulders to the north of the mine. Found by one of the authors

(RU) as small fragments in massive goethite at the copper shaft in association with pyrite and covellite.

CHALCOSIDERITE $\text{CuFe}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$

Identified as a very small, dark green aggregate of short prismatic crystals (to 0.5mm) in a phosphate-rich sample, associated with kidwellite and goethite (Fig. 7c). Its Raman spectra is a near match to those published of chalcosiderite (Frost *et al.* 2013). Also, as dark green crystalline patches, a few millimetres across, in corkite-rich goethite, identified by XRD. Analysis by EDS of the prismatic crystals indicated Fe, P, O and Cu in approximately the expected proportions.

Table 7—Three individual spot analyses from electron microprobe data of corkite-kintoreite with unusual compositions.

Sample	PbO	SO ₃	BaO	P ₂ O ₅	Fe ₂ O ₃	CuO	ZnO	As ₂ O ₅	Al ₂ O ₃	Balance
ii-1	32.85	6.22	0.60	17.22	20.15	0.37	0.03	0.40	11.50	10.67
iii-1	31.40	4.46	0.24	13.66	33.85	0.81	0.03	6.11	0.20	9.24
xii-1	14.72	8.21	12.18	15.06	35.31	0.04	0.03	0.23	1.89	12.34

ii-1 has molar Al:Fe 0.23:0.25, close to plumbogummite.
iii-1 had the highest As content measured.
xii-1 has molar P/(P+S) = 0.67, so in the corkite range, but molar Ba:Pb is 0.079:0.066.

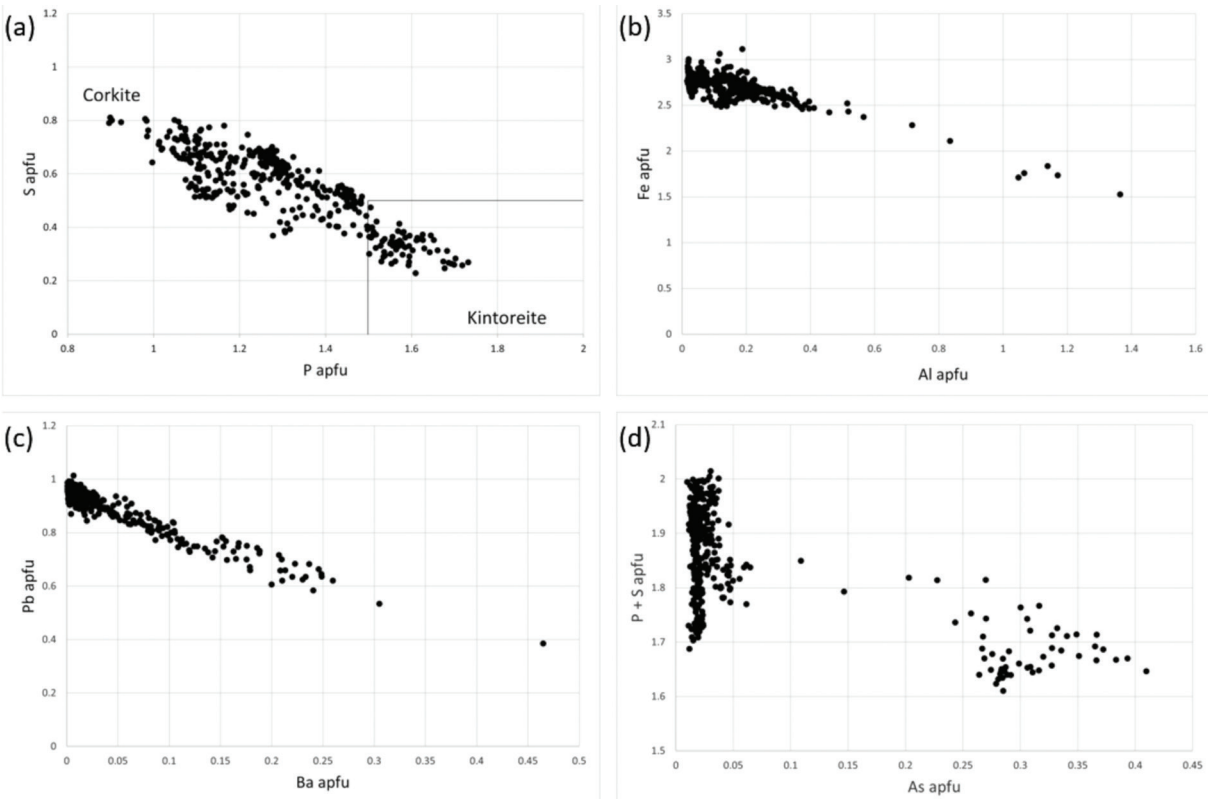


Fig. 4—Plots of atoms per formula unit (apfu) showing relationships between elements that may substitute for each other in corkite/kintoreite from Glandore Mine, Co. Cork: S, P; Fe, Al; Pb, Ba; As, P.

CHURCHITE-(Y) YPO₄·2H₂O

Radiating sprays of slender, snow-white needles 2mm in length, in a cavity of iron-rich material (Fig. 7b) were found by EDS to be yttrium phosphate with approximately 5% each of Gd and Dy, and around 1%–2% each of Sm, Er and Yb. The molar ratio of combined rare earth element (REE) to phosphorus was 1:1, and to oxygen was 1:7. Theory would predict 1:6 ratio for the latter, but EDS is only semi-quantitative. It also helps to distinguish it from the exceedingly rare

rhabdophane-(Y) (REE:O = 1:5; known only from one locality in Japan). Churchite-(Y) is typically found in iron- and manganese-rich environments where it is deposited by meteoric waters (Anthony *et al.* 2000). It is very widespread globally, but this is the first report of the mineral from Ireland.

CONNELLITE Cu₁₉(SO₄)(OH)₃₂Cl₄·3H₂O

Formerly quite common as thin coatings and found within copper-rich samples from the Copper Shaft,

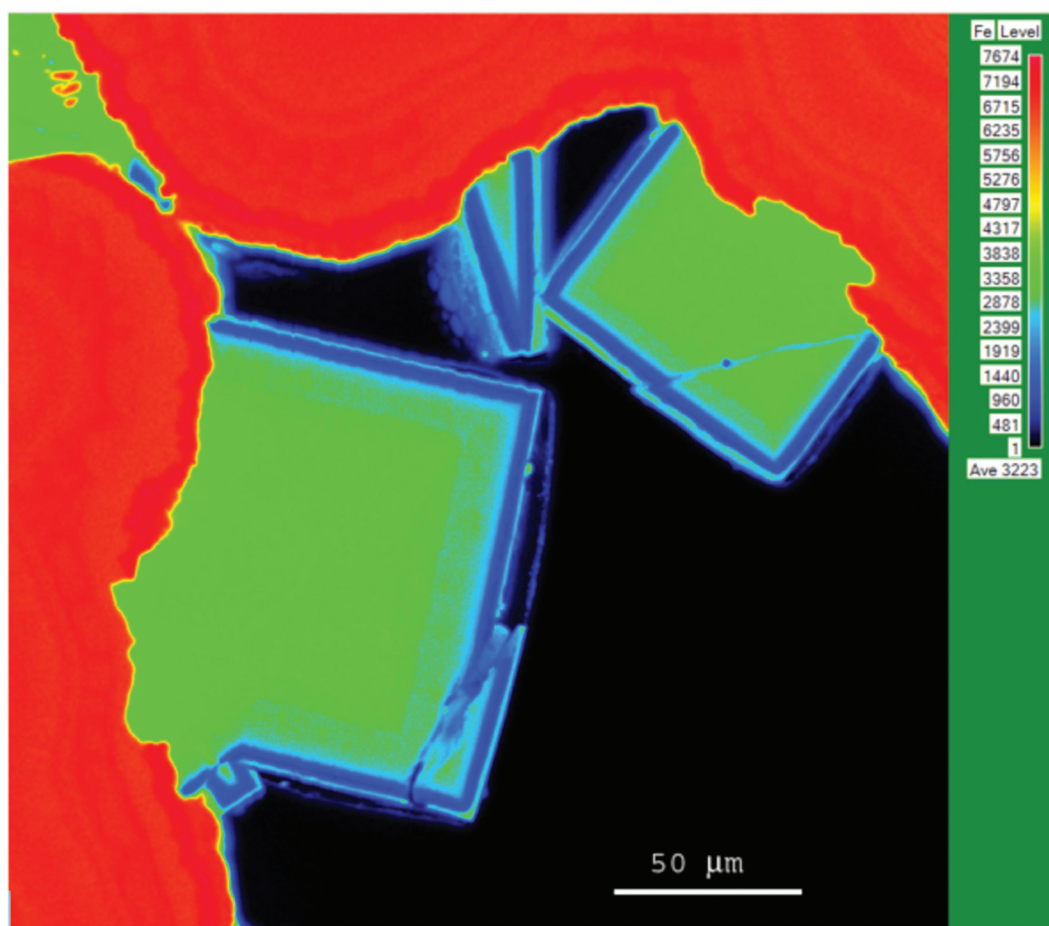


Fig. 5—Element map of zoned pseudocubic corkite (green), nucleated on goethite (red), showing Fe-depleted rims (blue). The scale bar at right indicates the number of counts in the detector which is proportional to the amount of Fe detected.

connellite is now hard to find at Glandore. Rarely found as lustrous, translucent blue acicular groups, with individual crystals to 0.5 mm. Early reports of azurite may have been a misidentification of connellite. Confirmation by Raman.

COPPER Cu

Reported by Anon. (1870) and again by Grennan (1969) who observed it in drill core. Native Cu has been found by the authors at the Copper Shaft, where it accompanies cuprite and malachite as dendritic crystal groups up to several millimetres in length. Its close association with cuprite can be seen with some dendritic groups being formed of both minerals (Fig. 7d). Identified by its colour and malleability.

CORKITE $PbFe_3(PO_4)(SO_4)(OH)_6$

Lustrous crystals, usually of pseudocubic habit, but sometimes in other forms (Figs 8 and 9a, b),

occur rarely as cavity linings in massive goethite ore. Crystals do not normally exceed 1mm across, but one unusually rich boulder contained much larger pseudocubic crystals. These were mostly around 1.5 – 2.0mm across, a single exceptional one measuring 6 mm across. This boulder provided sample 'A' in Table 4. The colour is variable, from sulphur yellow (the smallest crystals) to honey brown, to dark brown and greyish brown. The small crystals are often quite gemmy, the larger ones opaque. Some crystals are coated with mixed Mn–Fe oxide/oxy-hydroxides (EDS indicated Mn > Fe in one example), rendering them almost black. Occasionally, corkite forms yellow earthy coatings on goethite, and yellow radiating forms. Sometimes it has an outer yellow zone. One such yellow zone analysed by EDS gave a normal corkite composition. Identification was by XRD, EDS, XRF and WDS.

Another phosphate-rich sample, from surface mine waste, contains corkite ranging from sulphur

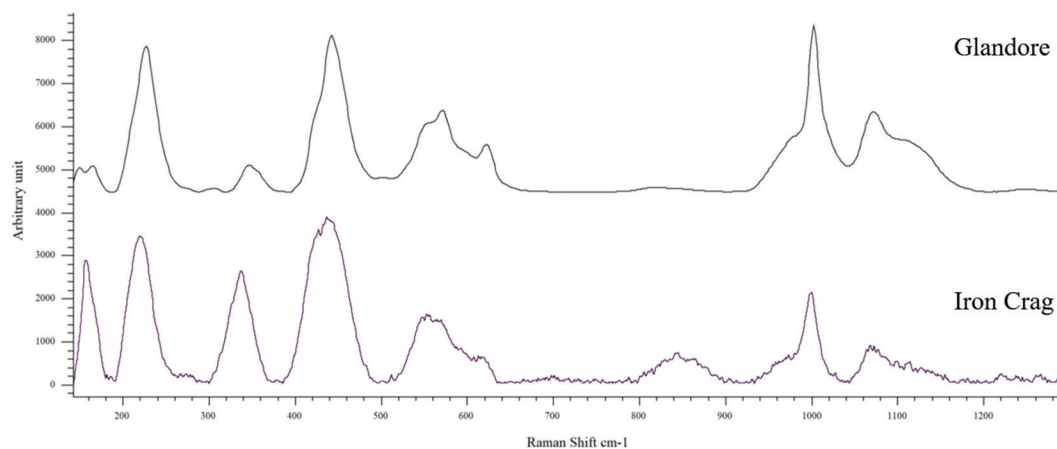


Fig. 6—Typical unoriented 532nm Raman shift spectrum of corkite from Glandore Mine (RU collection), with a comparative spectrum from Iron Crag, Caldbeck Fells, Cumbria, UK (RRUFF database no. R070491).

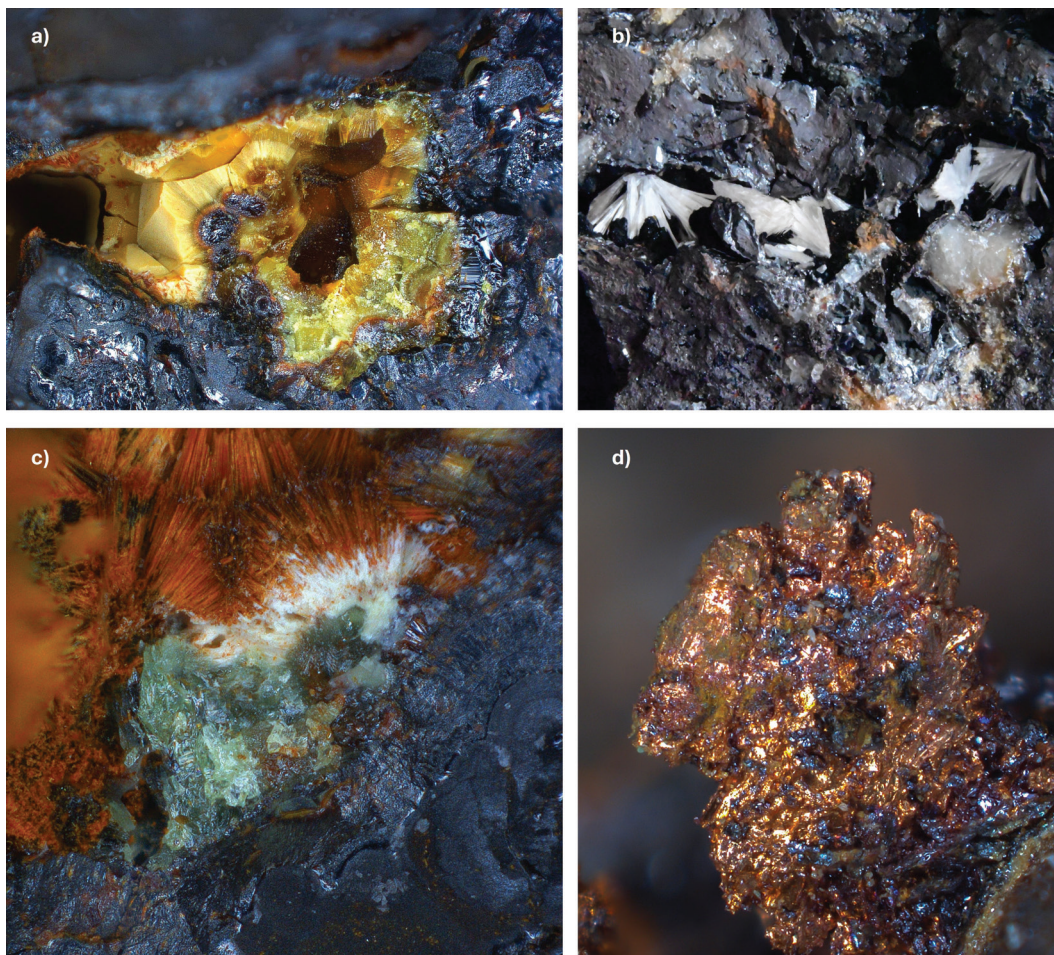


Fig. 7—a) Radial yellow to brown acicular crystals of cacosenite, associated with yellow-green corkite on goethite from Glandore Mine. Field of view approximately 2mm. Specimen and photo RU; b) Radiating white sprays to 2mm of churchite-Y on goethite from 'Big Pit', Glandore Mine. Specimen and photo SM; c) Apple-green aggregate of chalcosiderite crystals with acicular white kidwellite and rust coloured goethite (field of view approximately 1mm) from Glandore Mine. Specimen and photo RU; d) Small, 1mm group of native copper intergrown with cuprite from the Copper Shaft, Glandore Mine. Specimen and photo RU.

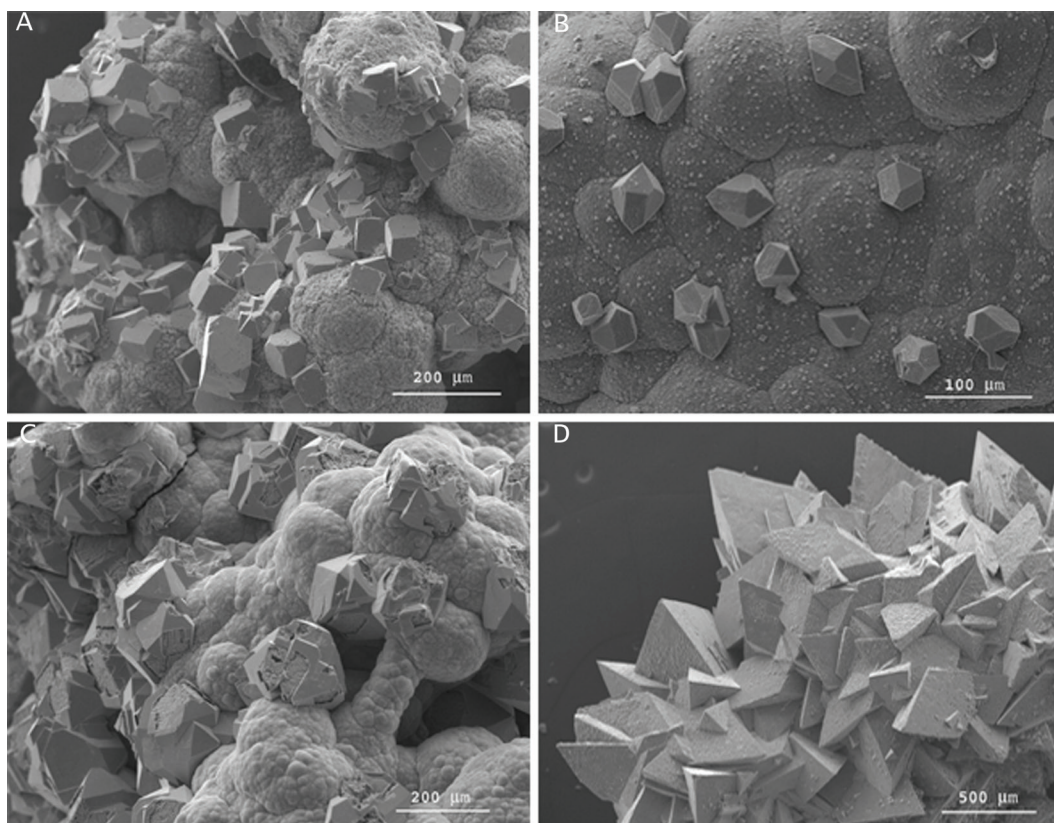


Fig. 8—Montage of SEM images showing the various habits exhibited by corkite-kintoreite from ‘Big Pit’ Glandore Mine. a) Pseudocubes, the most common habit; b) Second most common habit in which the crystals are lengthened along the c-axis, with loss of the pinacoid; c) Complex form, although some faces look similar to those in b; d) Unusual lozenge-shaped crystals, possibly a result of further extension along c-axis.

yellow to orange-brown and olive green. Crystal habit varies from typical pseudocubic to more complex forms and crystal groups, rarely acicular. Identification by Raman using published spectra from Frost and Palmer (2011).

COVELLITE CuS

Forms thin alteration rims around grains of chalcopyrite in samples from the copper shaft. Observed in polished section and confirmed by Raman.

CRYPTOMELANE $K(\text{Mn}^{4+}_7\text{Mn}^{3+})\text{O}_{16}$

The main manganese ore is cryptomelane. It occurs mostly as massive, fine-grained, dark grey to black, dull to slightly steely veins and masses cementing wall-rock. Occasionally it may be stalactitic in cavities in iron-rich material, the stalactites being only a few millimetres wide and up to 2cm long, although a much larger example of ‘psilomelane’ stalactites is preserved in the collections of the National Museum of Ireland (specimen G385.1980). Radial aggregates of silvery acicular crystals to 0.2mm within massive

manganese ore yield Raman spectra matching those of cryptomelane. Identified by XRD and XRF (Tables 2 and 3).

CUPRITE CuO

Reported by Anon. (1870) and found occasionally at the Copper Shaft, confirming reports that this was an important source of copper at the deposit. It occurs as dark red isometric crystals, mostly octahedra (Fig. 9c), as individual crystals (to several millimetres) or groups of crystals in cavities of goethite (several centimetres). It also occurs in patches and veins throughout the ore and could be described as ‘tile ore’ where thicker veins are exposed as surfaces. Well-crystallised samples are almost always associated with malachite, ranging from small circular patches on cuprite crystal faces to a complete cavity fill where the cuprite is only observed when the cavity is broken open. Very small (sub-millimetre), unaltered octahedra of cuprite have been observed in cavities with no malachite. Massive cuprite, intimately intergrown with goethite, is sometimes

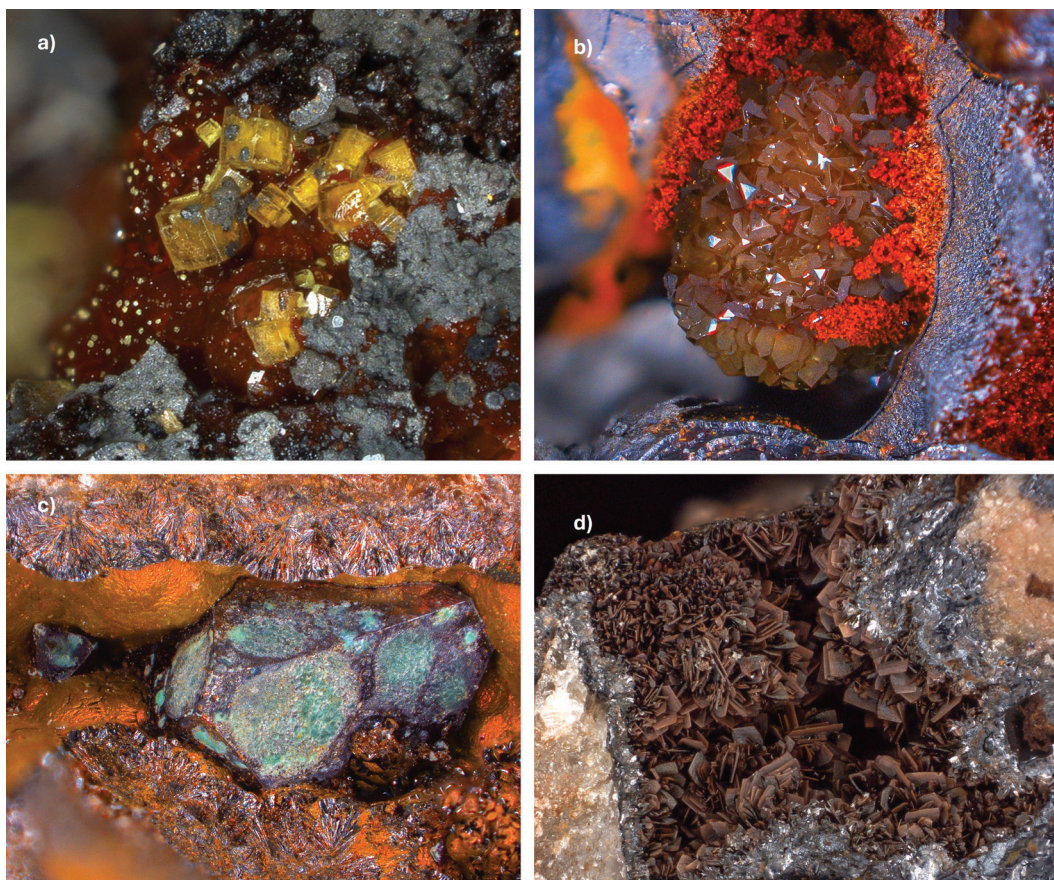


Fig. 9—a) Zoned yellow pseudocubic crystals of corkite on orange-brown goethite and dark grey cryptomelane. Field of view approximately 1mm. Specimen ii, 'Big Pit', Glandore Mine. Photo RU; b) Orange-brown aggregate (1.5mm) of corkite, displaying elongation of c-axis (see Fig. 8), on metallic grey to 'rust' orange goethite from Glandore Mine. Collection and photo RU; c) Modified octahedral cuprite (1.5mm) on iridescent goethite from Copper Shaft, Glandore Mine. Collection and photo RU; d) Cavity with bladed goethite in brecciated quartz. Field of view approximately 1cm from Glandore Mine. Collection and photo RU.

associated with dendritic native copper. Confirmed by Raman and visual observation.

DELAFOSSITE CuFeO_2

Delafossite has been identified in a sample from the Copper Shaft as small (400 micron) broken grey metallic hemispherical aggregates on goethite with adjacent cuprite and malachite. Confirmation by Raman.

GOETHITE $\text{FeO}(\text{OH})$

Goethite is the main component of the iron ore, as indicated by XRD of 4 representative samples, and is also the matrix mineral of the corkite, as shown by XRD, EDS, and Raman. Mostly, it is massive, orange-brown, grey-brown to near black, with numerous small cavities, and as a cement to brecciated quartz and/or baryte. In some well-crystallised specimens, goethite has been observed as groups of thin platy aggregates (Fig. 9d), as radiating acicular groups with colour-banding, and as lustrous orange-brown crystal

groups, sometimes forming typical 'bow-tie' habits. Often it forms brilliant black patches and small lustrous black spherules <1mm across (identified by EDS and their yellow-brown streak). Lustrous, black, stalactitic, and botryoidal masses form attractive hand specimens, especially when they have a thin iridescent coating, and can be found across the mine site. The 'limonite' of Grennan (1969) and the hematite of many authors may be goethite.

HEMATITE Fe_2O_3

Hematite was reported by Jukes and Kinahan (1861) and by Grennan (1969). In this study, it was found only occasionally as earthy red-brown patches in the massive iron ore and is associated with massive baryte. Identification was by its red-brown colour, and EDS, which found only iron and oxygen. Small (300µm) spheres of hematite (Fig. 10a) have been identified by Raman in a goethite-lined cavity from a phosphate-rich sample.

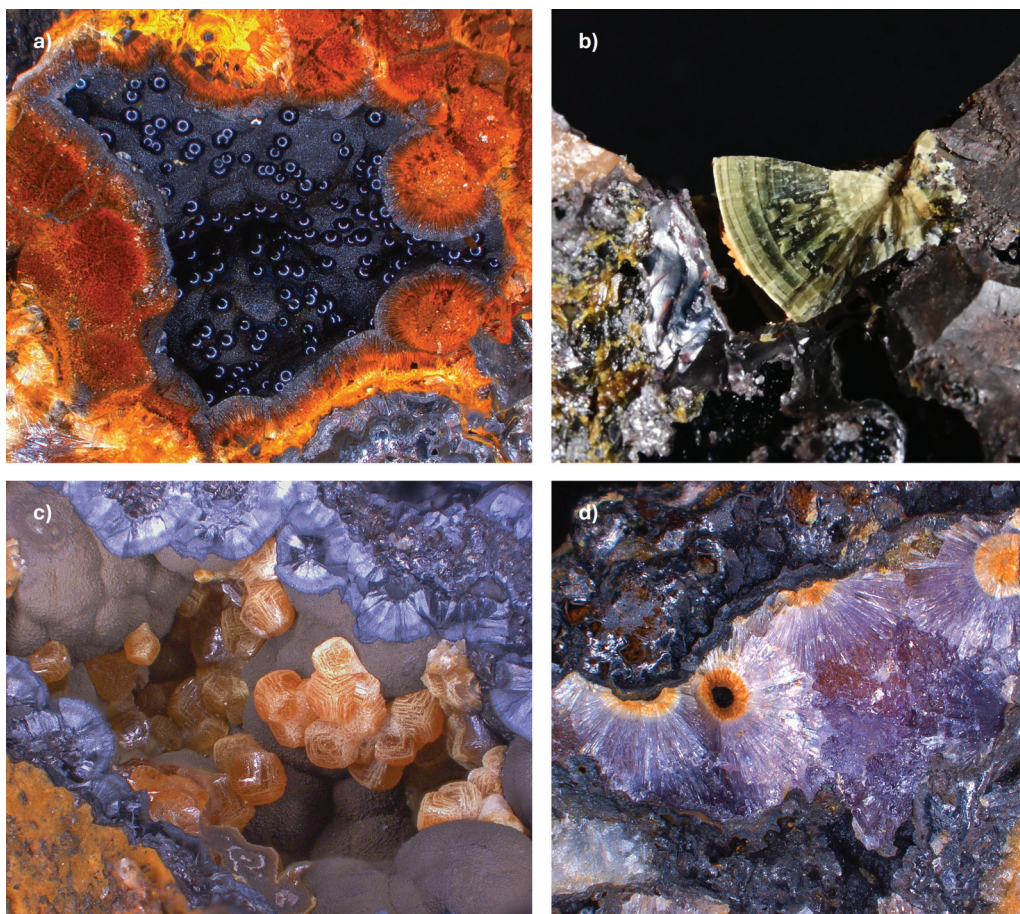


Fig. 10—a) Small spheres of hematite on altered goethite. Field of view approximately 6mm from Glandore Mine. Collection and photo RU. b) Radial group (4mm) of green, zoned kidwellite on goethite from 'Big Pit', Glandore Mine. Specimen and photo SM. c) Orange pseudocubic crystals of rhodochrosite on manganese oxides. Field of view approximately 7mm from Glandore Mine. Collection and photo RU. d) Radial groups of pink to violet coloured strengite, associated with minor pseudocubic corkite (top right) infilling a cavity in goethite. Field of view approximately 8mm from Glandore Mine. Collection and photo RU.

HOLLANDITE $Ba(Mn^{4+}_6Mn^{3+}_2)O_{16}$

Hollandite occurs in an identical manner to cryptomelane (above) and is distinguishable only by analysis (Table 3).

KIDWELLITE $NaFe^{3+}_{9+x}(PO_4)_6(OH)_{11} \cdot 3H_2O$,
 $x = 0.33$

Kidwellite is a rare mineral found as white radial aggregates (to 0.5mm) associated with chalcosiderite (Fig. 7c) and altered radial goethite. Confirmation by Raman. Another specimen consists of a greenish radial mass 4mm wide with yellowish bands (Fig. 10b). Identification was by XRD (Mike Rumsey, Natural History Museum, UK) and supported by EDS, which gave Fe, P, O and minor Na.

KINTOREITE $PbFe_3(PO_4)(PO_3OH)(OH)_6$

Kintoreite occurs in an identical manner to corkite (above) and is distinguishable only by analysis.

Usually, it occurs as zones of kintoreite composition in crystals that are mostly corkite. In only two cases did it dominate (see discussion). Kintoreite was not observed in the Raman analyses.

LEPIDOCROCITE $FeO(OH)$

This polymorph of goethite has been found as crystalline, radiating, red-brown bladed aggregates up to several millimetres across in cavities in the iron ore, occasionally accompanying corkite. Confirmed by XRD, by EDS (which found only Fe and O) and by Raman.

MALACHITE $Cu_2(CO_3)(OH)_2$

Reported by Anon. (1870) and Grennan (1969). Malachite is common as tufts of slender crystals up to 1 cm long in ore from the Copper Shaft, and as a post-mining coating on the wall of a level underground. Identified by Raman and by effervescence in acid.

Manganite $Mn^{3+}O(OH)$

Reported by Grennan (1969) but without details or method of identification.

MUSCOVITE $KAl_2(AlSi_3O_{10})(OH)_2$

Small quantities of muscovite were identified by XRD and XRF in the manganese ore (Tables 2 and 3). It is visible in both Mn and Fe ore samples as tiny flakes <1mm across. Soft, silky white coatings in cavities in goethite give a composition by EDS consistent with muscovite. In all cases, it is likely derived from the wall rock.

PYRITE FeS_2

Pyrite occurs in samples from the Copper Shaft as fractured and altered grains associated with the earlier sulfide mineralising event.

PYROLUSITE MnO_2

Reported by Grennan (1969) but without details or method of identification. Confirmed in this study as black, fibrous crystalline crusts, several millimetres thick, lining cavities in Mn ore. Identified by XRD and XRF. An old specimen of similar material labelled 'pyrolusite' is in the National Museum of Ireland collection (specimen G339.1980).

QUARTZ SiO_2

The main gangue mineral is massive brecciated milky quartz. Colourless prismatic crystals to 1cm, embedded in goethite, are derived from former crystalline vugs in the massive quartz. The XRD of four samples of massive iron ore also found quartz to be present.

RHODOCHROSITE $MnCO_3$

Three specimens have been found to date that contain pseudocubic rhodochrosite crystals up to 1 mm. The mineral is hosted in manganese ore and can vary from colourless to yellow and orange (Fig. 10c), which presumably reflects the amount of Fe present. In one sample, dull yellowish grey botryoidal rhodochrosite is associated with small blades of baryte. Confirmed by Raman.

STRENGITE $FePO_4 \cdot 2H_2O$

Some phosphate-rich specimens contain radiating aggregates of transparent pale pink to violet crystals up to several millimetres in length (Fig. 10d). Analysis by XRD found these to be the rare iron phosphate mineral, strengite. Elemental content by EDS confirmed Fe, P and O in the expected molar

ratios. In one sample, translucent, pale pink strengite appears to partially and completely pseudomorph radiating aggregates of goethite (confirmed by Raman).

This is only the second report of strengite from Ireland. The first is the phosphate deposit at Ballycormick, south of Shanagolden, Co. Limerick (Ryback and Tandy 1992).

Sulphur *S*

Reported by Grennan (1969) as a coating on manganese ore in a dump on the west side of the mine. The method of identification is not stated. It may be a mistaken identification of corkite (see discussion).

TENNANTITE $Cu_6[Cu_4(Fe,Zn)_2]As_4S_{13}$

Observed in brecciated quartz sulfide veins from the Copper Shaft in association with chalcopyrite and pyrite. Identified in polished section and confirmed by Raman following Apopei *et al.* (2017).

Tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$

Reported by Grennan (1969) but without analytical data it could be tennantite or another grey copper ore.

Discussion

Manganese oxides are notoriously tricky to characterise, in large part owing to their poorly crystalline nature. Nevertheless, XRD of the samples examined here match cryptomelane, whether by the automatic search software, or visually. Cryptomelane is a member of the coronadite group within the hollandite supergroup (Biagioni *et al.* 2013). Coronadite group minerals have the general formula AMn_8O_{16} , where A = Ba (hollandite), Na (manjiroite), K (cryptomelane), Pb (coronadite) or Sr (strontiomelane). The ratio Mn:A is 8.0 in ideal material. Charge balance is maintained by varying the oxidation state of the Mn, although examples are known in which charge balance is maintained by Fe^{3+} substituting for Mn^{4+} , as in ferrihollandite (Biagioni *et al.* 2013). The structure consists of MnO_6 octahedra forming tunnels, the cation A occupying sites in the tunnels (Post 1999). Because the structure is similar throughout the group, XRD will not reliably distinguish individual members. For this, an accurate analysis of the tunnel cations is needed to determine which is dominant, and, hence, the species. Cryptomelane and hollandite are already known from Co. Wicklow (Moreton *et al.* 2006).

Scott (2000) summarises the current classification for members of the beudantite group. Members have the general formula $\text{PbA}_3(\text{XO}_4)_2(\text{OH})_6$ where A is Fe(III) or Al, and X is P, As, or S. When P or As is dominant, the anion may be protonated (i.e. $[\text{PO}_3\text{OH}]^{2-}$) to maintain charge balance. In the case of the sulfate end-members, significant substitution of A by Cu can occur, further adding to the diversity of combinations possible. Figure 3, derived from Scott (2000), illustrates the currently accepted classification scheme.

All samples analysed here, whether by EDS, WDS, XRF or Raman, are members of the corkite–kintoreite series. None have sufficient As to enter the composition ranges of beudantite–segitite, and none have enough Al to be plumbogummite or hinsdalite. Over a fifth of the individual spot analyses have kintoreite compositions (Table 5), but most of these are zones within crystals whose overall compositions are corkite. Only two of the thirteen crystals analysed by WDS were kintoreite overall (samples vii and xii), although two others (iii and vi) were borderline. A similar proportion (about a quarter) were found to be probably kintoreite based on EDS. No correlation was seen between colour, crystal habit and composition.

It is noteworthy that, of the analyses reported here, those with the lowest $\text{P}/(\text{P} + \text{S})$ ratio (samples AT1 and AT2), and, hence, closer to mid-range corkite, were of a sample found on surface and, therefore, possibly from a different part of the mine to the ore pile underground that furnished all the other samples analysed here. The lowest $\text{P}/(\text{P} + \text{S})$ ratios (i.e. the most sulfate-rich) are the historical analyses (Table 1). Taken together, this suggests that the compositions of ‘corkite’ specimens from Glandore may vary according to where in the deposit they were derived. Those analysed here are toward the phosphate-rich end of the series, passing into kintoreite in some cases.

Figure 4 shows the relationships between the key elements. Some are unsurprising, such as Al substituting for Fe, and Ba for Pb, as is expected from their valence. One single Al analysis (Table 7) comes close to plumbogummite, but still has $\text{Fe} > \text{Al}$, keeping it within the kintoreite range. The Al distribution is not random. There are several crystals with Al-enriched, Fe-depleted, outer zones, and this is confirmed by the iron distribution map (Fig. 5), which shows the iron-depleted (hence Al-enriched) outer zones of some pseudocubic crystals.

Several samples were enriched in Ba. Figure 4 shows a simple linear relationship as Ba replaces Pb.

One single spot analysis (sample xii-1) stands out. It has molar $\text{Ba} > \text{Pb}$, suggesting it is the barium analogue of corkite. Such a mineral is theoretically possible but has not yet been reported. The closest are dussertite: $\text{BaFe}^{3+}_3(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})_6$, gorceixite: $\text{BaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$, and an unnamed phase with the formula $\text{BaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ (Izbrodin *et al.*, 2011). This last, the barium analogue of svanbergite, $\text{SrAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$, remains poorly characterised, such is the difficulty of working with tiny samples as inclusions or zones in other phases. Treating As as P, the apfu values calculated for the Ba-rich spot analysis in Table 7 are a reasonable fit for the formula $(\text{Ba}_{0.46}\text{Pb}_{0.39})(\text{Fe}_{2.59}\text{Al}_{0.22})(\text{PO}_3\text{OH})_{1.26}(\text{SO}_4)_{0.60}(\text{OH})_{6.38}$, but both di- and trivalent cations fall slightly short of ideal values. More, and better, data are required.

Arsenic is scarce and found in significant amounts in only two samples (iii & ix). The highest level detected was 6.11% As_2O_3 in sample iii (Table 7). Arsenic does not correlate with P, or any other element in isolation, but does show some association with $\text{P} + \text{S}$ together (Figure 4). Arsenic is associated with lower $\text{P} + \text{S}$ values. There are 49 spot analyses with $\text{As} > 0.2$ apfu of which all but 3 are associated with $\text{P} + \text{S}$ values < 1.8 apfu. 33 of the 49 are associated with $\text{P} + \text{S}$ values < 0.7 apfu. Adding the As apfu in these 49 to the corresponding $\text{P} + \text{S}$ values gives totals all within the range 1.9–2.1, matching the theoretical 2.0 apfu.

There remains a population with essentially no As, but $\text{P} + \text{S} < 0.8$ apfu. This can be explained if there was another anion not analysed for, substituting for phosphate and/or sulfate. A likely candidate is carbonate. This has been reported in other lead-bearing members of the alunite supergroup. Pring *et al.* (1995) measured 0.73% CO_2 in an analysis of kintoreite, and Grey *et al.* (2011) found 3.1%–6.3% CO_2 in analyses of plumbogummite. Prompted by this, sample ‘A’ was analysed for carbon content, this being the only one for which sufficient pure material was available. 0.3% CO_2 was detected. This would amount to 0.05 apfu. To achieve the 0.2–0.3 apfu carbon needed to balance the analyses with low $\text{P} + \text{S} + \text{As}$ would require 1.2%–1.8% CO_2 , which is plausible considering the literature values cited for kintoreite and plumbogummite.

The report of sulphur on manganese ore by Grennan (1969) could not be confirmed. Some corkite found during this study occurred as fine-grained bright yellow coatings on goethite. It is possible Grennan mistook goethite for manganese ore, and corkite for sulphur. His reports of manganite

and braunite, although possible, have not been confirmed.

Although ankerite was reported by Grennan (1969) this could not be confirmed. Ankerite is uncommon in the veins of Co. Cork, although siderite is often present. Either could serve as a source of manganese, which commonly substitutes for iron. It is more likely, however, that the manganese was derived from shallow circulating groundwater during a deep weathering period. Similar supergene events have been noted in Ireland, including the formation of the secondary orebodies at Tynagh, Co. Galway (Clifford *et al.* 1986), and Ballygowan, Silvermines, Co. Tipperary (Boland *et al.* 1992). Closer to Glandore, Mn-rich mineralisation, associated with deep weathering, has been noted by one of the authors (RU) in limestone quarries in the Cork region. Some deposits associated with subtropical weathering in SW Ireland have been dated from the Middle Jurassic (Higgs and Beese 1986) to Tertiary (Mitchell 1980).

Conclusions

The Mn–Fe–Cu–Ba deposit at Glandore represents a complex series of mineralising events, beginning

with large syn-basinal extension features that were later brecciated during basin inversion. Intense oxidation turned most of the Cu sulfides into oxide minerals and the Fe into goethite. Subsequent groundwater movements replaced the goethite in the higher parts with cryptomelane–hollandite.

The primary ore minerals were arsenic-poor, and the groundwaters phosphate-rich, resulting in a suite of rare supergene phosphate minerals. Minor Pb gave rise to corkite–kintoreite, Cu chalcocite, and Fe strengite, kidwellite and cacoxenite. At least two supergene mineralising events are indicated by early corkite–kintoreite being overgrown by later cacoxenite (Fig. 7), strengite (Fig. 10d) and sometimes a second generation of corkite.

Glandore is the type locality for corkite but, as analyses here show, some ‘corkite’ from Glandore is sufficiently phosphate-rich to bring it into the compositional range of the closely related mineral kintoreite or for corkite to contain zones of kintoreite. Variations in analyses of specimens found at different times, and in different places around the mine site, suggest that the composition of the corkite varies according to its position within the deposit. However, as all specimens are now no longer in their original *in situ* locations, and the parts of the mine

Table 8—Table of specimens donated to UCC (University College Cork), NMI (National museum of Ireland) and NHM (Natural History Museum, London).

<i>Mineral</i>	<i>Sample Number</i>	<i>Accession Number</i>	<i>Institution</i>
Cryptomelane	Mn 1	CKGM M 03880	UCC
Hollandite	Mn 2	CKGM M 03881	UCC
Cryptomelane	Mn 3	CKGM M 03882	UCC
Cryptomelane	Mn 4	CKGM M 03883	UCC
Cryptomelane	Mn 5	CKGM M 03884	UCC
Cryptomelane/Hollandite	Mn 6	CKGM M 03885	UCC
Cryptomelane	Mn 8	CKGM M 03886	UCC
Cryptomelane	Mn 9a	CKGM M 03887a	UCC
Cryptomelane	Mn 9b	CKGM M 03887b	UCC
Cryptomelane	Mn 10	CKGM M 03888	UCC
Corkite		BM.2024,51	NHM
Corkite/kintoreite	Sample B	NG:G2396	NMI
Corkite/kintoreite	Sample B	CKGM M 03879	UCC
Corkite	i	NG:G2397	NMI
Corkite	ii	NG:G2398	NMI
Corkite/kintoreite	iii	NG:G2400	NMI
Corkite	viii	NG:G2399	NMI
Corkite/kintoreite	xii	BM.2024,52	NHM
Corkite/kidwellite	xiii	BM.2024,49	NHM
Corkite/kidwellite	xiii	BM.2024,50	NHM
Corkite	Sample A	NG:G2395	NMI
Corkite/chalcocite		BM.2024,54	NHM

from where they were derived are now inaccessible, this cannot be investigated further.

Historical specimens of corkite from Glandore in museum collections may merit analysis to determine if they are, or include, kintoreite.

The Mn ores described in this study have been deposited with University College, Cork (UCC). Examples of corkite have been lodged at UCC, the National Museum of Ireland (NMI), and the Natural History Museum, London (NHM). The last also holds a piece of the high-Ba corkite-kintoreite and examples of kidwellite and chalcosiderite (Table 8).

Acknowledgements

The late Sonny Mahoney (former owner of main site), Leo O'Connor and Faulkner Cahalane are thanked for site access. The late John Lawson, Max Hilton, Monika Razkova and Klaudia Kertowska kindly assisted in fieldwork. Andrew Tindle (emeritus Open University) is thanked for his probe analysis of corkite, Mike Rumsey and Jens Najorka (Natural History Museum, London) for XRD confirmation of kidwellite, and John Spratt (Natural History Museum, London) for assistance with the WDS measurements. The reviewers and editors are also thanked for helpful suggestions that greatly improved the manuscript. The late Matthew Parkes (National Museum of Ireland) is thanked for providing access to historic specimens from Glandore in the National Museum of Ireland.

References

- Adam, G.J. 1869 Tableau Minéralogique, *Annals de Mines*, series 6, **15**, 405–626.
- Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols, M.C. (eds) 2000 *Handbook of Mineralogy*, **IV**, Mineralogical Society of America, Chantilly, VA 20151–1110, USA.
- Anon. 1870 The Glandore mines. *The Cork Examiner*, 5 October.
- Apjohn, J. 1844 On the constitution of jade; and also of two ores of manganese, from the south of Cork. *Proceedings of the Royal Irish Academy* **2**, 598–602.
- Apopei, A.I., Damian, G., Buzgar, N., Buzatu, A., Andras, P. and Milovska, S. 2017 The determination of the Sb/As content in natural tetrahedrite–tennantite and bournonite–seligmannite solid solution series by Raman spectroscopy. *Mineralogical Magazine* **81**(6), 1439–56.
- Biagioni, C., Capalbo, C. and Pasero, M. 2013 Nomenclature tunings in the hollandite supergroup. *European Journal of Mineralogy* **25**, 85–90.
- Boland, M.B., Clifford, J.A., Meldrum, A.H. and Poustie, A. 1992 Residual base metal and barite mineralization at Silvermines, Co. Tipperary, Ireland. In A.A. Bowden, G. Earls, P.G. O'Connor and J.F. Pyne (eds) *The Irish minerals industry 1980–1990*, 247–60. Dublin. Irish Association for Economic Geology.
- Clifford, J.A., Ryan, P., Kucha, H. 1986 A review of the geological setting of the Tynagh orebody, Co. Galway. In C.J. Andrew, R.W.A. Crowe, S. Finlay, W.M. Pennell and J.F. Pyne (eds) *Geology and genesis of mineral deposits in Ireland*, 419–39. Dublin. Irish Association for Economic Geology, Dublin.
- Cole, G.A.J. 1922 Memoir and map of localities of minerals of economic importance and metalliferous mines in Ireland. *Memoirs of the Geological Survey of Ireland, Mineral Resources*. Dublin. HMSO.
- Daly, H.J. 1918 *Report upon Glandore manganese mines*. Unpublished report to the Ministry of Munitions, held by the Geological Survey Ireland.
- Dauber, H. 1857 Ueber Svanbergit und Beudantit. *Annalen der Physik und Chemie* **176**(4), 579–80.
- Frost, R.L. and Palmer, S.J. 2011 A vibrational spectroscopic study of the mineral Corkite $\text{PbFe}_3^{3+}(\text{PO}_4)_2(\text{OH})_6$. *Journal of Molecular Structure* **988**(1–3), 47–51.
- Frost, R.L., Xi, Y., Scholz, R. and de Brito Ribeiro, C.A. 2013 The molecular structure of the phosphate mineral Chalcosiderite – a vibrational spectroscopic study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **111**, 24–30.
- Greg, R.P. and Lettsom, W.G. 1858 *Manual of the Mineralogy of Great Britain and Ireland*. London. J. Van Voorst.
- Grennan, E. 1969 *Report on the present status of the Glandore prospect, prospecting licence 998, for Irish Metal Mining Company Ltd*. Unpublished report held by Geological Survey Ireland.
- Grey, I.E., Shanks, F.L., Wilson, N.C., Mumme, W.G. and Birch, W.D. 2011 Carbon incorporation in plumbogummite-group minerals. *Mineralogical Magazine*, **75**(1), 145–58.
- Hallissy, T. 1923 Barytes in Ireland. *Memoirs of the Geological Survey of Ireland, Mineral Resources*. Dublin. HMSO.
- Hartley, E.G.J. 1900 On the constitution of the natural arsenates and phosphates. *Mineralogical Magazine* **12**, 234–8.
- Higgs, K. and Beese, A.P. 1986 A Jurassic microflora from the Colbond Clay of Cloyne, County Cork. *Irish Journal of Earth Sciences* **7**(2), 99–109.
- Izbrodin, I.A., Ripp, G.S. and Doroshkevitch, A.G. 2011 Aluminium phosphate and phosphate-sulphate minerals in kyanite schists of the Ichetuyskoye area, West Transbaikalia, Russia: crystal chemistry and evolution. *Mineralogy and Petrology* **101**, 81–96.
- Jukes, J.B. and Kinahan, G.H. 1861 Explanations to accompany sheets 200, 203, 204 and 205, and part of 199 of the map of the Geological Survey of Ireland, illustrating part of the County of Cork. *Memoirs of the Geological Survey of Ireland*. Dublin. HMSO.
- Kane, R. 1844 *The industrial resources of Ireland*. Dublin. Hodges and Smith.
- Lang, J., Meere, P.A., Unitt, R.P., Johnson, S.C., Solferino, G., Torremans, K., Selby, D. and Kyne, R. 2020 The vein-hosted copper deposits of the Allihies mining area, SW Ireland; a new structural and chronological evaluation. *Journal of the Geological Society* **177**, 671–85.
- Lafuente, B., Downs, R.T., Yang, H. and Stone, N. 2015 The power of databases: the RRUFF project. In T. Armbruster and R.M. Danisi (eds) *Highlights in mineralogical crystallography*, 1–30. Berlin, Germany. W. De Gruyter.
- Miers, H.A. 1900 Note on the Hitchcockite, Plumbogummite and Beudantite analysed by Mr Hartley. *Mineralogical Magazine* **12**, 239–43.
- Mitchell, G.F. 1980 The search for Tertiary Ireland. *Journal of Earth Sciences, Royal Dublin Society* **3**, 13–33.

- Moreton, S., Green, D.I. and Tindle, A.G. 2006 Manganese oxide minerals from veins in the Leinster granite. *Irish Journal of Earth Sciences* **24**, 29–36.
- O'Sullivan, P. 2002 Glandore mines, County Cork: History and survey. *Journal of the Mining Heritage Trust of Ireland* **2**, 51–9.
- Post, J.E. 1999 Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proceedings of the National Academy of Sciences of the USA* **96**, 3447–54.
- Poyraz, A.S., Huang, J., Zhang, B., Masrchilok, A.C., Takeuchi, K.J. and Takeuchi, E.S. 2017 Synthesis of cation and water free Cryptomelane type OMS-2 cathode materials: The impact of tunnel water on electrochemistry. *MRS Advances* **2**, 407–12.
- Pring, A., Birch, W.D., Dawe, J., Taylor, M., Deliens, M. and Walenta, K. 1995
- Kintoreite, $\text{PbFe}_3(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$, a new mineral of the jarosite-alunite family, and Lusungite discredited. *Mineralogical Magazine*, **59**(394), 143–48.
- Quinn, D., Meere, P.A. and Wartho, J. 2005 A chronology of foreland deformation: ultra-violet laser $^{40}\text{Ar}/^{39}\text{Ar}$ dating of syn/late-orogenic intrusions from the variscides of southwest Ireland. *Journal of Structural Geology* **27**(8), 1413–25.
- Rammelsberg, C. 1857 Ueber die Zusammensetzung des Beudantits, *Annalen der Physik und Chemie* **176**(4), 581–3.
- Reilly, T.A. 1986 A review of vein mineralization in SW County Cork, Ireland. In C.J. Andrew, R.W.A. Crowe, S. Finlay, W.M. Pennell and J.F. Pyne (eds) *Geology and genesis of mineral deposits in Ireland*, 513–44. Dublin. Irish Association for Economic Geology, Dublin.
- Reilly, T.A. and Graham, J.R. 1972 The historical and geological setting of the Glandore mines, southwest County Cork. *Geological Survey of Ireland Bulletin* **1**, 253–65.
- Rundall, W.H. 1939 *Manganese mining prospects at Glandore*. Unpublished report for Pellew Harvey and Co., London. Held by the Geological Survey Ireland.
- Ryback, G., Nawaz, R. and Farley, E. 1988 Seventh supplementary list of British Isles minerals (Irish). *Mineralogical Magazine* **52**, 267–74.
- Ryback, G. and Tandy, P.C. 1992 Eighth supplementary list of British Isles minerals (English). *Mineralogical Magazine* **56**, 261–75.
- Sandberger, F. 1857 Ueber den Beudantit und seine Modificationen. *Annalen der Physik und Chemie* **176**(4), 611–9.
- Scott, K.M. 2000 Nomenclature of the alunite supergroup: Discussion. *Canadian Mineralogist* **38**, 1295–7.
- Weaver, T. 1837 On the geological relations of the south of Ireland. *Transactions of the Geological Society of London* **5**(1), 1–68.
- Wen, N., Boyce, A.J., Fallick, A.E., Ashworth, J.R. and Ixer, R.A. 1996 The genesis of Cu-bearing quartz veins by metamorphic remobilization from stratiform red bed deposits, SW County Cork, Ireland. *Mineralogy and Petrology* **57**, 73–89.

RICHARD UNITT (corresponding author)
School of Biological, Earth and Environmental Sciences
University College Cork
Cork, Ireland
E-mail: r.unitt@ucc.ie
ORCID – 0000-0002-7504-1451

STEPHEN MORETON
33 Marina Avenue
Great Sankey, Warrington, Cheshire WA5 1HY
England, UK

SIMON KOCHER
Colorado School of Mines
1500 Illinois Street, Golden, Colorado CO 80401
USA

ROBERT LAWSON
Allanton
Castle Douglas, Dumfries and Galloway, DG7 1EN
Scotland, UK