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The Ballynoe Stratiform Barite Deposit, Silvermines, County Tipperary, Ireland

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Posted Date: 26 February 2024

doi: 10.20944/preprints202402.1481.v1

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The Ballynoe Stratiform Barite Deposit, Silvermines, County Tipperary, Ireland

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Abstract: The Ballynoe barite deposit is a conformable, mineralized horizon of Lower Carboniferous age overlying a diastem and mass faunal extinction demarking the transition from a quiet water environment to one of dynamic sedimentation. The geometry of the barite orebody correlates with the palaeo-topography of the footwall, which acted as an important control over the lateral extent, thickness and nature of the mineralization. Sedimentary features within the barite horizon suggest that it was precipitated in the form of a cryptocrystalline mud which underwent major diagenetic modification resulting in extensive stylolitisation, recrystallisation and remobilization. There is abundant and compelling geological and isotopic evidence for early local exhalation from the presence of a hydrothermal vent fauna consisting of a delicately pyritized worm tubes hosted and haematized filaments of apparent microbial origin. The worm tubes are remarkably similar to examples from modern and ancient volcanic-hosted massive sulphide deposits, and the filamentous microfossils have similarities to modern Fe-oxidizing bacteria. Strontium in the barite has a $^{87}Sr/^{86}Sr$ ratio indistinguishable from sea-water between 350 and 344Ma whilst oxygen isotopes from barite and chert suggest a diagenetic origin in equilibrium such sea-water around 60-70°C. Fluid inclusion studies have shown that, in general, low temperature inclusions are very saline (20-25%) whilst at higher homogenization temperatures they are more dilute (9-12%).

Keywords: stratiform; lower carboniferous; barite; Silvermines District; exhalation

1. Introduction

The carbonate-hosted Irish Midlands Orefield is ranked first in the world in terms of zinc metal discovered per sq. km, and second for lead [1,3] with in excess of 14 Mt of contained zinc metal has been found to date. The largest deposit at Navan exceeding 150 Mt of production and remaining resources, with four deposits (Tynagh, Silvermines, Lisheen, Galmoy) having been brought into production since 1962, and a further 20 prospects discovered to date. The Orefield has also historically been a major producer of barite (an EU designated critical raw material) and all of the deposits contain barite to some degree, and this is briefly described in the Addendum to this paper which specifically focuses on the largest barite deposit at Ballynoe in the Silvermines area.

The deposits in the Irish Midlands such as Navan, Tynagh, Silvermines, Lisheen, Galmoy and Pallas Green and others that host this vast resource show varying host-rocks, mineral textures, thermo-chemical and isotopic signatures that together neither equate to SedEx or MVT types. However, amongst this apparent diversity lie some major similarities that form the basis of the definition of being "Irish-type" [1]. The Silvermines deposits together form the type example of Irish-type Zn-Pb deposits iIlustrating the relationship between epigenetic ore zones (interpreted as feeders) and exhalative to near surface replacement stratiform sediment-hosted orebodies [1–3].

The base-metal and barite deposits in the Silvermines area occur on the northern flank of the Silvermines Mountains, some 8km south of the market town of Nenagh in north County Tipperary in the Irish Midlands. The earliest description of the deposits dates back to 1861 with the first series sheet memoirs of the Geological Survey of Great Britain [4] whilst Griffith [5], Rhoden [6], Barrett [7], Taylor & Andrew [8], Taylor [9], Andrew [1,10], Mullane & Kinnaird [11] have described the contemporary knowledge of the mineralization in detail. Additional data on the deposits have been

 doi:10.20944/preprints202402.1481.v1

contributed by Greig *et al* [12], Coomer & Robinson [13], Larter *et al* [14], Bruck [15], and Boyce *et al* [16,17] However, these publications have largely focused on the base-metal mineralization.

The Ballynoe barite zone is a substantial part of the Silvermines mineralizing system although literature is sparse on the barite ore zone itself with only Barrett [7] and Mullane & Kinnaird [11] specifically describing its setting and features. This paper is a review of the existing published data on the Silvermines system, focussing on the Ballynoe barite zone and attempts to draw together some of the available information from a number of unpublished sources.

The Silvermines orebodies consist of three contiguous stratiform zones, two of which (the Upper G and B-Zones) contained economic Zn-Pb-Ag grades hosted in massive pyrite, siderite and barite whilst the third (the Ballynoe deposit) comprises massive barite with only traces of Zn-Pb. These mineralized zones totalling some 17.7Mt @ 6.4% Zn, 2.5% Pb also contain 0.64Mt of massive barite in addition to the 5.27Mt mined from the Ballynoe section and are developed at a single horizon and genetically may be considered as a single entity. Cross-cutting mineralization of Zn-Pb-Fe sulphides and barite is seen at lower stratigraphic levels and may be logically assumed to represent conduits to the stratiform ore horizon.

2. History

The discovery of barite at Ballynoe must be credited to the Geological Survey of Great Britain who mapped the area between 1856 and 1860. In 1956 the Silvermines Lead and Zinc Company Limited commenced quarrying the barite at outcrop and shipped 3,800 tonnes at 80% $BaSO_4$ to England. In the following year the company commenced drilling the deposit with the hope of locating base-metal mineralization associated with the barite completing 23 holes with little base-metals but defining a substantial deposit of barite. In May 1959 the Magnet Cove Barite company ("Magcobar") took out a lease over the property and extending the drilling to eventually define over 5Mt of barite at an average grade of 85% $BaSO_4$ [18].

In October 1962 the Canadian International Mogul Mines, also concluded a farm-in agreement with the Silvermines Lead & Zinc Company to explore an 80 km^2 area at Silvermines. Drilling commenced in June 1963 and by December 1964 almost 10Mt of economic zinc-lead ore had been defined. Underground mining operations commenced in 1968 until closure in July 1982, having milled 11.86Mt of ore grading 2.83% Pb and 7.35% Zn from underground workings on a number of orebodies, of which the B and G zones, located at the same stratigraphic horizon and part of the same orebody as the Ballynoe barite, were economically the most substantial.

Magcobar Ireland Limited (latterly Dresser Minerals International Inc) mined of 5.27Mt barite (~90% $BaSO_4$) from the Ballynoe open-pit (Figures 1 and 3) (and latterly a small tonnage from underground workings) between 1963 and April 1993 [2,18] (Figures 1, 2 and 3). To access this ore around 8.5 to 9 Mt of overburden and waste rock were stripped and largely dumped above the open pit. These dumps have recently been landscaped and revegetated whilst the pit is now completely flooded.

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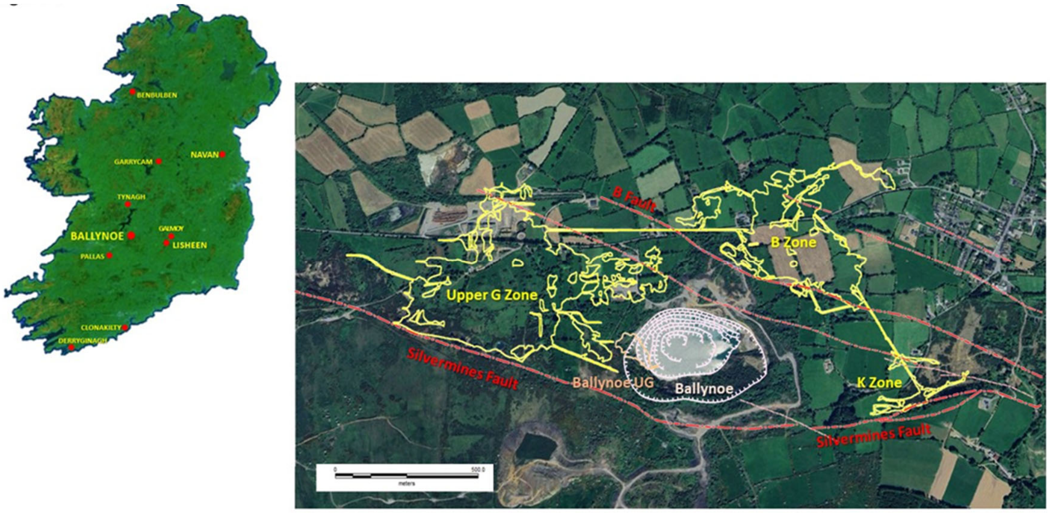

Figure 1. Location map of Ballynoe in central Ireland showing other barite occurrences and satellite image of the Silvermines District showing the underground workings of the Mogul Mine and the open pit and underground workings at Ballynoe.

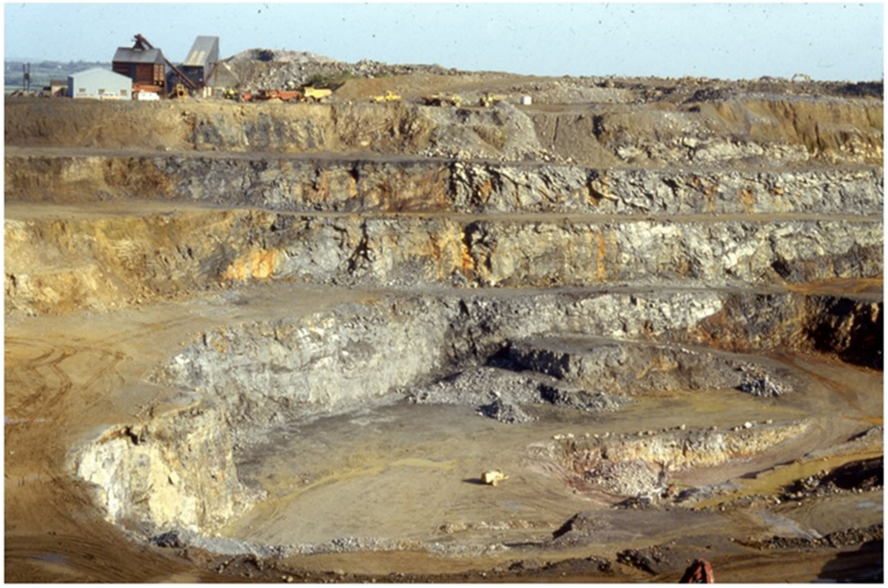

Figure 2. General view of the Ballynoe Pit (Magcobar) facing to the NNE with pit bottom on Bench 5 – July 1986.

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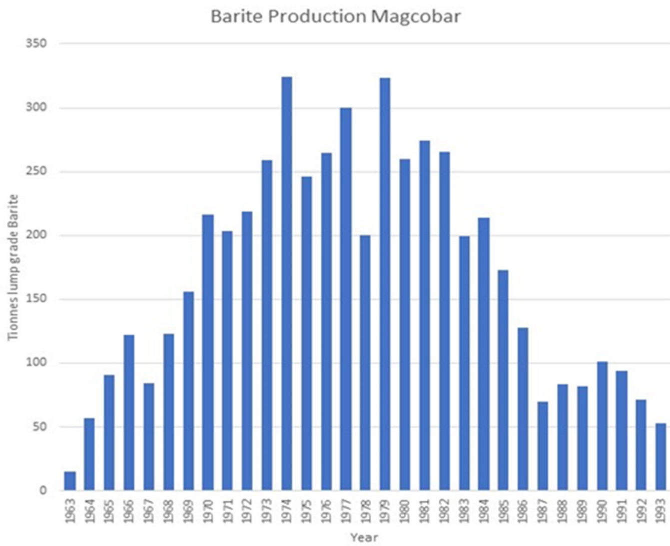

Figure 3. Production of lump grade (>85% $BaSO_4$) from the Ballynoe Mine between 1963 and closure in 1993.

3. Geological Setting

The stratigraphy of the Silvermines District has been described by Taylor and Andrew [8], Taylor [9] and Andrew [2] and its regional setting by Brück [15] and Philcox [19]. In simple terms the local Silurian basement is overlain by a clastic sequence of red, green and white siliciclastics of early Tournaisian age which pass conformably up into a marginal marine transgressive sequence of, initially, silty mudrocks and upwards into a sequence of oolitic and argillaceous bioclastic limestones (the Ballysteen Formation) before seeing the development of the regionally extensive Waulsortian mudbank limestone comprising pale grey stromatactid biomicrites and its equivalents [20–22] Depositional patterns and thicknesses were strongly influenced by the development of basinal areas, which generally follow earlier ENE and NE'erly Caledonian structural trends in the pre-Carboniferous basement, have been described in detail [1,19,23–26].

In the Silvermines District a sharp formational boundary at the top of the argillaceous limestones of the Ballysteen Formation is defined by mass extinction of fauna and by a thin (0.05-1.0m) distinctive greenish argillite which may have a tuffaceous component as seen at Lisheen and Pallas Green where it has been dated at between 350.5 to 348.2Ma [27]. Above the Green Shale at Silvermines the Waulsortian equivalent marks the transition from a quiet water environment to one of dynamic sedimentation and comprises a sequence of complex limestone and dolomite breccias that most authors familiar with Silvermines consider to be chaotic debris flows, focussed down palaeoslope from the points of maximum throw on the ore controlling fault system (Figures 4, 5 and 6).

The principal structural setting comprises a WNW-trending, NNE dipping, array of left-stepping fault segments with maximum displacements between 130 and 375m, linked by relay ramps and generally referred to as the Silvermines Fault zone [28] (Figure 6).

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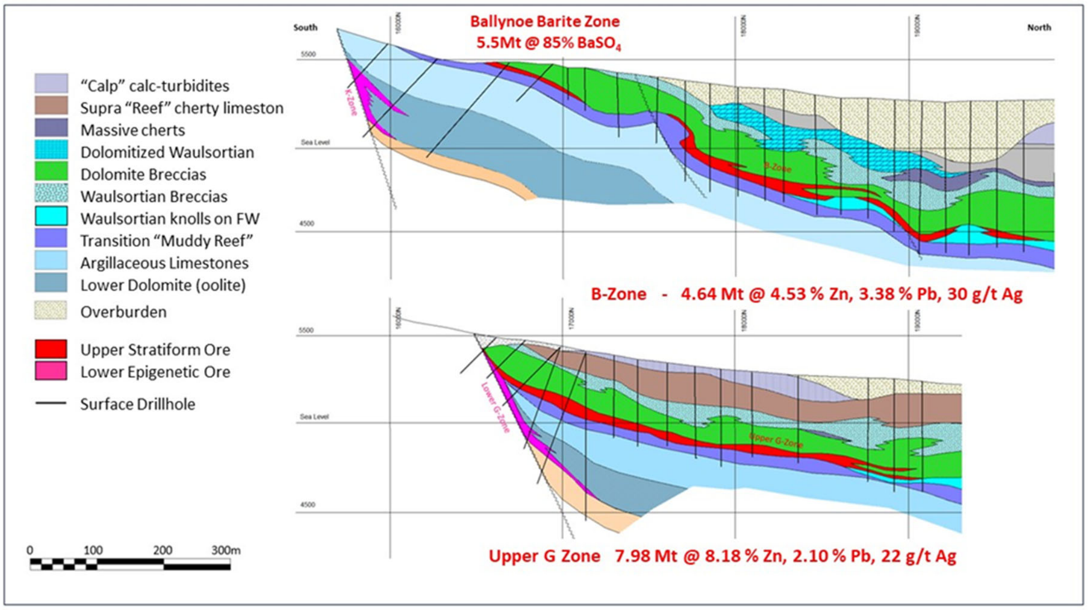

Figure 4. N-S Sections through the Silvermines orebodies. [8].

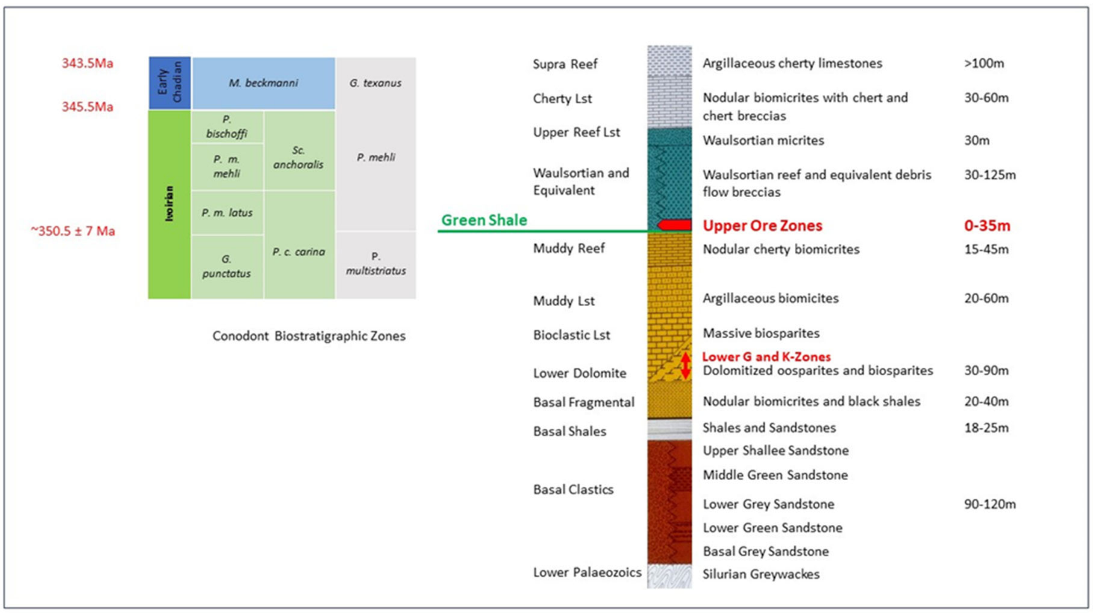

Figure 5. Stratigraphic column for the Silvermines and Ballynoe area.

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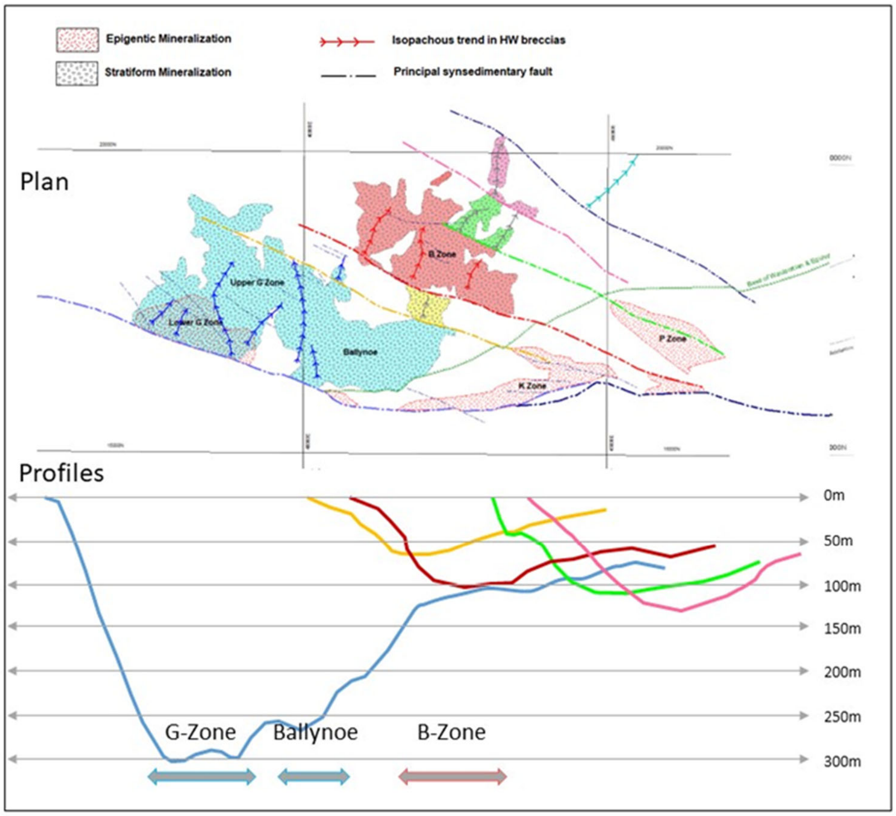

Figure 6. Plan and displacement profiles of the various branches of the Silvermines Fault Zone, showing the changes in vertical displacement for each of the segments, the principal trends of thickened hangingwall breccias and the extent of the stratiform ore zones.

3.1. Setting of the Barite Orebody

Immediately underlying the strongest base-metal and barite mineralization at Silvermines the Muddy Reef Limestone is extensively replaced by chert in the upper part of the succession, and black chert lenses up to 5m thick are of common occurrence below the barite horizon. A similar thickness of chert is reported underlying the 'Upper G Zone' orebody [29].

The Muddy Reef Limestone is generally capped by an irregular development of green argillite ("Green Shale" of previous authors [2,8–10] which also interdigitates with the barite horizon. The thickest development of this shale is found to occur in minor surface depressions at the top of the Muddy Reef Limestone, ranging from a few cms up to a

maximum of around 1.2m. Slump structures are evident in the thicker shale lenses and rare, angular, micro-fragments of bioclastic limestone are sometimes incorporated into the slumped argillite. Barrett [7] noted that on the basis of its constituent mineralogy the green argillite may be divided into two facies: *(a)* a chlorite-illite-quartz shale ± barite and, (*b)* a siderite-chlorite-illite-quartz shale.

Type (a) has the most widespread distribution in the vicinity of the barite zone and also comprises numerous shale intercalations within the basal part of the barite orebody indicative of density differential slumping.

Type (b) is defined by its siderite ($FeCO_3$) content and is a paler shade of green than type *(a)*, it is generally less laminated and not greatly affected by slumping. Type *b)* is preferentially developed underlying the siderite ore host lithologies in the B-Zone and the barren siderite developed to the north of the Ballynoe barite body.

The Ballynoe barite deposit is a complex interstratification of sulphate, sulphide, oxide, silicate and carbonate minerals. The mineralized horizon exhibits both lateral and vertical zonation which is of considerable genetic importance. The barite horizon is conformable with the top of the Muddy Reef Limestone and in both strike and dip the orebody is lenticular in shape, with ore-grade barite quickly pinching out into low-grade material towards the margin of the lens. Economic barite mineralization extends for approximately 700m along strike and for 400m down-dip from outcrop. The average thickness of the orebody is around 10m of massive barite, with a maximum thickness of close to 20m being developed in the west-central part of the deposit (Figure 12). The location, disposition and thickness of the barite body shows an intimate relationship to the topography of the footwall contact as described by previous authors [7,8.9,10 29].

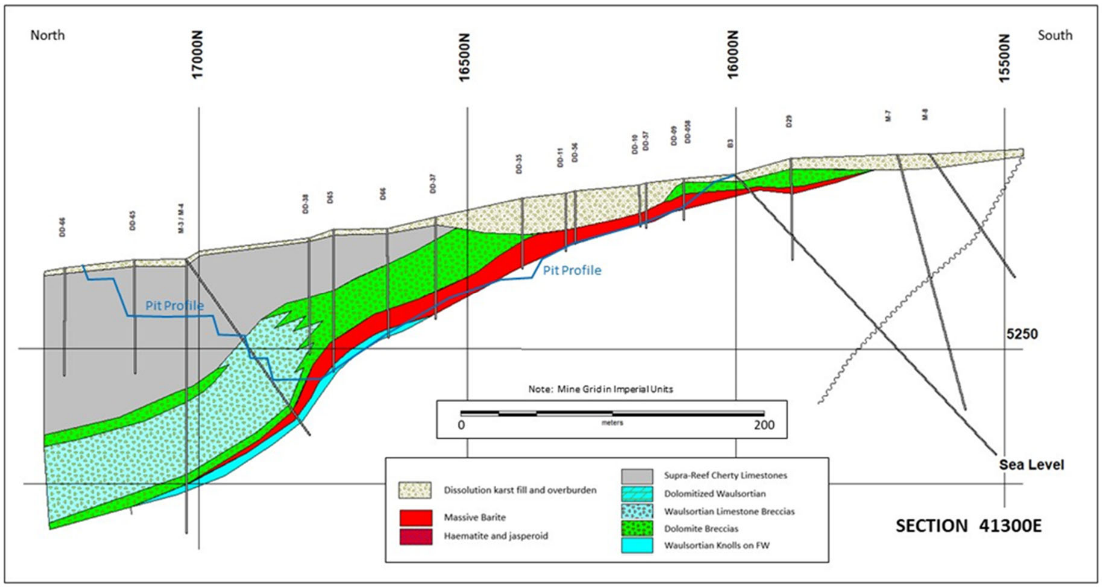

Figure 7. North-South Section 41300E through the Ballynoe Barite Zone and open pit.

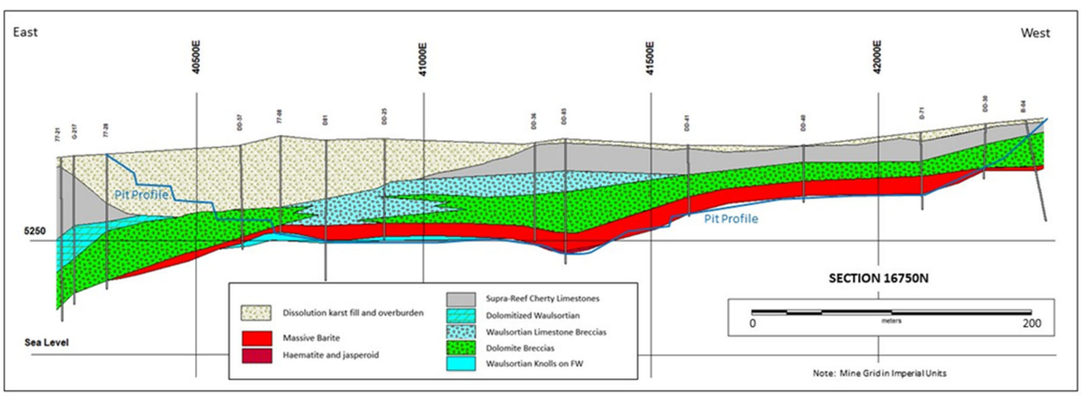

Figure 8. East-West Section 16750N through the Ballynoe Barite Zone and open pit.

Lying at the same horizon and partially connected to the west of the barite zone the stratiform Upper-G orebody occurs as massive partly brecciated pyrite at the base of a thick sequence of dolomite breccias, and immediately overlies the Mudbank Reef Limestone (Figures 4, 7 and 8). The maximum thickness of economic ore (30m) is attained in the southern portion of the orebody near the northwest-trending faults that define its southern limit. The southwestern and southeastern boundaries, which follow closely the limits of massive pyrite development, are straight and well defined, whereas the northern limits are irregular and reflect the uneven development of the footwall Reef Limestone against which the pyritic ore pinches out. The orebody base is in general lithologically sharp: it is marked by the abrupt change from massive pyrite to footwall sediments almost devoid of sulphides, but occasionally the sediments, with progressive increase in pyrite content, grade into the

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massive pyrite. The upper contact is, in contrast, always lithologically well defined: it is indicated by the change from massive pyrite to dolomite breccia or to thin shale bands overlain by dolomite breccia. Pyrite and marcasite, which constitute 75% of the sulphide content, sphalerite (20%) and galena (4%) are the dominant sulphides; trace quantities of chalcopyrite, tennantite, boulangerite, marcasite, bournonite, jordanite and pyrrhotite occur. Of the gangue minerals, dolomite, chert, clay minerals, calcite, barite, and quartz are present in descending order of abundance.

Also contiguous, to the NE of the barite zone, part of the B-Zone orebody is dominated by pale buff to pink brecciated fine-grained barite that contains distinctive inclusions of haematite and jasperoid at its base. The characteristic mineralization is of fine intraclastic disseminations of galena and pyrite with minor fine-grained sphalerite. The pyrite zone comprises massive or brecciated pyrite. The massive pyrite is either finely crystalline or colloform, and displays a variety of structures including spheroids, concentric bands, plumose bodies and framboids. It typically contains extremely fine-grained sphalerite and galena, as both disseminations and coarser replacements. Locally, the pyrite is in the form of a tightly packed poorly sorted breccia in an argillaceous or dolomitic matrix, partly replaced by fine-grained sphalerite and galena. The siderite zone is characterized by a breccia of clasts of line-grained buff to grey siderite, of varied size, angularity, and degree of packing, which appear locally stratified with interbeds of undisturbed shale.

The geometry of the barite, siderite and pyrite orebody host lithologies correlates with the palaeo-topography of the footwall, the topography acting as an important control over the lateral extent, thickness and nature of the mineralization which thins over Waulsortian footwall knolls and thickens in troughs between such knolls (Figures 9, 10, 11 and 12).

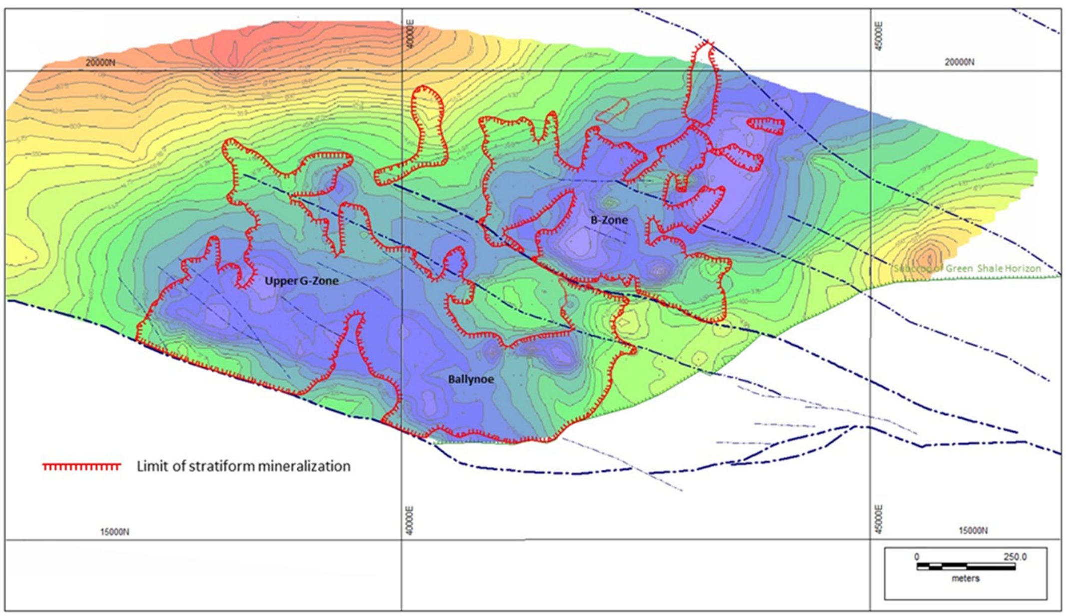

Figure 9. Connolly-type plan of the distance above a uniformly dipping plane of the footwall contact of the mineralized horizon (the Green Shale) showing the troughs (blues) and highs (reds). Plan also shows the extent of the stratiform mineralized horizon and principal structures of the Silvermines Fault zone. Note the spectacular correlation between the troughs and the extent of the mineralization.

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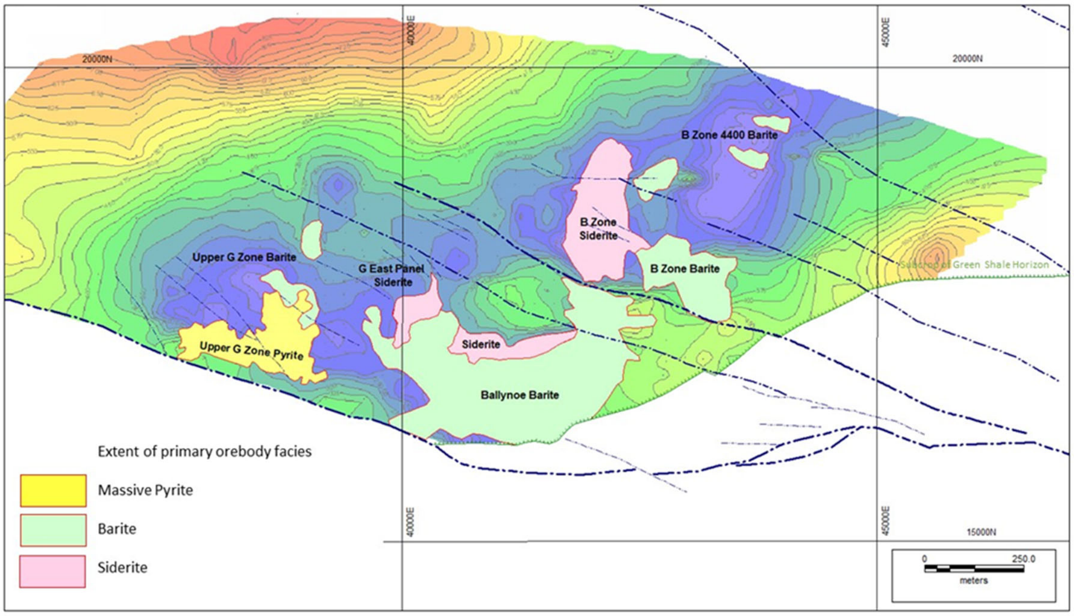

Figure 10. Similar Connolly plot as in Figure 9 but also showing the extent of the primary stratiform orebody host lithologies.

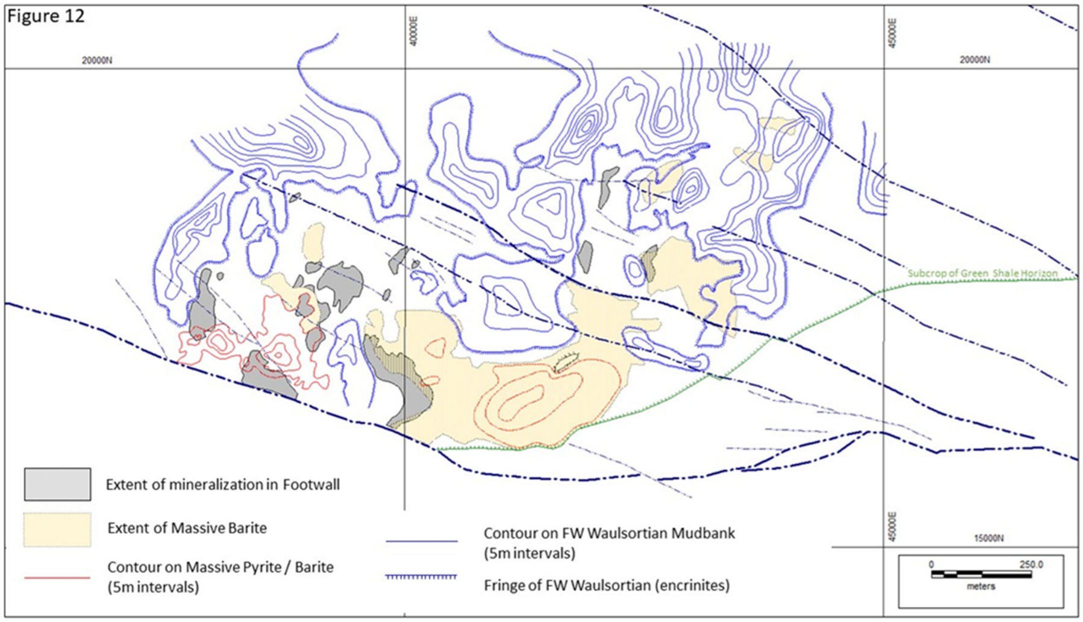

Figure 11. Plan showing the extent of chertification and mineralization in the uppermost beds of the footwall Muddy Reef Limestones, the extent of the massive barite orebody with isopachs and the development of the thickness and extent of the knolls of Waulsortian on the immediate footwall of the stratiform horizon.

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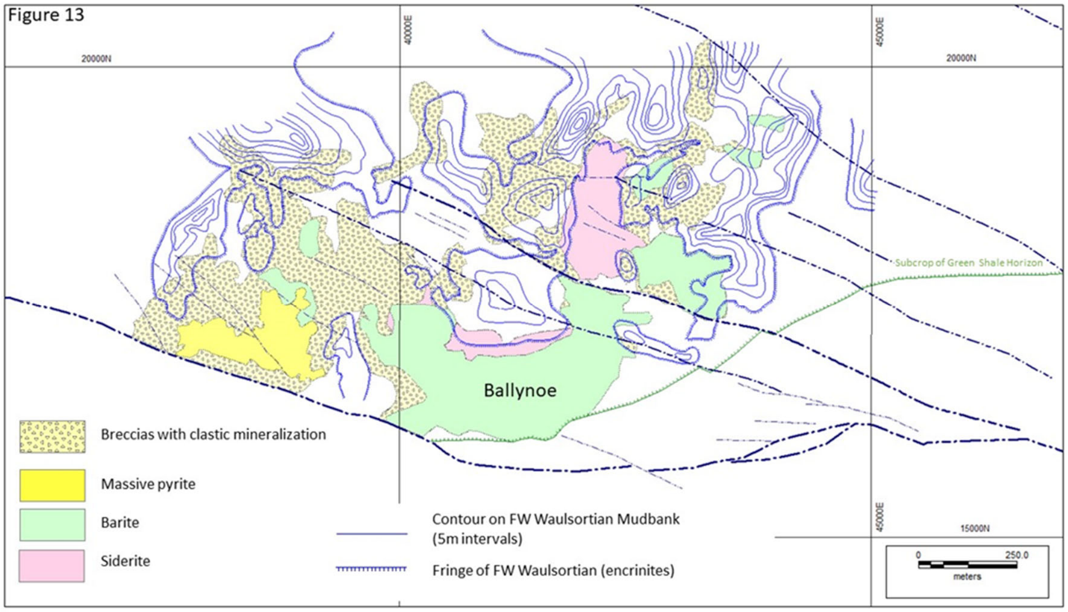

Figure 12. Similar plan to Figure 11 but showing the extent of the primary stratiform orebody host lithologies and the extent of the knolls of Waulsortian on the immediate footwall of the stratiform horizon.

3.2. Nature of the Barite Orebody

Barrett [7] and Mullane & Kinnaird [11] have defined a number of distinct stratigraphic units within the barite on the basis of differences in mineralogy texture and sedimentological features (Figure 13). However, these divisions are extremely variable in extent, and often co-exist.

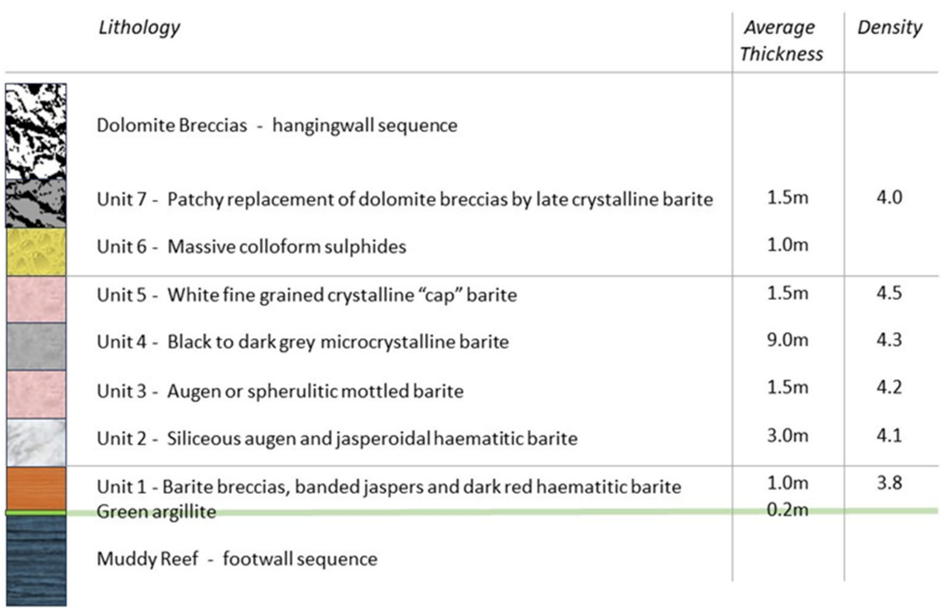

Figure 13. Sketch diagramme showing the various Units of the Barite orebody as defined on the basis of differences in mineralogy texture and sedimentological features [7,11].

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The basal Unit 1, typically 1-2m in thickness, may be sub-divided into the following types: 1a) barite breccia; 1b) banded haematite-barite with massive jasper; 1c) replacement of the footwall by barite and pyrite.

The development of barite breccia (Unit 1a) is associated with local changes of slope in the footwall, and its formation may be exemplified on the flanks of the 'eastern dome'. On the north-western flank of this footwall 'high', lensoid masses of siliceous, crinoidal debris are overlain by pyritic, green argillites and thence a thin, baritic breccia sequence (Figure 13). The barite breccia consists of scattered clasts of brick-red to pink barite set in a matrix of highly-slumped, green argillite. Fragments of bioclastic limestone are not infrequent in the breccia. The barite breccia clasts may be angular, rounded, or diffuse. The diffuse barite occurs in zones of intense slumping and is often sheared and invaded by slivers of green argillite parallel to the plane of movement. The slumped material has been subjected to secondary silicification and pyritization. The fact that the barite breccia is confined to the flanks of the 'eastern dome' suggests gravitational slumping and the existence of the topographical high during early barite deposition. The barite breccia sequence rarely exceeds 50cms in thickness. A zone of thick, barite breccia is developed in a 'low' situated in the south-east of the B Zone orebody. The brecciated sequence is up to 8.5m thick and consists of sub-angular clasts of micro-crystalline, brown barite, set in a muddy carbonate matrix.

The banded haematite-barite with jasper (Unit 1b) is quite complex, both mineralogically and texturally comprising quartz (as inclusion-rich equant crystals in jasperoid and as clear fracture-filling material), blood-red haematite (as the inclusions in jasperoid, sphalerite, pyrite, galena, boulangerite, barite, and minor calcite [30].

The banded haematite unit is a conformable, ironstone horizon is analogous to the Tynagh bedded ironstone formation [31], although developed on a very much smaller scale. The bedded haematite at Ballynoe is unique to the barite deposit, and no comparable formations being reported from the 'Upper G' or 'B' zones. The haematite horizon averages 0.6m in thickness and is best developed under the southern half of the barite body, pinching out entirely downdip to the north. The horizon consists of lenses of massive haematite (up to 0.3m thick) in a matrix of haematitic-barite and interlayered with goethite and jasper. Rare magnetite has been identified from crushed samples of massive haematite. Evidence such as graded particulate sediments and soft sediment slump fabrics suggests that the haematite was laid down as a sediment in a dynamic environment. Catlin [32] and Danielli [30] found no evidence that the jasperoid replaced an earlier-formed carbonate rock and concluded that it had formed as a sea- floor precipitate. Soft-sediment slumping and penecontemporaneous micro-faulting occur frequently throughout the horizon and are often pseudomorphically replaced by fine grained aggregates of euhedral and subhedral pyrite. Wherever the haematite horizon is underlain by green argillite the sequence is balled-up and highly brecciated. It is possible that the upper surface of the Green Shale acted as a plane of decollement to the overlying haematite formation and initiated the slumping.

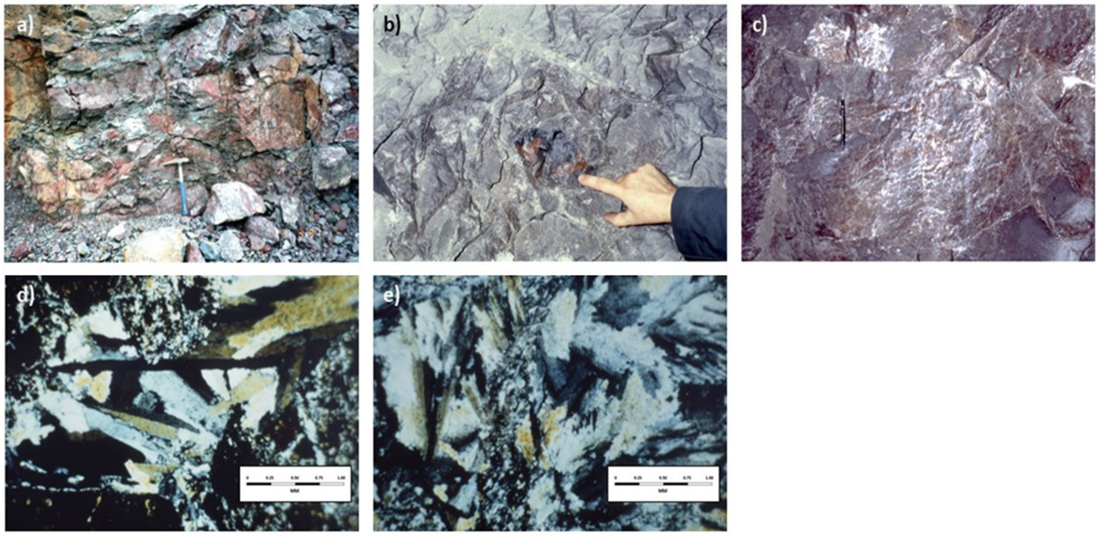

Figure 14. a): Haematitic / jasperoidal barite, Ballynoe pit south-west face Bench 6. (**b)**: Clast of jasperoid set in massive grey-brown barite; 'B-Zone' 4937 Room. (**c):** Massive brown and white mottled barite with lamination parallel to bedding; 'B-Zone' 4939 Room. (**d):** Barite (white to grey to yellow) filling voids in fractured and brecciated jasperoid (dark brown to black). 'B-Zone' 49 area. Transmitted light with crossed polars; [32]. (**e):** Massive barite (white to grey to yellow) with minor opaque iron sulphides. 'B-Zone' 49 area. Transmitted light with crossed polars; [32].

A massive micritic carbonate mudbank is present in the northwest corner of the Ballynoe pit and the barite ore body abuts this mud bank along its northern margin, indicating that the mudbank was present prior to mineralization.

The gradual transition from 'bedded ironstone' into siliceous, iron-rich barite is marked by streaks and lenses of brilliant-red jasper (Figure 15a and 16a). Two types of jasper have been identified and probably represent different generations. A colloform variety is associated with haematitic barite whilst a second variety replaces pyrite euhedra. The colloform jasper is composed of coalescing spherulites about 100 microns in diameter which encloses amorphous, vuggy jasper often infilled by late crystalline white barite. A feature common to the colloform jasper and not the replacement variety are dehydration (syneresis) cracks, also often infilled with white barite. The cracks which are wedge shaped, pinch out towards the centre of the jasper lens typical of the texture when dehydration of a silica gel takes place [33,34].

The morphology of the barite which replaces the footwall rocks (Unit 1c) is very distinctive and is easily differentiated from the allothigenic barite found in the basal green argillite sequence. This barite normally occurs as displacive growth stellate crystal groups and is always white to translucent in colour. Although the stellate barite crystals are developed in a very siliceous environment up to 3m below the footwall contact with the principal mineralized-horizon, they are free from any silicification suggesting emplacement post-dating the chertification of the Muddy Reef Limestone.

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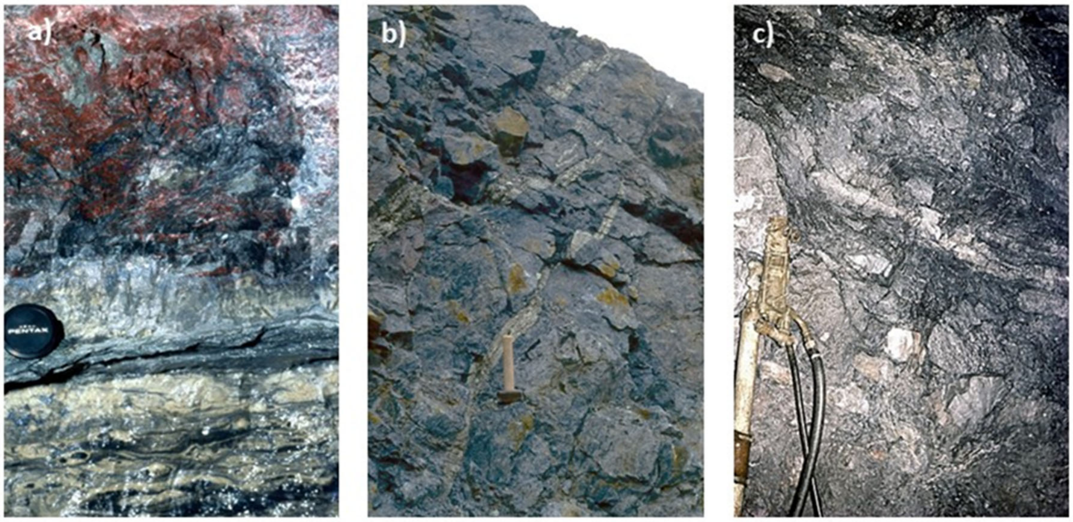

Figure 15. a): Footwall contact of the haematitic massive barite sitting on 3-4cms of the Green Argillite overlying strongly silicified and well mineralized (pale yellow sphalerite) Muddy Reef Limestone. Upper G Zone, East Panel, 2 Level. (**b):** Crustiform collomorph marcasite veins cutting massive grey barite. Ballynoe open pit. **(c):** Slumped debris flow of polymictic blocks set in argillaceous carbonate matrix, Two angular clasts of white and pink barite mid-lower centre. Jackleg drill for scale. B-Zone, 4510 Stope.

Two important periods of brecciation can be discerned with early-formed, haematite-bearing jasperoid being brecciated and then recemented by clear silica and minor pyrite. This material was in turn brecciated and recemented by barite, pyrite and base-metal sulphides (with pyrite earliest), and minor calcite. The second brecciation/re-cementation event was accompanied by a "bleaching out" of the haematite on the edges of jasperoid clasts, giving a greenish-tan colour rather than a blood-red colour to the edges of the jasperoid clasts (Figures 15a and 15b).

The gradual transition from bedded ironstone into around 3m of siliceous, jasperoidal haematitic barite of Unit 2 is marked by streaks and lenses of brilliant-red jasper (Figure 14a). The high silica content of the basal barite is not only due to jasper which is normally restricted to areas of haematitic barite but primarily due to the extensive replacement of barite by up to 10% of free silica. The pattern of this replacement is controlled by the crystalline fabric of the barite and as a result a tabular meshwork of barite and quartz is often developed. Unit 2 passes gradually into Unit 3 which is dominated by “augen” or spherulitic mottled barite up to 1.5m thick.

In Unit 3 layers of spherulitic and coarsely-crystalline, nodular barite are associated with the zones of stylolitisation and aggregations of spherulites around 0.02-0.05m in diameter form thin, colloform layers of red to pink barite which are conformable with the bedding and maybe followed along strike for tens of metres. Stylolitic and spherulitic barite is confined in development to the central and thickest section of the orebody, the zone being very poorly defined in the east where the barite thins rapidly over the 'eastern dome’. An empirical relationship is observed between the formation of stylolites and the occurrence of spherulitic textures in the barite.

Unit 4 comprises the greater part of the orebody and consists of well-bedded, grey to black barite of a microcrystalline barite and of uniform texture. In appearance specimens resemble either dark anhydrite or a bituminous limestone. The fabric of the massive grey-black barite consists either of a compact aggregate of randomly orientated microplumose crystals or looser aggregates of microspherulites up to 0.5mm in diameter and probably represent the primary crystalline state of the barite, a stage which is often obscured by diagenetic-recrystallisation.

The microcrystalline grey-black barite of Unit 4 is rarely in direct contact with the hangingwall dolomites and is normally overlain by a sequence of white barite (Unit 5) or massive pyrite (Unit 6)

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carrying disseminated galena and sphalerite up to 1m in thickness, which is best developed over the western end of the Ballynoe barite orebody. This sulphide horizon attains its maximum thickness in troughs controlled by the uneven undulating upper contact of the barite with thinner development of pyrite overlying the crests of the undulations and carries less galena/sphalerite.

Zones of extensive stylolitisation in fine-grained grey-black barite of Unit 4 tend to be overlain by layers of coarse, spherulitic barite crystals, the spherules often being pink to dark red in colour due to tiny inclusions of haematite. Horizontal-simple stylolites tend to be independent of the original barite fabric which is truncated at random. The very carbonaceous composition of the stylolites probably represents the insoluble residue left from the original barite. Such stylolites are considered to have formed early and at shallow depths [36]. In contrast to the simple stylolites, the horizontal-sutured variety are narrower in width, display a greater amplitude and tend to be localised along the margins of megacrystalline barite 'fans'.

Three facies of macrocrystalline barite in Unit 5 were recognized by Barrett [7]:

5a) barite conformable with the stratification and capping the orebody barite.

5b) irregular patches of white barite replacing the black, microcrystalline barite within the orebody.

5c) extensive hangingwall replacement by the white barite.

The macrocrystalline (type 5a) barite is hereafter described as the 'cap' barite and is pure white in colour and is composed of a coarse aggregate of macroplumose crystals up to 0.1m in length. The horizon varies up to 1m in thickness and was originally best developed near the surface over the 'eastern dome'. Masses of collomorph pyrite are not uncommon within the basal development of the 'cap' barite (Figure 15b).

Associated with the development of secondary barite are crosscutting veinlets of thin barite (2-3cms wide) which extend across the orebody from footwall to hangingwall, a vertical distance of more than 10m. The veinlets trend NE-SW (the dominant joint trend) and invariably dip to the east at between 70-85^{o}. The vein barite carries no sulphides.

The Ballynoe barite deposit is a complex interstratification and exhibits both lateral and vertical zonation. As such the zonal divisions within the barite horizon can be extremely variable in extent, and often co-exist. For example, layers of spherulitic barite (Unit 3 type) may be developed throughout the black, microcrystalline barite of Unit 4. The white, crystalline barite of Unit 5 may be found as disseminations within Units 4 and 6. Units 2 to 4 carry ore-grade barite and constituted around 85% of the total tonnage mined.

Synsedimentary slumping is well developed throughout the barite ore body, particularly in Units 4 and 5. It is most obvious when the barite is of different colours and when it is intercalated with pyrite, as in Unit 4. Debris-flow clasts of red silicified barite and jasperoidal haematite are present in the lowest parts of the barite body (Figures 14b and 15c). [2,7–9,11,35]. They vary from angular to sub-rounded and have sharp margins. These originated as rip-up clasts from the erosion of the underlying unit. Another example of rip-up clasts, emphasized through colour contrasts, occurs close to the contact between barite Units 3 and 4. Angular clasts of Unit 3 (black) are incorporated at the base of Unit 4 (fawn-brown). The upper surface of Unit 3 is also scoured.

4. Geochemistry

At Ballynoe, the silica content of the immediate footwall to the barite body attains levels of up to 60% and then diminishes upwards through the barite orebody from 10% near the base in Units 1 and 2 to less than a few hundred ppm in Unit 4 (Figure 16) [7]. This silica within the barite is amorphous and cryptocrystalline and often associated with haematite as jasperoid in the lowermost parts of the orezone. As at Tynagh the iron-silica zone infills a palaeo-topographic low or sag on the downthrown side of the fault complex [31].

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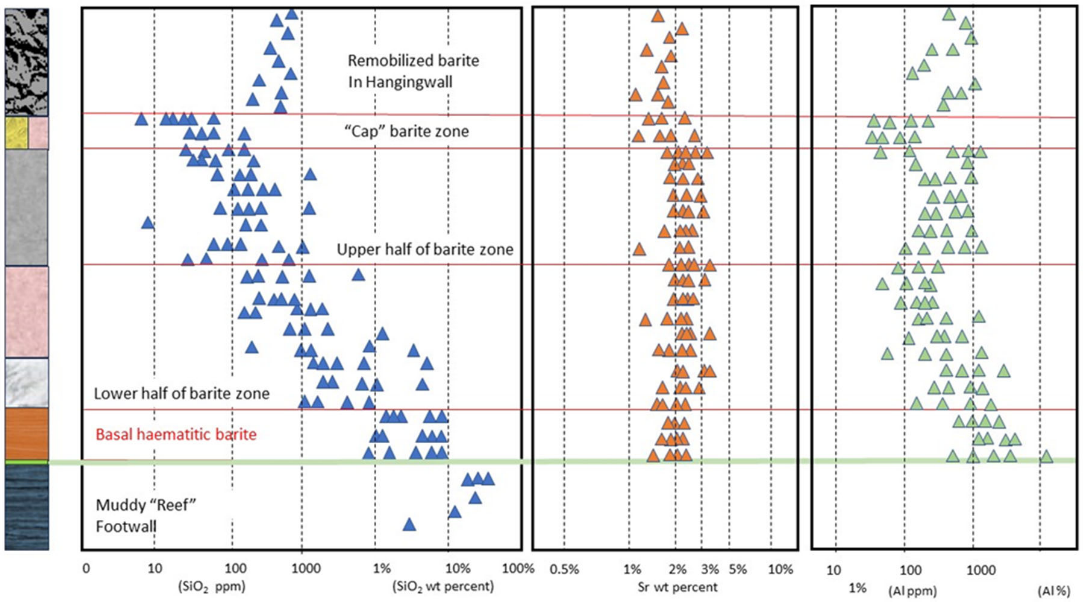

Figure 16. Geochemical profiles through the barite orebody in Ballynoe for silica, strontium and aluminium. Data all from Barrett [7].

The wallrock geochemistry at Ballynoe and as a result suggested that the dispersion of anomalous Ba values is strictly confined to the mineralized-horizon directly overlying the Muddy Reef Limestone and Fe and SiO_2 reveal the only major association with the initial emplacement of the barite [7]. Ba and Fe appear to have been co-precipitated from an aqueous solution in the presence of amorphous silicon in a semi restricted marine lagoon. The subaqueous precipitation of barite is supported by sulphur and oxygen isotope data which suggests that contemporaneous seawater sulphate played a significant role in the deposition of the barite. In the more restricted areas of the lagoon (cut-off by carbonate mudbanks), lower Eh and pH conditions led to the precipitation of iron as siderite and/or pyrite. In such conditions the Ba would likely have remained in solution.

4.1. Biota in the Barite Orebody

There is significant evidence for contemporaneous environmental impact of the onset of the mineralizing process as towards the top of the Muddy Reef succession, the diameters of individual crinoid ossicles tend to increase in size until an abrupt extinction of the crinoid population occurs and crinoids are absent from the topmost 0.1m [7,11]. A plot of the ossicle enlargement trend is shown in Figure 17. This size increase seen up stratigraphy may be a direct consequence of changing physio-chemical environments during sedimentation, the crinoids reflecting these conditions until for some reason mass extinction occurred. The crinoidal lenses may also exhibit severe slumping. A similar phenomenon is seen within a single bed of the uppermost Muddy Reef in the B-Zone where the crinoid ossicle size gradually increases laterally towards the chertification whereupon the crinoids cease to be found before passing laterally into grey and black non-fossiliferous cherts sometimes with distorted laminated pale sphalerite (Figure 15a). On the fringes of the chert development crinoid ossicles show partial or total replacement by silica [7]. These two factors strongly suggest that towards the uppermost Muddy Reef and the diastem to the breccia sequence, a change in the physiochemistry of the depositional environment had an impact on the nature of the crinoid population.

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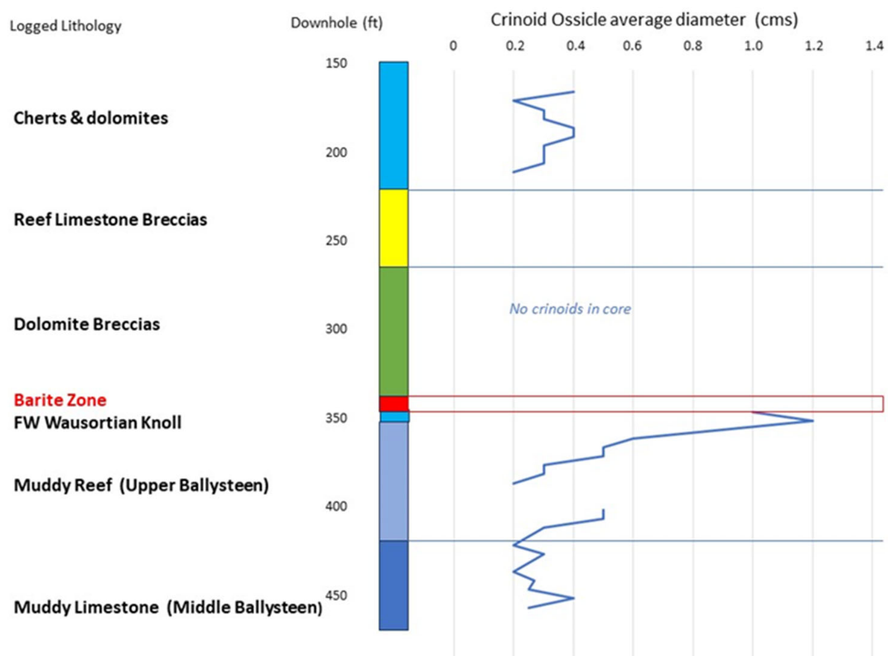

Figure 17. Plot of average crinoid ossicle diameters showing the notable increase towards the top of the Muddy Reef Limestone (Ballysteen Fm.). [7].

Barrett (1975) noted that in the massive sulphide Unit 6 of the barite body, the pyrite may develop tube-like structures which are up to 10cm long by 1cm in diameter which he considered to resemble pyritic crinoid stems, now considered more likely to be worm casts and hydrothermal chimneys as described by Larter *et al* [14], and Boyce *et al* [17].

Larter *et al.* [14] identified the occurrence of fossil hydrothermal vents and a highly pyritic vent field at the south-western part of the Ballynoe pit at Silvermines. These fossil polychaete worms, which occur in pyritic mounds have affinities to Paravinella, an organism that lives attached to hydrothermal chimneys at the Juan de Fuca hot spring site in the Northeast Pacific [36,37]. Stratiform beds of iron oxides (usually haematite) and silica – 'jaspers' – are commonly associated with sulphide deposits in volcanic rock sequences in the geological record and are usually considered to be the product of low-temperature, diffuse hydrothermal venting, because of their close similarity to seafloor mineral deposits at modern vent sites and on seamounts [39,40]. Tubes of haematite cemented by silica, similar to iron oxidizing bacteria such as Gallionella that are typical of both fossil and modern submarine vent sites; and specimens of a finely annulated pyritized tube worms sharing features in common with small alvinellid polychaetes observed in the Devonian Sibay and Cretaceous Bayda vent assemblages [41,42].

Additionally, the presence of pyrite microbialites and the presence of sub-micron, filamentous hollow tubes of haematite cemented by quartz suggest fossil iron-oxidising bacteria, which could indicate the existence of a chemoautotrophic, near-seafloor habitat typical of both fossil and modern seafloor hydrothermal systems. The interpreted presence of fossil vent-related worm tubes suggests that sea-floor exhalative hydrothermal activity could have occurred at Silvermines and Tynagh around 350-360Ma [14,16,17,38,43].

Filamentous haematite microfossils in Ballynoe (Silvermines) jasper were also described showing a strong similarity to Fe-oxidizing bacteria and provide evidence of microbial activity, a feature typical of modern and ancient vent fields [17]. Such filaments, identified as fossilized microbial communities [43,44] are mainly twisted hollow tubular structures and some are filled with later silica and typically are 1-20µm in diameter and up to 200µm long and are coated by sub-micron scale haematite crystals. All of the filaments are cemented by later silica phases, which can be either quartz or chalcedony. The fact that filaments often cross quartz and chalcedony crystal boundaries

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proves that the silica post-dates haematite filament formation [44]. Kucha [43] also noted the presence of sub-micron, filamentous hollow tubes of haematite cemented by quartz interpreted to be fossil iron-oxidising bacteria, support the existence of a chemo-autotrophic, near-seafloor habitat that is typical of both fossil and modern seafloor hydrothermal systems.

Fossil evidence of the presence of a vent-related worm tube provides compelling evidence that sea-floor exhalative hydrothermal activity did occur at Silvermines and Tynagh. This implies that at least some of the mineralization occurred contemporaneously with deposition of the carbonate host rocks during the Ivorian Stage about 348Ma [16]. The worm tubes are remarkably similar to those seen around modern and fossilized around ancient volcanic-hosted massive sulphide deposits, and the filamentous microfossils have similarities to modern Fe-oxidizing bacteria. There is no correlation between the worm tubes and normal Ivorian fossil assemblages such as crinoids, whose replacement by pyrite in the immediately underlying Ballynoe footwall is seen to destroy the original morphology. Convincingly the sulphur isotope composition of the worm tube and host pyrite is essentially identical to that of the vent field pyrite and the main sulphide ore stage of Silvermines sulphides, all having a mean value about -20‰, indicating an open-system bacteriogenic sulphide source.

4.2. Fluid Inclusions

Mullane & Kinnaird [11] in their study on Ballynoe barite reported that two-phase liquid-vapour inclusions *('L+V')*, are very irregular in shape. *L+V* inclusions lack solid phases and have a wide range of homogenization temperatures, from 68 to 223°C, with two peaks - one at 70-80°C and the other at 190-200°C (Figure 23). Salinities are in the range 9-25 equiv. wt% NaCl, again with two peaks - one at 10-11 equiv. wt% and the other at 23-24 equiv. wt% NaCl. In general, low temperature inclusions are very saline (20- 25%) and higher temperatures inclusions are more dilute (9- 12%). There is a distinct break in sequence between these two fluid end-members implying that there were two fluids, one of moderate temperature and low salinity and the other of low temperature and high salinity. Low-temperature, high salinity inclusions were present in all the units sampled, including one from a late-stage barite vein. The low-temperature, high-salinity inclusions display a general increase in homogenization temperature from 68 to 110°C between barite in Unit I and the crystalline cap barite in Unit 5. The moderate-temperature, low-salinity inclusions, exhibit a similar pattern, from 150°C to 220°C (Figure 18).

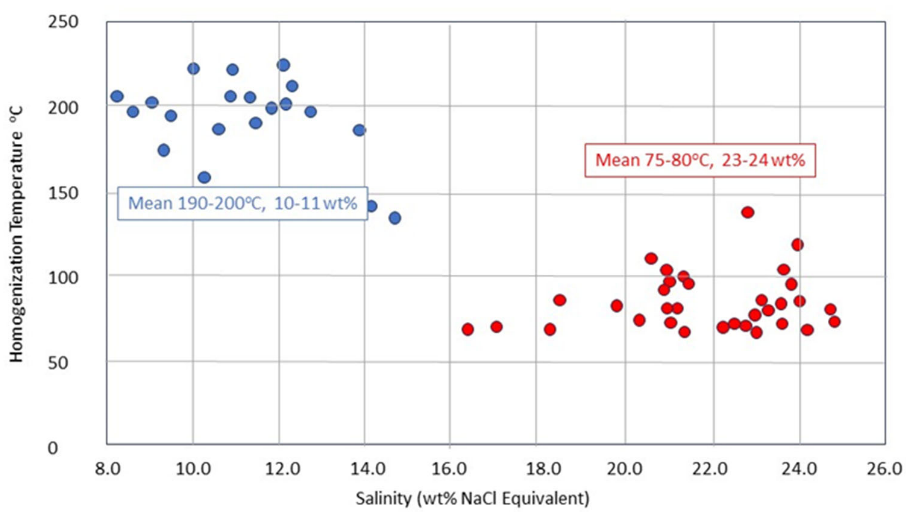

Figure 18. Fluid inclusion data from Ballynoe barite samples [11].

Samson & Russell [44] in their study of the Silvermines sulphide orebodies record that fluid inclusion salinities range from 8 to 28 equiv. wt% NaCl with modes at 14 and 19 wt% NaCl. Leachate studies show the fluids to have high sodium concentration with lesser variable amounts of potassium

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and calcium and uniformly low magnesium concentrations (K/Na = 0.03-0.23; Ca/Na = 0.03-0.28; Mg/Ca = 0.1-0.67). Homogenization temperatures range from 50° to 260°C, with most between 140° and 220°C with a mode at 190°C and a subsidiary group around 140°C. Samson & Russell [45] suggest that the required pressure corrections are less than 5°C, thus if the pressure within the epigenetic ore zones (Lower G and K-Zones) was purely hydrostatic, as is reasonable, a minimum seawater depth of c.80m is required to prevent boiling of some fluids.

Samson & Russell [45] record those inclusions in diagenetic barite from the stratiform Ballynoe orebody which grew in unconsolidated mud, close to the seafloor [16], also have high salinities. This supports a model in which the upper parts of the system contained high-salinity fluids and further suggests that a brine pool existed on the sea floor during mineralization**.**

4.3. Strontium Content and Isotopic Ratios

Barrett [7] reported that the barite from Ballynoe has a remarkably consistent content of strontium ranging from 1.96% $SrSO_4$ wt% in the basal haematitic barite to 2.45% wt% in the main orebody for a statistical average content of 2.33% $SrSO_4$ wt% (n=105). The apparent lower value of $SrSO_4$ in the basal haematitic barite may be explained by the high SiO_2 and Fe_3O_4 content of the ore (up to 15% plus combined) which correspondingly reduces the $BaSO_4$ content and, thus proportionally the $SrSO_4$ content.

The Sr isotope record of the Dinantian seawater is characterized by a decline in $^{87}Sr/^{86}Sr$ ratio from 0.7082 at the Devonian/Carboniferous transition from a high of 0.7080 in the early Hastarian to a low of 0.70765 in the late and mid-Chadian, with an early Chadian maximum at 0.7079. Superimposed on this trend are higher-order fluctuations with a periodicity in the Ma range. The Dinantian seawater curve may potentially serve as a geochronological and correlation tool, particularly for the Hastarian to lower Chadian interval, where the attainable resolution is ~1 Ma [45,46]. Snoeck et al [48] provide extensive Sr isotope data over the island of Ireland showing that the Lower Carboniferous succession in the Irish Midlands all fall within a range of $^{87}Sr/^{86}Sr$ equal to 0.7080 to 0.7090.

Sr isotope data indicate that strontium in the Ballynoe barite predominantly has an $^{87}Sr/^{86}Sr$ ratio of 0.7079 [48] indistinguishable from that demonstrated for Lower Carboniferous (Ivorian and early Chadian) sea water between 350-349Ma and 345-344Ma respectively [46,50] (Figure 19).

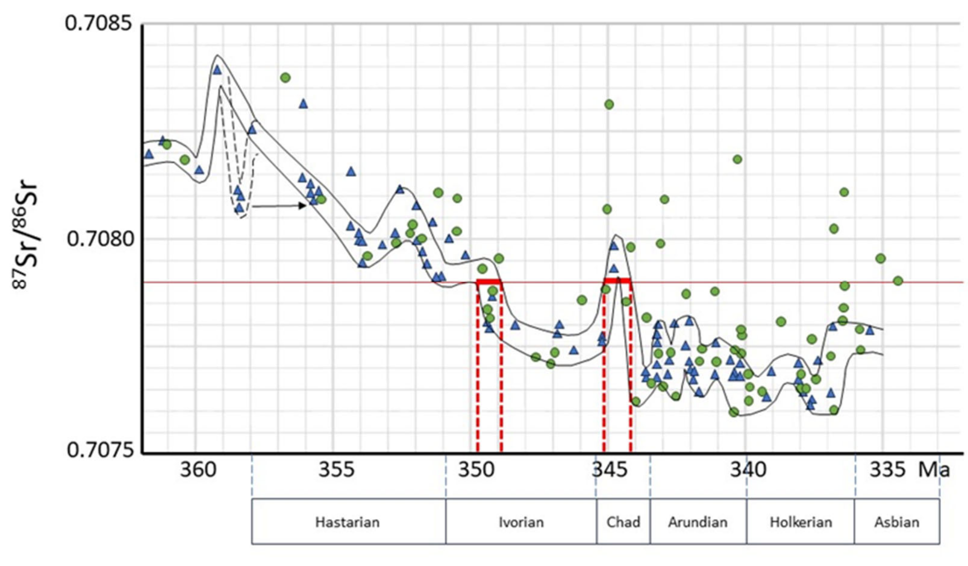

Figure 19. $^{87}Sr/^{86}Sr$ ratios of Ballynoe barite plotted on the LOWESS statistical regression function (*LOcally WEighted Scatterplot*) of Strontium Isotope Stratigraphy through the Lower Carboniferous Note correlation of Sr ratios with dates in the Ivorian and Chadian Stages [46,50].

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4.4. Stable Isotopes of Hydrogen, Oxygen and Sulphur

Fluid inclusion waters have δD values of -24 to -49‰ for quartz, -23 to -29‰ for dolomite-, -41 to -55‰ for barite,- 46‰ for sphalerite and -58‰ for galena. The $\delta^{18}O$ values of the mineralizing fluids, calculated from mineral values range from +1.1 to +7.7‰ for quartz and +1.8 to +5.7‰ for dolomite [45].

Oxygen isotope analyses of black chert from the immediate footwall to the barite in the Ballynoe open-pit show little isotopic variation (+25 to +27‰), which is consistent with a diagenetic origin for the cherts in equilibrium with a fluid similar to Lower Carboniferous sea water at temperatures around 60-70°C [13].

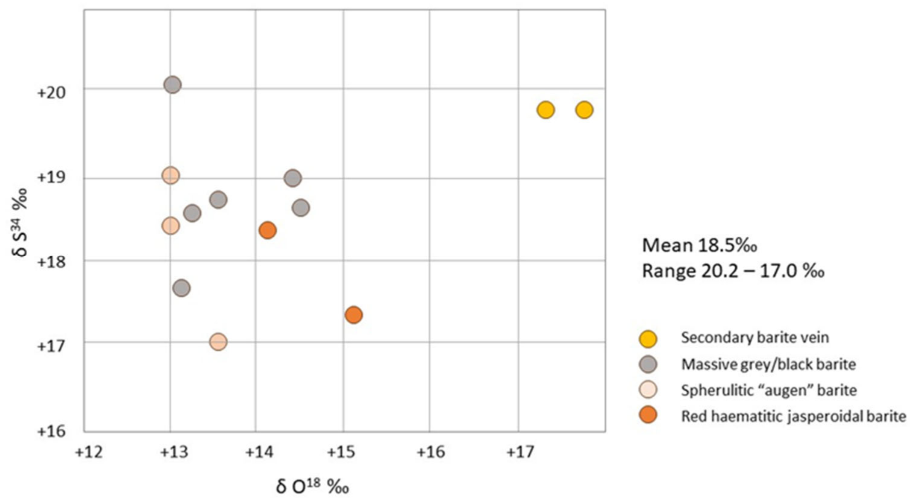

Figure 20. S and $\delta^{18}O$ values obtained for Ballynoe barite [13].

Isotopic values for the main orebody barite (Units 1 to 4) of $\delta^{18}O$ are in the range of +13.0 to +14.5‰. Little variance from orebody isotopic values was obtained from samples of secondary white 'cap' barite of Unit 5 with the isotope values for $\delta^{18}O$ +14.5‰ [13] (Figure 20).

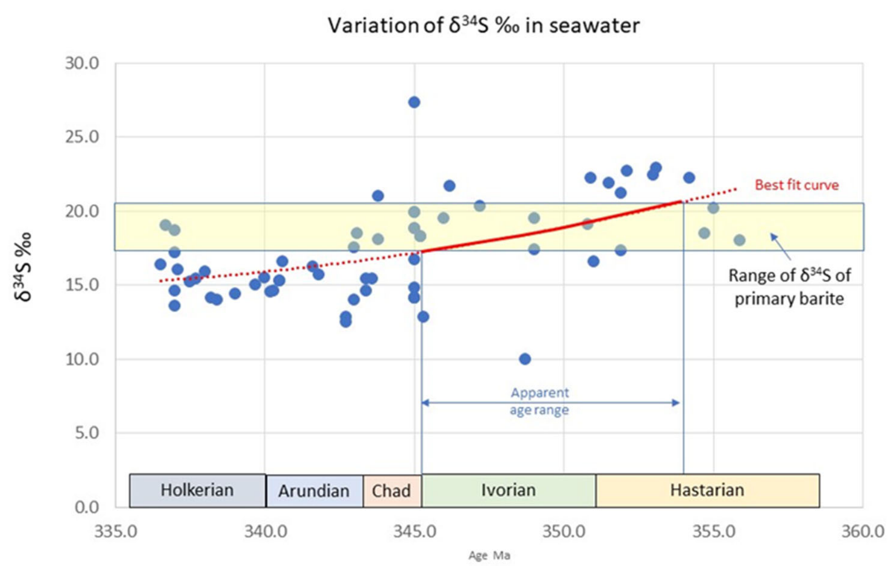

Figure 21. Diagramme showing the range of seawater sulphate $\delta^{34}S$ values through the Lower Carboniferous and the extent of the ranges obtained from Ballynoe barites showing a coincidence between 354 and 345Ma in the upper Hastarian to Ivorian [53].

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The isotopic values for the orebody barite are clustered in the range $\delta^{34}S$ +18.6 to +19.0‰ [13]. Greig *et al* [12] found that the barite at the distal end of the stratiform 'Upper G' zone and barite from the Ballynoe deposit had consistent isotope values around $\delta^{34}S$ +18.5‰, whilst Coomer & Robinson [13] report that for the orebody barite $\delta^{34}S$ values are clustered in the range $\delta^{34}S$ +18.6 to +19‰, all consistent with direct derivation from Ivorian seawater sulphate [16,53].

The sulphur isotope signature ($\delta^{34}S$) from the base-metal stratiform orebodies (Upper G and B Zones) is dominated by a signature about –20‰ indicative of an open-system bacteriogenic sulphide source, typical of Irish-type deposits [52]. The $\delta^{34}S$ values for the orebody barite fall within the range obtained for contemporaneous, Lower Carboniferous, seawater sulphate [51]. Figure 21 shows the range of seawater sulphate $\delta^{34}S$ values through the Lower Carboniferous and the extent of the ranges obtained from Ballynoe barites showing a coincidence between 354 and 345Ma in the upper Hastarian to Ivorian [53].

Isotopic analysis on pyrite containing the worm tube fossils return a $\delta^{34}S$ of -23.2‰; whereas pyrite from a small section of worm tube gave a value of –18.4‰ [16,17]. Both of these values fall within the range of the dominant bacteriogenic signature from the stratiform deposits [12,13]. Collomorph pyrite and marcasite from throughout the barite open pit but outside the vent site, although having an average value about –19‰, has a very broad isotopic range (-40.4 to +6‰). This large range contrasts to the worm tube-related pyrite and associated vent-type pyrite in chimneys, which has a very restricted range of -18 to -19‰ [17].

All the isotopic results firmly place the Ballynoe barite within the hydrothermal field interacting with contemporaneous seawater [55].

4.5. Hangingwall Breccias

The hangingwall sequence to the tabular stratiform barite body comprises a sequence of well bedded biomicrites and dolomite breccias. In the lower half of the succession the limestone has been dolomitised and heavily brecciated. This brecciation was initially interpreted to be the product of soft sediment slumping, and debris flows probably induced by gentle movements along the Silvermines Fault zone (Figure 22) [29]. The breccias are extremely variable in lateral extent and horizons of brecciation intercalate with massive dolomites and Waulsortian reef limestones and show multiple well-developed slump planes, multiple brecciation and graded bedding of the breccia clasts (Figures 24a, 24b and 24c). Subsequent authors intimately familiar with the geology of the Silvermines district reiterated the interpretation of debris flows and *in situ* brecciation of soft sediments [2,7,8,9,10,14,16,35, 54) Whilst also having certain similarities to evaporite dissolution collapse breccias, there is no evidence for evaporites being present in time equivalent sequences in this part of the Irish Midlands.

Mullane & Kinnaird [11] described sedimentary cycles within the hangingwall breccia sequence, which is up to 32m thick in the Ballynoe pit, with flow boundaries being well defined due to the presence of basal slip planes separating three distinct lithofacies: 1) a basal debris flow breccia, with bioclasts at the base, overlain by 2) dark banded limestones and 3) bioclastic breccias.

These debris-flow deposits typically around 1m in thickness, are pale-grey, poorly bedded, poorly sorted and matrix-supported debris-flow deposits, with angular, sometimes imbricated clasts ranging in size from 0.03 to 0.30m. The clasts are mainly of calcite, but there are some of low-iron dolomite. *In situ* brecciation of the clasts is common, ranging from a single fracture to intense brecciation. The breccias are separated by thin, subordinate, impersistent horizons of bioclastic breccia, typically 20cm thick, and minor lenses of banded limestone.

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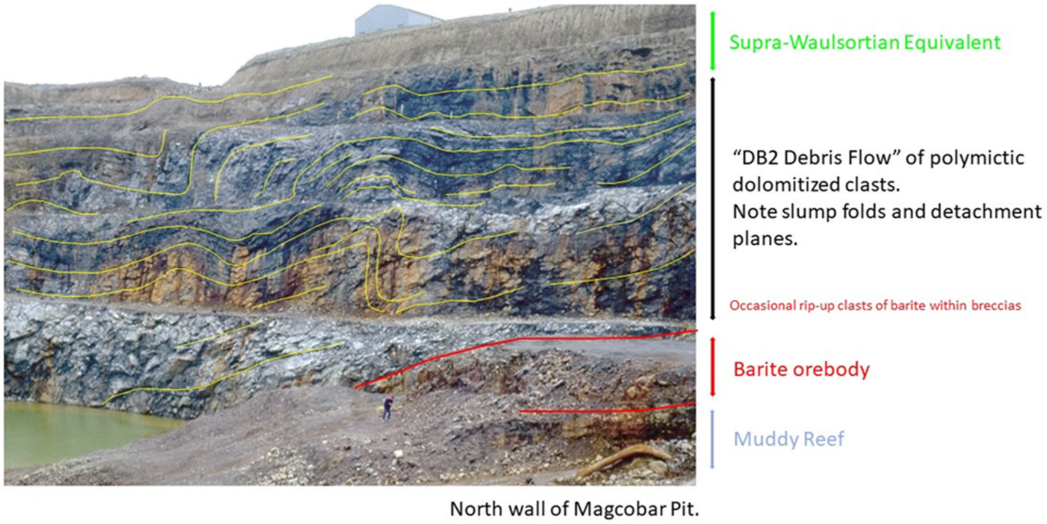

Figure 22. Annotated photograph of the north wall of the Ballynoe (Magcobar) open pit showing the slumped bedding and detachment folding within the "DB2" debris flow sequence overlying the barite orebody seen bottom right of photo.

Lee & Wilkinson [35] described individual breccia units as varying in thickness from 1 to 10m, commonly with gradational boundaries. Sub-horizontal alignment of clasts is very common, and normally graded intervals up to 0.5m thick are occasionally observed. Clasts of reworked limestone breccias demonstrate that there were multiple brecciation events.

Barrett [7] noted a very distinctive and continuous horizon within the dolomite breccia comprising a 1.5-3.0m thick unit of very thin, filamentous, dolomite laminae he regarded as being "*of a possible stromatolitic affinity*" which probably equates to the crenulated carbonate laminae within the banded argillaceous limestones in the cyclic unit recognized by Mullane & Kinnaird [11] (Figures 23a and 23b).

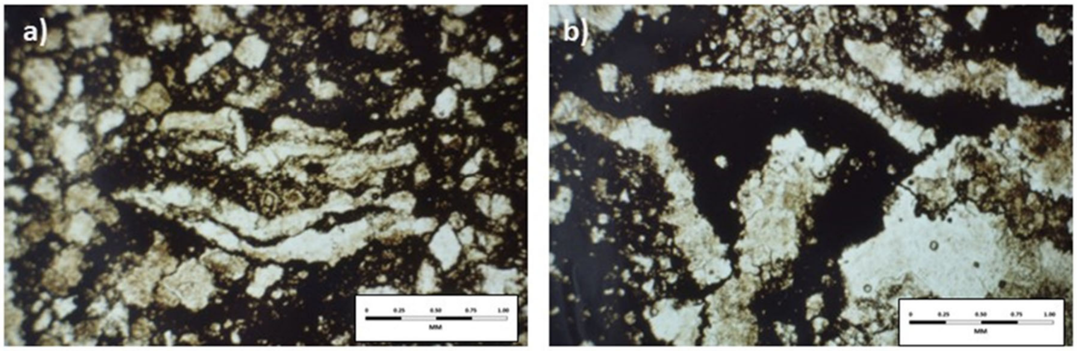

Figure 23. (a): Vermicular fabric of dolomite. Note double growth direction from central membrane of organic material. Curving from soft sediment compaction. 'Upper G-Zone' drillhole G-112, c. 38m. **(b):** Elongate and wavy section of dolomite around an area of organic-rich carbonate mud. 'B Zone' drillhole B- 190, c. 136m.

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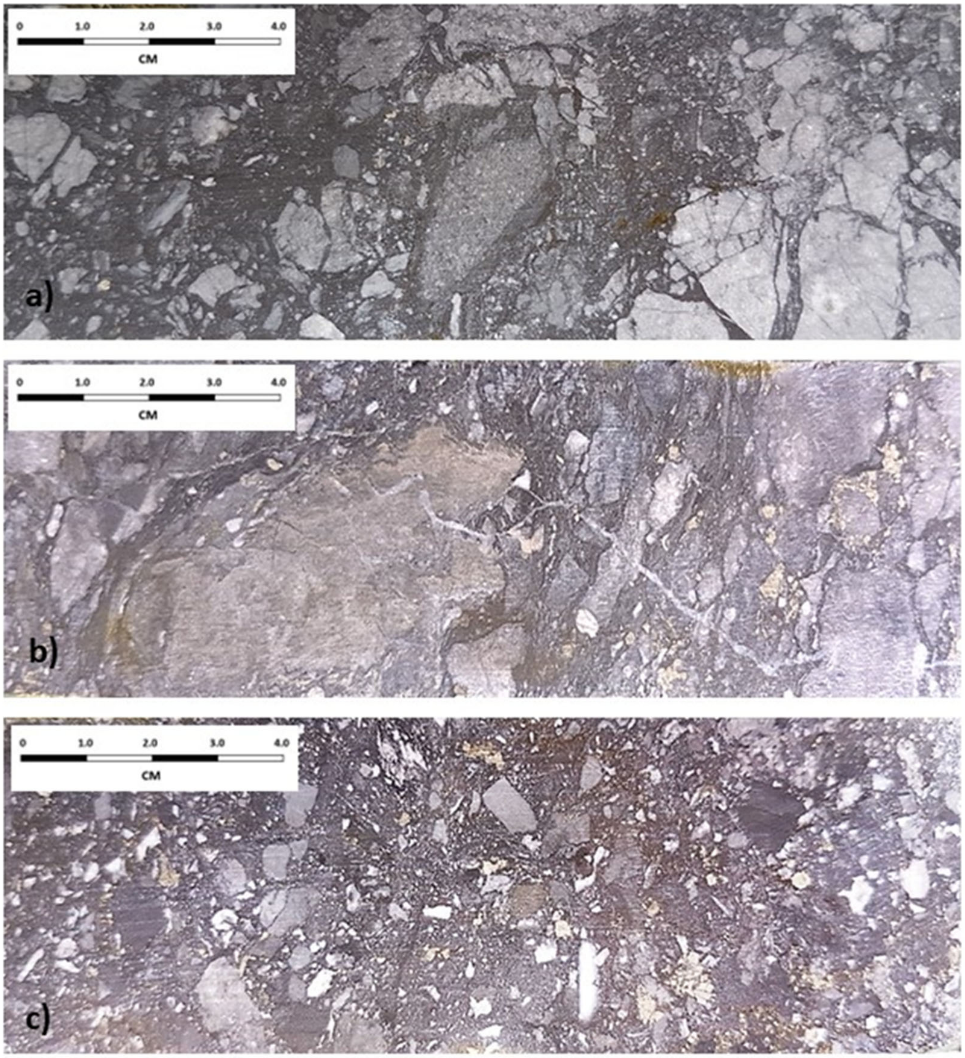

Figure 24. a): Slightly pyritic Dolomite Breccia of dolomitized clasts set in a black dolomitic mud matrix. Note mixture of jigsaw breccias and rounded coated clasts, 'B Zone' drillhole B- 190, c. 138m. **(b):** Limestone Breccia with small angular clasts of pyrite and a large, somewhat ragged, clast with pale brown sphalerite mineralization. Both clasts and matrix are calcareous. 'B-Zone' drillhole B-56, c. 70.1m. **(c):** Polymictic fine grained debris flow Dolomite Breccia with abundant angular clasts of pyrite. Upper G-Zone drillhole G-112, c. 96.1m.

Close to the basal contact of the breccia sequence with the underlying orebody up to 15% of the clasts are angular and include angular rip-up clasts of lithified barite and flame or loading structures of pyrite into the base of breccia sequence [2,7–9,11,29,35,54].

Isolated clasts of barite, colloform sphalerite and laminated pyrite are commonly present in the lowest beds of the breccia sequence and can attain ore grade (>5% Zn+Pb) in the outer fringes of the Upper G and B-Zones (Figures 24b and 24c). These sulphide clasts range from rounded to angular and are typically 3 to 40mm across with reworked clasts of banded sphalerite commonly showing evidence of dissolution during later (post lithification?) dolomitization, confirming that both phases did not precipitate from the same hydrothermal fluid [8,35].

In clasts of Waulsortian-type limestones the stromatactis is mainly infilled with coarse subhedral calcite, but in the lower part of the geopetal infill is framboidal pyrite. The orientation of the

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stromatactis within the clasts typically shows evidence of disturbance from its original depositional / crystallization environment suggestive of mass chaotic flow [11]

In the upper half of the succession, the Dolomite Breccias tend to become more argillaceous and are increasingly replaced by a black or grey chert. In many instances only the carbonaceous zones within the Dolomite Breccia are replaced, and examples are known of angular, dolostone clasts being set in a matrix completely replaced by a black, homogeneous chert [7]

Dolomitization of the hanging wall sequence is a distinctive feature of the rocks at Silvermines, with more than one generation of dolomite present in the breccias and mudbanks. Textures range from almost complete preservation of the original sedimentary features, through hazy recrystallisation, to almost total destruction of the original fabric leaving a saccharoidal and vuggy mosaic.

5. Discussion

Considerable controversy exists as to the timing of the important Mississippian carbonate-hosted Irish-type Zn + Pb +/- Ba +/- Ag deposits. The Silvermines stratiform ore zones including Ballynoe have been defined as an end member of this style in that in part they can be demonstrated to display textures indicative of on or near contemporaneous sea-floor deposition.

One of the strongest arguments in favour of this interpretation are the reports) of a hydrothermal vent field, including pyritic chimneys in the Ballynoe open-pit barite deposit [16,17,52] of delicately pyritized worm tubes hosted by massive pyrite and haematized filaments of apparent microbial origin [17].

These discoveries provide compelling evidence for the exhalative nature of parts of the Silvermines orebodies and imply that mineralization had begun in the Irish ore field by the late Hastarian (around 350 Ma). This is consistent with interpretations of local exhalative activity at Silvermines based on a range of geological and palaeontological features [14,17,35]. In addition, a number of isotopic dating methods focus around similar ages [49].

The earliest manifestation of the mineralizing processes is defined by the increasing influence of warm hydrothermal fluids accumulating in palaeotopographic lows influencing the size of crinoid ossicles and deposition of silica. Such palaeotopographic lows developing perpendicular to the principal fault trends indicating synsedimentary activity.

The onset of synsedimentary tectonism appears to be contemporaneous to early hydrothermal activity as indicated by faunal flourishment and mass extinction towards the top of the Muddy Reef Limestone [7]. The increase in crinoid size and density apparently representing optimum conditions of nutrient and heat supply for growth followed by metal or sulphide toxicity. The Green Shale demarks a significant tectonostratigraphic diastem defining the onset of dynamic basin development and synsedimentary faulting. Immediately post-dating the Green Shale, the haematite, barite, and siderite appear to have been deposited coevally, and due to the tight palaeotopographic and stratigraphic control along with other evidence are most likely to have been formed at or just below the sediment / water interface.

In the B-Zone and parts of the Upper G-Zone the barite / siderite is overlain by massive pyrite. This massive pyrite is strongly texturally zoned with coarse collomorph mounds developed close to the Silvermines Fault (in the case of the Upper G Zone) and the B Fault (in the case of the B Zone) immediately above either the haematite/barite or siderite or the Green Shale. Flanking the collomorph mounds is a fringe of coarse exfoliated colloform clasts which pass down slope into progressively finer grained laminated pyritic clastites and sulphidites. Above the massive pyrite, dolomite, and debris-flow limestone polymictic breccias contain angular clasts of pyrite and, locally, barite (Figures 16c, 24b and 24c).

Subsequent base-metal mineralization appears to post-date the barium-iron facies with fine grained galena and schallenblende type sphalerite infilling primary porosity (as in the colloform pyrite) and replacing argillaceous matrix in the polymictic breccias. Metal zoning shows lead and silver enriched close to the main faults and also becoming increasingly lead-rich up stratigraphy.

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Barrett [7] demonstrated that late crystalline barite (the "cap" barite) formed by up dip migration of fluids post main stage mineralization.

Some contrarian opinions have suggested that the hangingwall breccias are collapse or dissolution features formed by hydrothermal activity with the barite and sulphides being deposited at the base of a giant cavity system. There are issues with such an interpretation including fundamental issues such as there being no evidence of fracturing penetrating supra-Waulsortian Equivalent (or indeed sub-Waulsortian) units as seen in the classical MVT-type deposits in Kildare [56,57].

At Silvermines there is no doubt that the breccias are thicker overlying the stratiform upper ore zones (Upper G Zone and B-Zone). In these areas the breccias equivalent to the entire Waulsortian is thickened clearly contradicting a dissolution and collapse mechanism. The interpretation must surely be that that the breccias are dominantly debris-flows and this is supported by the presence of clasts of mineralization included within the breccias, graded beds, rip-up and flame structures and scouring. If they were formed by dissolution and collapse the sequence would, logically, have to be thinner over mineralization as at, for example, Lisheen and Galmoy [58]. In addition, there is no evidence of a "roof" to sustain the collapse nor is there any subsidence of the supra-Waulsortian units which exhibit a layer-cake stratigraphy above a generally evenly dipping sedimentary interface. Such differences render an interpretation of dissolution and collapse difficult at best.

An additional important observation is that the footwall rocks at Silvermines are generally evenly bedded and maintain a uniform pattern until the very uppermost beds immediately below the footwall to the upper orebodies. Hence as both the underlying and overlying sequences to the breccias have a well-developed tabular "layer-cake" disposition with little if any thickness variation and, as such demonstrate that the breccia sequence represents an anomalous time period in the sedimentary record.

6. Summary

Barrett [7], Andrew [2] and Mullane & Kinnaird [11] regarded the massive barite at Ballynoe (Silvermines) as being sedimentary in origin and all described bedding features, slumping/debris flows and rip-up clasts as all having a primary sedimentary origin. Barrett [7] convincingly demonstrated that the wallrock geochemistry at Ballynoe suggests that the dispersion of anomalous Ba values is strictly confined to the mineralized-horizon directly overlying the Muddy Reef Limestone and the knolls of Footwall Waulsortian knolls. The stratiform nature of the Ba anomaly is still evident in areas well away from the effects of the main mineralization. Iron and silicon were the only major elements which were associated with the initial emplacement of the barite.

A waning of the iron-rich phase heralded the bulk of the barite mineralization which initially was very siliceous. The microspherultic fabric of the barite suggests a rapid crystallisation. With the possible exception of minor (biogenic?) pyrite the barite was free of accessory mineralization possibly due to bottom water conditions being sufficiently oxic to support a marine bottom fauna (at least episodically during barite precipitation) would have been insufficiently reducing and sulphidic to induce efficient precipitation of metals. A gradual cessation of barite mineralization witnessed the introduction of sphalerite and galena muds which were the forerunners of the stratiform, sulphide cap to the orebody.

It is evident that the barite horizon has undergone considerable diagenetic modification since its original precipitation in the form of a cryptocrystalline mud and the stylolitisation of the barite horizon must have been initiated during the early compaction and lithification of the deposit. There is compelling evidence that the barite body must have lithified quickly as angular rip-up clasts of barite, exhibiting identical features to that in the main orebody, are seen in the immediate hangingwall breccias (see Figure 16c) [2,7–11,35,54] . Similarly, Graham [29] described evidence of upward projecting tongues of pyrite into the hangingwall breccias along the hangingwall contact of the 'Upper-G' zone massive pyrite body, which he attributed to the weight of the overlying debris flow sediments on the still plastic sulphides. Together this evidence strongly suggests that both the barite (siderite) and massive pyrite bodies were formed rapidly within the constraints of the

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palaeotopography and covered relatively quickly by flows of limestone and dolomitized limestone debris triggered by episodic movements on the Silvermines fault array.

Such features suggest strongly that the ore depositional environment was on or just below the contemporaneous seafloor at around 348 Ma. This date agrees with various isotopic dates of between 350.5-348.2Ma for the Green Shale [27], the $^{87}Sr/^{86}Sr$ ratio at between 350-349 Ma or 345-344 Ma and the $\delta^{34}S$ ‰ suggesting 354-345 Ma.

Thus, it is reasonable from the geological and isotopic evidence to conclude that the Ballynoe barite deposit formed by early local exhalation of ore-host facies (barite, siderite, pyrite) around 348Ma marginally predating base-metal mineralization which *mainly* occurred sub-seafloor by void-fill and locally by replacement of carbonates during early diagenesis during shallow burial, during slumping and *in situ* (soft sediment) brecciation. The main depositional mechanism was by the mixing of high temperature metal-bearing brines with low temperature bacteriogenically active H_2S-rich modified seawater.

There is abundant evidence of tectonism contemporaneous to mineralization and this is likely to have assisted in the rapid burial and early onset of diagenetic recrystallization and stylolitisation of the barite at shallow burial depths. This, associated with the overall sag coincident with the extent of the mineralization revealed from Connolly plots (Figures 10 and 11) clearly shows that contemporaneous tectonism was active at the time of the formation of the stratiform ore zones.

Recent U-Pb dating on a single unusual apatite crystal obtained from the hangingwall sequences spatially and geologically unrelated to the barite body at Ballynoe have returned ages of 331±5.6Ma [59] which corresponds to the age of basin inversion in the Limerick-Clare areas immediately to the west [26].

The age of mineralization is geologically and isotopically closely constrained and is contemporary with the Courceyan to late Chadian mineralization elsewhere in the Irish orefield,[1] predating the onset of basin collapse and late Chadian volcanism. Most workers support a model of formation at shallow depths typical of Irish-type deposits.

Ballynoe is part of the Silvermines district of the classic typomorph of Irish-type early syndiagenetic Zn-Pb-Ba-Ag ore deposits hosted in shallow water shelf limestones and bears similarities to deposits in the Selwyn Basin and Kechika Trough in Western Canada (Anvil, Tom, Jason, Howards' Pass) and to parts of the giant Red Dog group of deposits in Alaska. Elsewhere in Europe bedded barite is associated with sediment-hosted Pb-Zn deposits in Germany (Meggen and Rammelsberg), Belgium (Chaudfontaine). The Cretaceous agreed Zn-Pb (±Ag±Ba) deposits in the Malayer-Esfahan Metallogenic belt of Iran have been described as Irish-type and have many features in common with Ballynoe (Silvermines) [61–63].

ADDENDUM

Barite Elsewhere in the Irish Midlands Ore District and Surrounds (Figure 1)

In most of the Irish-type deposits in the Midlands barite is difficult to quantify. Economically extracted barite at Ballynoe and Tynagh suggests that it is higher in the west of the orefield and, taken with Garrycam, suggest that base of Waulsortian deposits may host higher levels of the mineral although no significant levels of barite have been discovered along the Rathdowney Trend (Lisheen, Galmoy and Rapla) [58]. Perhaps notably, there is no discrete barite lens at Navan, by far the largest Irish-type deposit in the Midlands, however, barite is a common gangue in the Navan orebody, so the amount of barite is clearly significant, but is as yet, unquantified [3].

At the Tynagh deposit (12.3Mt @ 4.5% Zn, 4.6%Pb, 0.4% Cu, 52 g/t Ag) barite is a significant component of Stage 3 of the mineralizing paragenesis occurring as veining and replacement of the host rocks and earlier ore textures by an assemblage dominated by tennantite, medium to coarsely crystalline galena, and coarse barite and in certain bands comprises the major component. Milchem operated a retreatment plant on the Zn-Pb-Ag tailings recovering between 50,000 to 100,000 tpa for a total of 460,000 tonnes of barite from approximately 8.6Mt of tailings suggesting a content of around 5.3% barite in the Tynagh orebody.

 doi:10.20944/preprints202402.1481.v1

The Keel Zn-Pb deposit occurs as disseminations and as stockwork sulphide mineralization in Upper Devonian and Lower Carboniferous clastics and carbonates faulted against Lower Palaeozoic metasediments. Diamond drilling and underground exploration have outlined indicated and inferred resources of 1.85Mt grading 7.71% Zn, 1.04% Pb, 0.12% Cd and 39.6g/t Ag. The Garrycam barite deposit is less than 1km distant and is genetically related to the Keel mineralization. The stratiform barite (with some sphalerite) is hosted in basal Waulsortian (Lower Carboniferous) micrite. The deposit contains 1.35Mt grading 2.67% Zn, 0.18% Pb and 36.14% $BaSO_4$. [60].

Vein type deposits in County Cork at Clonakilty, Dereenalomane and Derryginagh carry almost monomineralic white saccharoidal barite with traces of pyrite and specularite along fault zones up to 10m in width over vertical depths in excess of 150m.

The existence of barite at the Lady's Well barite mine near Clonakilty in County Cork was noted from the early 1800's with intermittent production around 1952 and again up to 1922 Milchem Ltd. reopened the mine in early 1979 following dewatering and a 12-hole drilling programme completed in 1978 indicated a recoverable reserve of 230,000t (to the -710 Level some 90m below the lowest contemporary extant mine level) with a target annual production of 50,000tpa. The deposit comprises an almost vertical E-W vein averaging 2m in thickness, but locally up to 5m thick. The barite is generally high grade (locally of chemical grade) and has been in production sporadically since 1855. Records show that approximately 5,000tpa had been produced from 1876 to 1901. More recently 36,000 tpa had been produced between 1979 and 1985 initially by Milchem and later by NYM limited to the -610 level.

The Derryginagh mine near Bantry, County Cork, was worked in the period 1864-1922 with mine workings extending over a strike length of 200m and to a depth of 90m. In the 1980s four holes drilled by Dresser Minerals International Inc. intersected the barite vein over an average true width of 2.4m at about 100m below surface and over a total strike length of 200m. Further drilling by Sunrise Resources in 2012 led to the publishing of a scoping study for 278,340 tonnes of minable barite grading 67% $BaSO_4$ with further downdip potential below 180m but nothing further ensued.

The Benbulben (Glencarbury) mine in County Sligo, Discovered in the latter part of the 19th century, a vertical vein of barite cuts the massive Lower Carboniferous limestones of Benbulben Mountain, Co. Sligo. Averaging 1.2m in thickness, the vein has been worked intermittently since 1875. Approximately 110,000t of barite was produced between 1942 and 1960. More recently, approximately 10,000tpa was produced between 1975 and 1979.

Acknowledgments: This paper is a review of the detailed observations and work of many earlier workers notably John Barrett and Eta Mullane whose detailed observations in the Ballynoe open pit during production operations are fundamental to our knowledge of the deposit and to them I am grateful. I had the pleasure to have worked at Silvermines with Stuart Taylor and Eamonn Grennan and although nearly 50 years ago now, I still recall their incisive comments and observations on the geology of these intriguing deposits.

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