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A NEW FOSSIL VENT BIOTA IN THE BALLYNOE BARITE DEPOSIT, SILVERMINES, IRELAND: EVIDENCE FOR INTRACRATONIC SEA-FLOOR HYDROTHERMAL ACTIVITY ABOUT 352 Ma

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Abstract

Considerable controversy exists as to the timing of the important Mississippian carbonate-hosted Irish-type Zn + Pb ± Ba ± Ag deposits. The Silvermines deposits have been defined as an end member of this style in that they have been interpreted to display textures indicative of sea-floor deposition. One of the strongest arguments in favor of this interpretation was the report of a hydrothermal vent field, including pyritic chimneys in the Ballynoe open-pit barite deposit. This paper adds to that body of evidence by describing a hydrothermal vent fauna from the same vent field, consisting of a delicately pyritized worm tube hosted by massive pyrite and hematized filaments of apparent microbial origin. The worm tube is remarkably similar to fossil worm tubes from modern and ancient volcanic-hosted massive sulfide deposits, and the filamentous microfossils have similarities to modern Fe-oxidizing bacteria. We have found no correlation between the worm tube and normal Mississippian fossils such as crinoids, whose replacement by pyrite in the immediately underlying Ballynoe footwall destroys original morphology. The sulfur isotope composition of the worm tube and host pyrite is essentially identical to that of the vent field pyrite and the main sulfide ore stage of Silvermines sulfides, all having a mean value about –20 per mil, indicating an open-system bacteriogenic sulfide source. These discoveries provide additional 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 Tournaisian (~352 Ma).

Introduction

Deep-sea hydrothermal vents are sites at midocean and arc-related spreading centers where hot, metal-bearing (including Fe, Cu, Zn) hydrothermal solutions that have been convected through newly formed basaltic crust are exhaled onto the sea floor. On exhalation, these fluids precipitate their metallic load to form large sulfide edifices and mounds (e.g., Herzig and Hannington, 1995). The chemical energy of these systems is utilized by complex animal communities whose primary production is based on chemoautotrophic bacteria (e.g., Grassle, 1986; Van Dover, 1995). Common constituents of these vent-associated communities are tube-forming annelid worms (vestimentiferans and alvinellids, especially). The vast bulk of vent phenomena (e.g., chimneys, edifices and associated fauna) are found at or near the interface between the exhaling solutions and the sea floor.

In contrast to modern ocean ridge and arc-related vent sites, central Ireland during the Mississippian, about 352 Ma, had a very different crustal setting dominated by intracratonic (non-oceanic), tectonically active, subsiding submarine basins (Boyce et al., 1983a; Andrew, 1986; Sevastopulo and Wyse Jackson, 2001). Carbonate sediments that formed in these basins are host to several base-metal deposits, which make Ireland currently the richest zinc province in the world in terms of tons of metal per square kilometer (Singer, 1995). Despite a wealth of published studies, controversy still exists as to whether any of the deposits exhibit features indicative of sea-floor deposition, yet this is critical to the understanding of the timing and origin of these important orebodies.

It is generally agreed that the bulk of the Irish-type deposits were precipitated subsea floor, as at Navan (Anderson et al., 1998), but for nearly 40 years the Silvermines ore deposits, in particular, have been argued to display textures indicative of sea-floor deposition. These deposits exemplify the Irish-type deposit because they also contain the clearest evidence of epigenesis, in the form of base-metal and barite veins crosscutting the Old Red Sandstone (the Shallee deposits, e.g., Taylor and Andrew, 1978) and massive stratiform replacement of the lower members of the Mississippian host lithologies (e.g., the Lower G zone; Taylor, 1984). Veins in the Old Red Sandstone were worked for many centuries before the discovery of the stratiform sulfide and sulfate horizons in the 1960s. The sedimentary exhalative view of the Silvermines deposits, which can explain both styles of mineralization, assisted the mining of the Mogul base-metal and Ballynoe barite deposits (the largest producers in the camp) by offering a conceptual basis that the mining geologists and engineers followed and refined (e.g., Taylor and Andrew, 1978; Taylor, 1984).

Larter et al. (1981) reported the occurrence of fossil hydrothermal vents and a highly pyritic vent field at the Ballynoe barite deposit in the Silvermines camp. These were among the first reported fossil vents in the world (Boyce et al., 1983b). Subsequently, Banks (1985) described the occurrence of both fossil vents and a vent biota at the Tynagh deposit. Despite this evidence, recent publications question the

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validity of these findings, and the existence of any exhalative features in this and other Irish deposits (Hitzman and Beatty, 1996; Johnston, 1999; Peace and Wallace, 2000). This encouraged us to initiate a new search for fossil vent biota in the putative vent field at Ballynoe, and in massive pyrite blocks exhibiting typical vent-type, colloform textures in and around the open pit. Here we report the discovery of a fossil vent biota consisting of a delicately pyritized worm tube and hematized bacterial filaments. The worm tube bears a remarkable resemblance to vent fossils from ancient volcanic-hosted sulfide deposits as indicated in the preliminary report of Boyce et al. (1999), and the filamentous microfossils, presented here for the first time, show a considerable similarity to Fe-oxidizing bacteria. Although there is certainly substantial, indeed classic, epigenetic (postlithification) ore at Silvermines (Taylor, 1984), the present findings add to the weight of evidence that there was also a component of syngenetic (synsedimentary) hydrothermal activity to the ore, and that hydrothermal fluids exhaled onto and near the sea floor at Silvermines during the Mississippian, about 352Ma.

Geological Setting

The two principal ore deposits in the Silvermines area, the Mogul base-metal deposit and the Ballynoe barite deposit, are described in detail by Taylor (1984) and Mullane and Kinnaird (1998). Both deposits occur at the same stratigraphic horizon and are contiguous with a thick (hundreds of meters) transgressive Mississippian (Tournaisian) carbonate sequence (Andrew, 1986). This overlies a thin, fluviatile Old Red Sandstone horizon (on the order of tens of meters or absent in central Ireland, with at least the top 20 m of Tournaisian age represented in this area Boyce, 1990), which in turn unconformably overlies a thick sequence (>4,000 m) of regionally metamorphosed and folded lower Paleozoic sandstones, mudrocks, and volcanic rocks. The immediate footwall of both the Mogul and Ballynoe deposits is known locally as the Muddy Limestone (regionally the upper Ballysteen Limestone), which in the top few meters is a silicified, crinoid-rich limestone. At Silvermines this unit may represent an off-bank facies of the regionally important Waulsortian Mudbank. Boyce (1990) argues for a topmost Tournaisian Tn3 stage (fig. 3.6b: Harland et al., 1989) assignment for this horizon. With reference to the published absolute time scales of Harland et al. (1989) and Ogg (1995), the top of the Tournaisian epoch is best defined at 352 Ma. Thus, we argue for an approximately 352 Ma age for top of Muddy Limestone. The ore deposits overlie the Muddy Limestone, with thicknesses of massive barite in Ballynoe reaching 31 m. More than 5 Mt of barite (sp gr 4.23) were mined from this orebody. At both the Mogul Zn + Pb + Ag ± Ba deposit and the Ballynoe deposit there is extensive evidence of synsedimentary faulting, affecting and controlling the ore horizons and the overlying Dolomite Breccia, indicating considerable tectonic activity accompanied ore deposition (e.g., Boyce et al., 1983a; Taylor, 1984; Mullane and Kinnaird, 1998; Lee and Wilkinson, 2002).

In the southeast corner of the Ballynoe open pit, on the exposed surface of the footwall (the footwall pavement; Fig. 1), Boyce et al. (1983b) noted the occurrence of a roughly triangular exposure approximately 120 × 100 × 80 m, which was extremely rich in pyrite. The area included a number of pyrite-dominated lenticular mounds, up to 2-m high and 3-m in diameter. Boyce et al. (1983b) interpreted the site as the remains of a fossil hydrothermal vent field. Much of the pyrite has a collomorphic texture, similar to that of pyrite-hosting vent fossils in volcanic-hosted massive sulfide (VHMS) deposits (Little et al., 1998). The pyrite is dominantly a pale green color, with a marked tendency to break down rapidly to hydrated iron sulfates through exposure. Barite in this area was among the first exposed during mining, but was not taken as ore because of the pyrite contamination. The immediately overlying barite horizon is rich in hematitic jasper (Mullane and Kinnaird, 1998). Specimens of the latter from the vent field were examined for this study (locations of the principal sample sites are marked on Fig. 1).

Associated with this field were the type II hydrothermal vents described by Boyce et al. (1983b): small tubular pyrite structures exhibiting radial textures, indicative of rapid precipitation. Earlier, Larter et al. (1981) had noted the first occurrence of vent phenomena from this pit (pyrite "chimneys"), which Boyce et al. (1983b) later described as type I structures. These were not found in situ, but instead came from the first waste dump, suggesting their extraction from the initial open cut, now the southeastern extremity of the present pit in the vicinity of the vent field on Figure 1 (Boyce, 1990).

The Worm Tube and Comparisons

A worm tube specimen (Fig. 2A) was found in a loose block on the footwall surface in the hydrothermal vent field (Fig. 1). The fossil is cylindrical, 21 mm long and 2.5 mm in diameter, and consists of a thin pyrite wall infilled with barite. The tube wall shows an external ornament of closely spaced concentric annulations with 0.06 to 0.1 mm spacing. Surrounding the tube are thick, concentric, collomorphic pyrite layers, which may represent earlier vent structures, or more likely later overgrowths on the tube (cf. Banks, 1985). We believe the Ballynoe tube is without doubt biogenic in origin as we cannot envisage an abiogenic process that could form a straight-sided tube with perfectly circular cross section and an external ornament of regular saw-tooth annulations.

The Ballynoe worm tube might be interpreted as merely a replaced Muddy Limestone fossil, and therefore not necessarily associated with active hydrothermal exhalation. However, we have been unable to find any published reports of a comparable Muddy Limestone or other Mississippian fossil. Superficially it resembles a crinoid stem, and because the immediate footwall Muddy Limestone is extremely rich in crinoids, some pyritized stems were examined for comparison. Examination of these shows clearly that crinoid pyritization in the footwall at Silvermines is destructive, progressively erasing the original morphology (Fig. 3). This style of preservation is different from that seen in the worm tube fossil.

Although the Ballynoe worm tube is unlike normal Mississippian limestone fossils, it does share many morphological characters with epifaunal fossil annelid worm tubes (vestimentiferans and polychaetes) found in Phanerozoic VHMS deposits (Little et al., 1998, 1999). At these sites the link between sea-floor exhalative mineralization and the vent-specific fauna is unequivocal. Like the Ballynoe worm, many

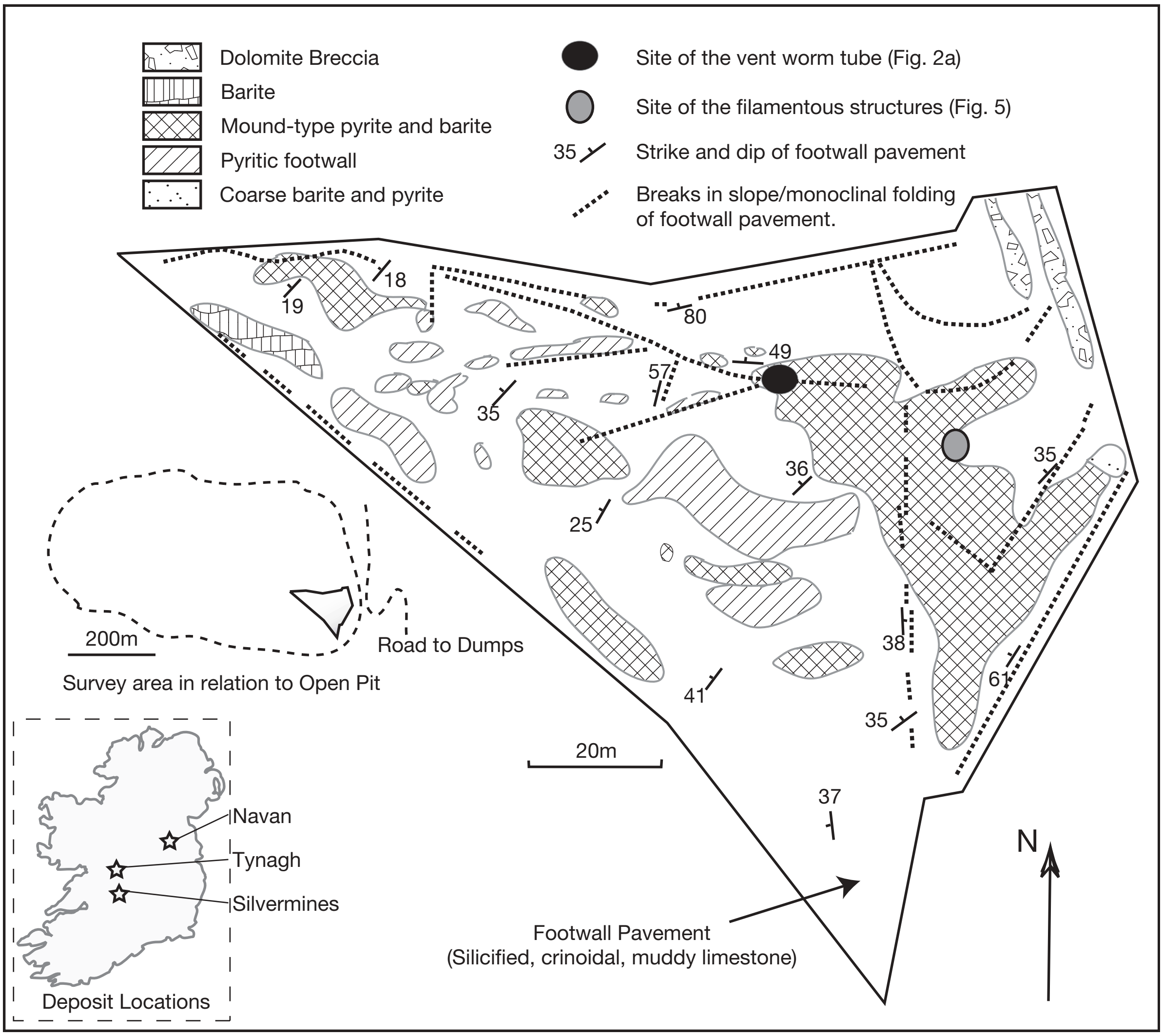

FIG. 1. Map of the surface geology of the Ballynoe vent field modified from Boyce et al. (1983b), showing the sites of the discoveries of the worm tube and filamentous microfossil samples. Insert maps indicate locations of the Irish-type deposits mentioned in the text, and the vent field in relation to the current open pit outline.

of the VHMS annelid worm tubes described by Little et al. (1998, 1999) are cylindrical and have pyrite tube walls with closely spaced concentric annulations (Fig. 2B).

The Ballynoe worm tube is also very like some of the fossils found in the coeval Tynagh base-metal deposit (Fig. 2C; Banks, 1985). These tubes are up to 0.8 mm in diameter, have annulated pyrite walls, and are infilled by barite. They are enclosed by concentric layers of collomorphic pyrite, which Banks (1985) suggested represented vent chimneys. Although the Tynagh worm tubes are smaller than the example described here, their close resemblance leads us to suggest that they are related and corroborates Banks' (1985) identification of the Tynagh tubes as biogenic in origin.

Unidentified worm tube fossils from early Carboniferous (340 Ma) bryozoan-microbial carbonate mounds in the Big Cove Formation, Newfoundland, are also associated with strata-bound sulfide (Zn-Pb-Fe) and sulfate (Ba-Sr) mineralization (Von Bitter et al. 1990, 1992; Dix and Edwards, 1996). However, the Big Cove tube worms are formed of carbonate, not sulfide, and are substantially larger than the Silvermines fossil, being 15 to 30 mm in diameter and up to 200 mm in length. Furthermore, they do not have any external ornament. In addition to the worm tube fossils, the Big Cove carbonate mounds contain a diverse fauna of bryozoa, brachiopods, conularids, serpulids, and crustaceans, but lack corals and crinoids. Whereas Von Bitter et al. (1990, 1992) suggested that the carbonate mound fauna was intimately associated with the mineralization and thus represented a hydrothermal vent community, Dix and Edwards (1996) have proposed that most of the mineralization was epigenetic and occurred some time after carbonate mound formation.

The Ballynoe fossil cuts through the layering in the surrounding massive pyrite at right angles. The most likely explanation for this orientation is that the tube was formed at or near the original sediment-water interface, sticking up into the water column. It is unlikely to represent a planktonic organism falling on to the sea floor as the resulting tube fossil would likely be found parallel to surrounding pyrite layers.

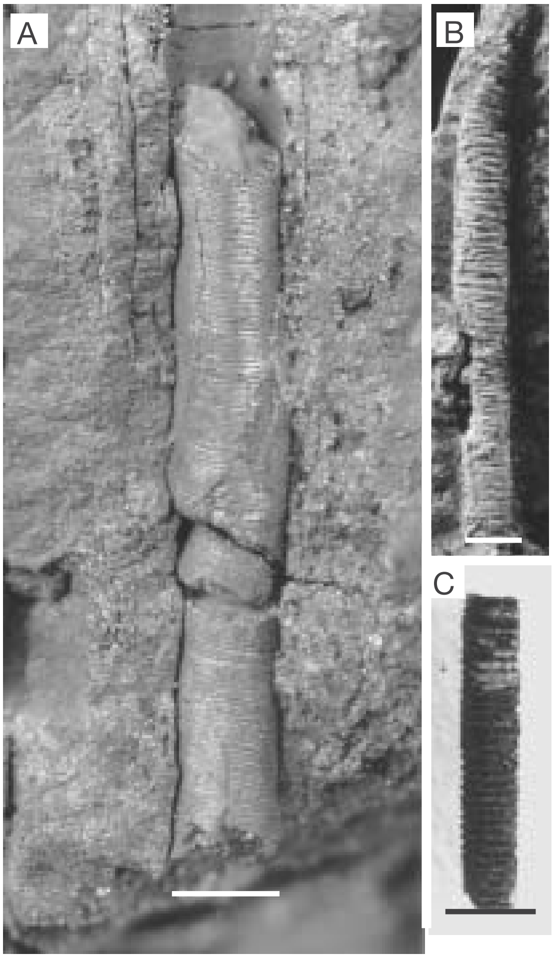

FIG. 2. Fossil hydrothermal worm tubes from Ballynoe, Yaman Kasy, and Tynagh. A. Ballynoe tube. B. Tube of ?polychaete *Eoalvinelloides annulatus* Little et al. (1999); Silurian age Yaman Kasy massive sulfide deposit, Russia. C. Tynagh tube. Scale bars for A and B = 2 mm. Scale bar for C = 1 mm.

Based on the above observations we conclude that the Ballynoe worm tube lived at the same time as the pyrite mounds formed. Following from this, we think it likely the worm tube was intimately associated with hydrothermal venting and, like modern vent annelids (e.g., vestimentiferans, alvinellids, and other polychaetes), may have been dependent on the vent fluid as an energy source, possibly via bacterial chemoautotrophic symbionts (Cavanaugh et al., 1981). Little significance can be attached to the solitary nature of the Silvermines worm tube because the block of sulfide hosting the fossil was not found in situ, and notwithstanding the vagaries of preservation, modern vent vestimentiferans are not always found in clusters (e.g., Southward et al., 2002). The tube wall of the Silvermines fossil probably was originally an organic structure, which would rapidly have been replaced by pyrite, probably very shortly post mortem. It has been well documented that scavenging and decay of unoccupied worm tubes occurs within a few years at modern hydrothermal vent sites (Tunnicliffe and Fontaine, 1987), unless they are pyritized or silicified (e.g., Juniper and Sarrazin, 1995; Maginn et al., 2002).

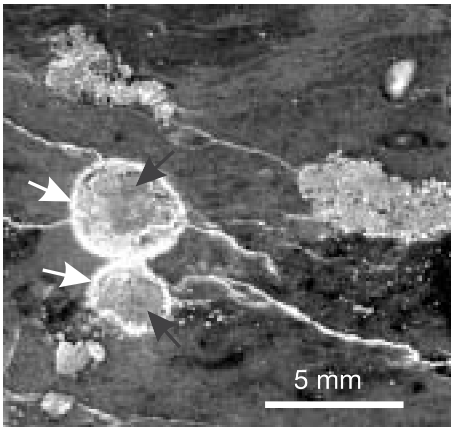

FIG. 3. Polished block of immediate footwall Muddy Limestone with crinoid ossicles and pyrite mineralization; reflected light. White arrows point to two ossicles in transverse section whose central areas have been replacement by coarse pyrite crystals (black arrows). Note that other pyrite mineralization in the block (top left and center right) is not associated with crinoid ossicles.

Other blocks of colloform pyrite from the Ballynoe open pit contain cylindrical to ovoid structures cutting through laminated pyrite (Fig. 4), both of which could be interpreted as biogenic in origin (cf. McGoldrick, 2000). These tubular structures are either hollow or contain weathered cylindrical pyrite cores lacking ornamentation. They are similar to the structures reported in Boyce (1990), which had cleiophane (white sphalerite) cores. Russell et al. (1989), in their discussions of the emergence of life from

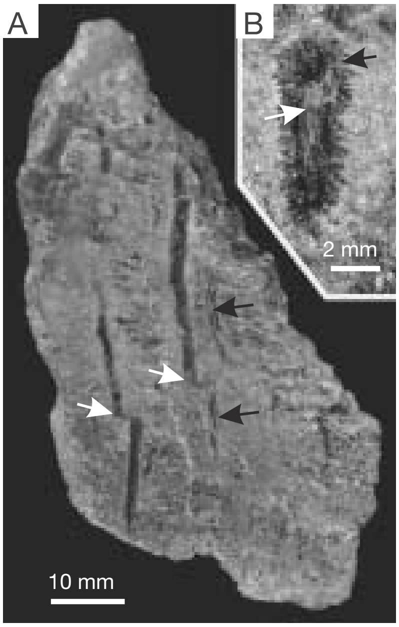

FIG. 4. Unidentified tubular structures in laminated pyrite. A. Block with several tubular structures perpendicular to the pyrite layering. Two of the tubes have significant offsets (white arrows); two have cylindrical pyrite cores (black arrows). B. Detail of another tubular structure with a cylindrical pyrite core (white arrow) and an irregular wall (black arrow). The latter is due to weathering of bladed radial pyrite crystals.

ancient hydrothermal sites, argued that these structures were fossil hydrothermal chimneys hosting inner casts of a vent-type worm. Alternatively, it is possible that these structures are fossils of the worms themselves, or volatile escape structures. Without obvious ornament such an interpretation remains contentious.

Filamentous Microfossils in Jasper

The jasper-rich barite horizon immediately overlying the vent field comprises dendritic hematite, quartz, and later barite veins. It contains domains of abundant filaments formed of tubular aggregates of submicron-scale hematite crystals infilled by quartz, and also cemented by clear quartz (Fig. 5). The filaments have branching and twisted morphologies, and are 2 to 5 μm in diameter and several hundreds of microns in length. These structures are very like the filaments illustrated from iron-silica beds associated with ancient (Juniper and Fouquet, 1988; Duhig et al., 1992; Rasmussen, 2000) and modern (Alt, 1988; Zierenberg and Schiffman, 1990; Emerson and Moyer, 2002) sea-floor hydrothermal vents which have been interpreted as fossilized bacteria, possibly sulfide- and iron-oxidizing chemoautotrophs. The twisted Ballynoe filaments are also very similar to the stalks of the iron-oxidizing bacterium *Gallionella feruginea* (e.g., Hanert, 1973), although given the inherent difficulties in identifying bacteria by morphology alone, we cannot formally ascribe the Ballynoe structures as *Gallionella*. It could be argued that the Ballynoe filaments have an abiogenic origin like the abiogenic twisted carbonate filaments grown by Garcia-Ruiz (1988). However, Ballynoe filaments have a much more regular shape than the crystals grown by Garcia-Ruiz (1988) and the chemical conditions are also considered to have been radically different. Therefore, the presence of what we interpret to be fossil microbes in the jasper leads us to suggest that this deposit formed on the sea floor, supporting the evidence from the fossil worm tube. It should also be noted that oxygen isotope analyses of hematite from this horizon are consistent with the oxygen involved in hematite transformation being derived partially from dissolved oxygen in seawater (Cruise et al., 1999), again linking this horizon with processes requiring proximity to the sea floor.

Sulfur Isotope Provenance

The sulfur isotope signature (δ^{34}S) from the pyrite of the vent field and the bulk of the Mogul base-metal stratiform ore, is dominated by a signature about –20 per mil (Fig. 6) indicative of an open- system bacteriogenic sulfide source, typical of the Irish-type deposits (e.g., Fallick et al, 2001). Barite throughout the deposit—and the vent site—has a δ^{34}S value of about 18 per mil, consistent with direct derivation from Mississippian seawater sulfate (Boyce et al., 1983b). This is further evidence that the Silvermines deposits were formed contemporaneously with the carbonate host rocks, as was postulated originally by Coomer and Robinson (1976). A new isotopic analysis on pyrite containing the worm tube fossil gave a δ^{34}S of –23.2 per mil; whereas pyrite from a small section of worm tube gave a value of –18.4 per mil. Both fall well within the range of the dominant bacteriogenic signature from the stratiform deposits (Fig. 6A and D). Pyrite from throughout the barite open pit but outside the vent site, although having an average value about –19 per mil, has a very broad isotopic range (-40.4 to +6 per mil), with a large standard deviation ($1\sigma = \pm13.8$ per mil: Fig. 6B). This large range is in stark contrast to the vent-type pyrite, which has a relatively restricted range ($1\sigma = \pm1.4$ per mil: Fig. 6C), It is notable also that the worm tube-related pyrite, which has textural similarities with vent-type pyrite, also has δ^{34}S falling within this restricted range. We believe this provides further evidence locating the provenance of the worm tube within the vent field.

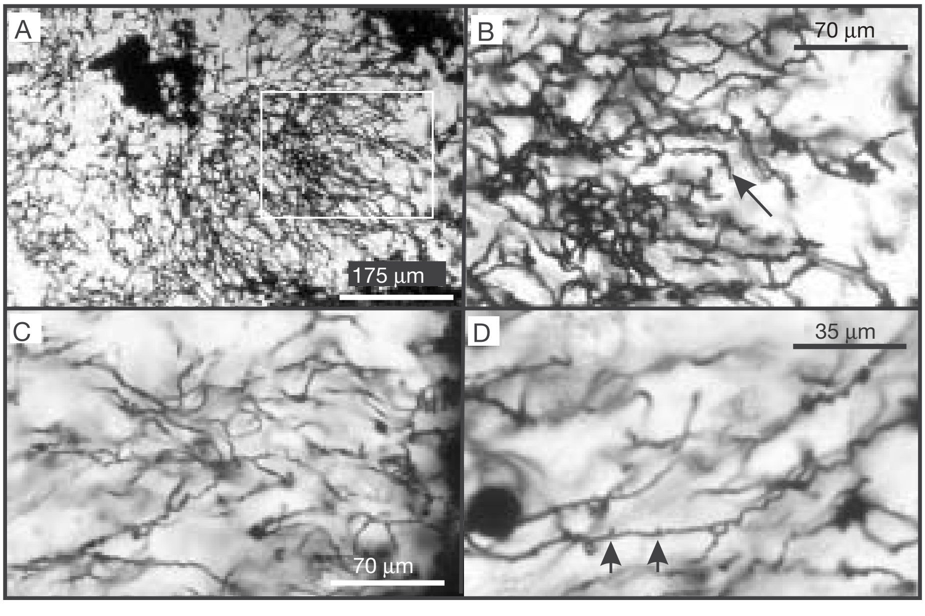

FIG. 5. Transmitted light photomicrographs of filamentous hematite microfossils in Ballynoe jasper. A. Domain of filaments in quartz matrix showing directed growth. B. Detail of white box area in A; black arrow points to twisted filament. C. Looser packed branching filaments. D. Filaments showing coiling and budding (black arrows).

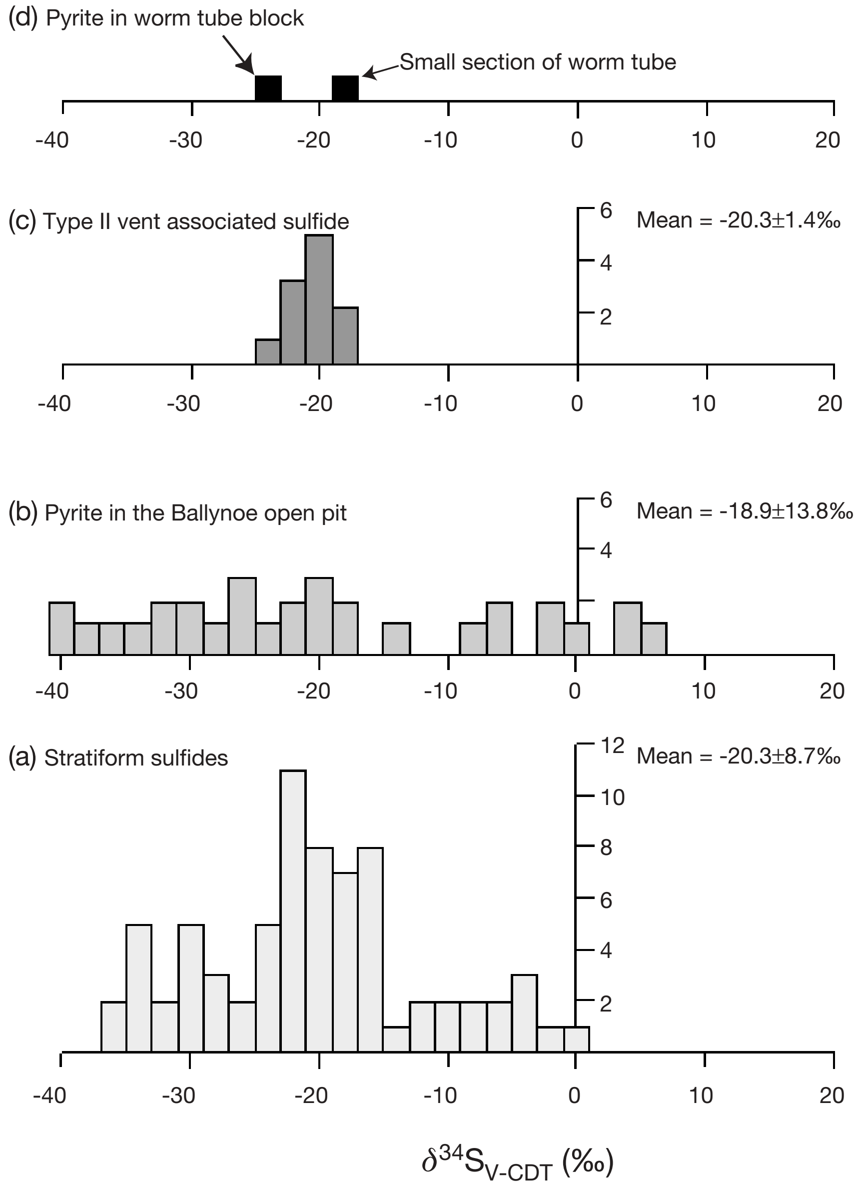

FIG. 6. Histograms of sulfide sulfur isotope data from the Silvermines deposits. (A) All sulfide data from the stratiform Upper G and B zones from the Mogul Zn + Pb + Ag deposit, and pyrite data from the Ballynoe barite horizon from Boyce, 1990. (B) Pyrite data from the Muddy Limestone, Barite Ore horizon, hanging-wall Dolomite Breccia and Chert horizons in the Ballynoe open pit from Boyce (1990). (C) Type II vent data, extracted from Boyce et al. (1983b). (D) Data from the worm tube and surrounding block. All data were carried out following the procedure of Robinson and Kusakabe (1975), with an error or reproducibility about ±0.2 per mil based on repeat analyses of laboratory and international standards. All data are presented in standard notation as per mil (‰) deviations from the Vienna-Canyon Diablo Troilite (V-CDT) standard. A detailed table of data is available from A.J. Boyce upon request.

Conclusions

Fossil evidence of the presence of a vent-related worm tube in the Ballynoe barite deposit provides strong evidence that sea-floor exhalative hydrothermal activity did occur at Silvermines. This implies that at least some of the mineralization occurred contemporaneously with deposition of the carbonate host rocks during late Tournaisian, about 352 Ma, as suggested by Boyce et al. (1983a, 1983b), Taylor (1984), Andrew (1986) and Mullane and Kinnaird (1998). In addition, microfossils with a strong similarity to Fe-oxidizing bacteria provide evidence of microbial activity, a feature typical of modern and ancient vent fields. On the broader scale, the observation of Chadian-Arundian aged mineralization at Navan (~345 Ma; Anderson et al., 1998; Blakeman et al., 2002) indicates that hydrothermal activity in the Irish ore field must have occurred over an extended period (>7 m.y.).

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