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Correspondence

Central Irish sulphur isotope data in the light of the rift geological-metallogenic model

Comment

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Deeny's recent interpretation (Deeny 1985) of sulphur isotopes in the Dinantian ore deposits of Ireland casts serious doubts on existing interpretations. Concentrating on the Silvermines deposits, I will defend the recent isotopic interpretations of Coomer & Robinson (1976) and Boyce et al. (1983a). Essentially, a similar defence can also be offered for the interpretation of the Tynagh sulphur isotope data, as given by Boast et al. (1981).

The thrust of Deeny's model is that when catastrophic sulphurous injections (emanating from his proposed E-W trending para-axial structures) coincide with metal-bearing fluid exhalations (from NW trending transverse structures), sulphur isotope fractionation took place 'by definition, in the immediate vicinity of the fumaroles' (Deeny 1985, p. 219). By fumaroles, Deeny must mean sites of seafloor venting, because of his reference to Boyce et al. (1983a). He argues that the sulphur isotope data are the result of fractionations between sulphur species in the exhaling fluid, the extent of fractionation being dictated by changes in fO_2, pH and temperature, under conditions of isotopic and chemical equilibrium; this is implicit in his references to the work of Ohmoto (1972) and Greig et al. (1971). Indeed, he stresses that one of the main purposes of his paper was to 'redraw attention to' the hypothesis of Greig et al. (1971).

Two serious criticisms must be levelled at this re-interpretation. Firstly, temperatures would not have been high enough for the attainment of isotopic equilibrium (I would suggest $\geqslant 175°$ C), at or near the sites of exhalation which created the Upper 'G' and 'B' orebodies (Samson & Russell 1984): equilibrium could only have been achieved if the solutions did not exhale. To the model of Greig et al. (1971), this factor presents little problem, since they do not suggest that the fluids exhaled onto the seafloor, merely that they passed up the main E-W fault, and percolated away from the fault to precipitate the ores in the appropriate host strata. Their thesis, therefore, demanded an epigenetic origin for the deposits. Myriad sedimentary features in and around the ores have shown the purely epigenetic model to be untenable (e.g. Taylor & Andrew 1978; Larter et al. 1981; Boyce et al. 1983b and Taylor 1984). There is no doubt that Deeny concurs with evidence for the syngenesis of these particular ores. Thus, the submarine exhalation of mineralized solutions at Silvermines makes it highly unlikely that isotopic equilibrium would have been attained during the precipitation of the great bulk of syngenetic ore (which represents $>70\%$ of the total ore reserves; Taylor 1984), because the temperature would have been too low, and the precipitation too rapid.

Furthermore disequilibrium is reflected, for example, in the erratic and unrealistic range of temperatures (assuming isotopic equilibrium) obtained from both the syngenetic (Upper 'G', 'B' and Ballynoe) and epigenetic (Lower 'G', Shallee, Gortnadyne and 'K') deposits. Temperatures range from less than 25° C to greater than 500° C. Disequilibrium is also reflected in the common occurrence of pyrite being isotopically lighter than apparently coexisting sphalerite and galena; and it is reinforced by a lack of any petrographic evidence for equilibrium.

Secondly, all fifty published and unpublished sulphate analyses from Silvermines group tightly around +18% (my results are $\times = +17.7$, $1\sigma = 1.78$, $n = 23$), isotopically indistinguishable from proposed Lower Carboniferous seawater sulphate (Claypool et al. 1980). Since the sulphates analysed come from syngenetic *and* epigenetic zones, these results point to the paucity of sulphate in the 'primary' mineralizing fluids. Under such circumstances, it is geochemically unlikely that the large spread in $\delta^{34}S_{sulphide}$ (+10.60‰ to −42.50‰) could be achieved by equilibrium fractionation in the manner Deeny suggests. In sulphate deficient systems the extent of equilibrium fractionation is considerably restricted, since by far the largest isotope effects are achieved by redox reactions involving sulphide *and* sulphate species. To illustrate this qualitatively consider, the following equation:

$$\delta^{34}S_{sulphide} \simeq \delta^{34}S_{fluid} - \Delta SO_4 \cdot (R/1 + R)$$

where ΔSO_4 is ($\delta^{34}S_{sulphate} - \delta^{34}S_{sulphide}$), and R is the mole ratio of $\sum SO_4/\sum$Sulphide (after Ohmoto & Rye 1979). Thus, when the sulphate content of the fluid is low the $\Delta SO_4 \cdot (R/1 + R)$ term is small, and consequently the $\delta^{34}S_{sulphide}$ is close to the total sulphur isotopic composition of the fluid (i.e. to $\delta^{34}S_{fluid}$, which at Silvermines is estimated at +3‰, Boyce et al. 1983a). Deeny's contention that the spread in $\delta^{34}S_{sulphide}$ could have been achieved by equilibrium fractionation, even if all sulphate were derived from seawater, is therefore refuted.

Deeny also offers the alternative that even if the $\delta^{34}S_{sulphate}$ were controlled by equilibrium fractionation, and not by direct precipitation from seawater sulphate, there would be no anomaly in his model. This claim is injustifiable since (1) all sulphate is isotopically indistinguishable from seawater sulphate and (2) all sulphate is in isotopic disequilibrium with co-existing sulphide.

Although both Coomer & Robinson (1976) and Boyce et al. (1983a) demand that bacteriogenic sulphur is the overwhelmingly dominant source of sulphide in the syngenetic zones at Silvermines, both also acknowledge the presence of a 'deep-seated' or hydrothermal sulphide in the deeper, epigenetic feeder zones. It is probable that in these latter zones some equilibrium fractionation did take place, and indeed, it is in these zones that the most realistic isotopically derived temperatures occur. It is evident, however, that this hydrothermal sulphide source did not provide sufficient sulphur for mineral precipitation in the syngenetic zones, and that it was only the presence of bacteriogenic sulphide which facilitated such deposition. Indeed, Russell (personal communication 1985) has pointed out, most pertinently, that if a forming Irish-type ore deposit did not have access to such a bacteriogenic sulphide reservoir, then that deposit will be of insufficient size to be economic at today's metal prices.

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Reply

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Boyce's insistence on the improbability of occurrence of the significant seafloor isotopic fractionation which which *he* assumes my model requires and his omission of the words '(lateral or vertical)' in his quotation from my note (Deeny 1985a, p. 219, 2nd para., line 19) suggests that in his 'refutation' of my hypothesis he may be attempting to apply current exhalative centre knowledge to fossilised phenomena (i.e. Irish ore deposits) which are only partly analogous. In my model's context (Deeny 1985a, b) the Irish ore sites, like their present day oceanic partial analogues, are grouped in a locality (central Ireland) characterised by plate edge tectonic activity (rifting is plate-edge or potential plate-edge activity). Observation of events at certain currently active exhalative centres *during major fault activity* might provide more pertinent facts on which to base an assessment of my model. Although of necessity (!) indirect, the available evidence (Gold & Soter 1985) is supportive of my thesis concerning gas injections during rifting (i.e. a rather major variety of earthquake activity).

My model suggests that a presumably sulphur-poor hydrothermal fluid (possibly metal-enriched modified seawater) which had previously (i.e. prior to rift activity) been 'busily convecting' in transverse structures (modern exhalative sites may be a manifestation of such a process) was suddenly catastrophically enriched in sulphur *throughout the plumbing system*, i.e. from seafloor vents to unknown depths in the sediment pile. A significantly greater proportion of the fluid's contained metals would suddenly precipitate, both within the plumbing system and at seafloor vents. In such circumstances and depending on the variety and nature of the physico-chemical mechanical parameters intrinsic to that particular event, significant equilibrium isotopic fractionation might occur at very shallow depths in the sediment pile and indeed, both at and within the exhaling sulphide emission at the seafloor. On cooling such isotopic compositions would be 'frozen into' the resultant sulphide-seawater-hydrothermal fluid mix, the sulphides *subsequently* depositing (depending on local submarine conditions) both proximal and at variable distances distal to the vents (sulphide deposition would, of course, be occurring within the feeder system also). Thus Boyce's refutation applies to a metallogenic mechanism not proposed by myself. I would argue strongly that central Irish sulphur isotope data (referenced in my original note – Deeny 1958a) are not inconsistent with the mechanism described above.

Boyce's reasoning concerning the origin of the syngenetic sulphate at Silverminss may likewise be coloured by preconceived ideas he has concerning the relative properties of the fluid*s* which precipitated the sulphides and sulphate. The dual nature of the fluids proposed in my model (i.e., separate sulphur-rich and sulphur-poor fluids) and the catastrophic nature of my proposed mixing mechanism – these factors alone suggest that caution should be exercised in assuming, as Boyce does, that the syngenetic sulphides and sulphate were a manifestation of one hydrotermal fluid.

In this respect the tectonic parameters described in my model (Deeny 1985a, b) are of some importance. Fig. 2 in Boyce et al.'s (1983) work illustrates this point. In this diagram NW-trending structures (transverse structures in my interpretation) are seen to intersect both the Upper G and B orebodies at Silvermines. Such structures are the loci of the metal-enriched, sulphur-poor convective cells of my model. No such structures intersect the spatially discrete baryte orebody. Thus in terms of my model's tectono-hydrotermal parameters, there is room for substantial compositional, precipitational and depositional variation between the fluid(s) which gave rise to the syngenetic sulphide bodies and that (those) which gave rise to the syngenetic barite deposit. In such a view Boyce's reasoning concerning the dissimilatiry in isotopic composition between the sulphur in the syngenetic baryte and syngenetic sulphide orebodies is possibly overly simplistic.

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