

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

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Received 7 June 1984; accepted in revised form 1 April 1985

Abstract

Deeny, D.E. 1985 Central Irish sulphur isotope data in the light of the rift geological-metallogenic model – *Geol. Mijnbouw* 64: 217-220

The current state of central Irish sedimentary-exhalative metallogenic theory is summarily reviewed. There is disagreement concerning the significance of primary sulphur in the genesis of the Tynagh/Silvermines ore deposits, the most popular view being that seawater sulphate, via biogenic reduction processes provided the bulk of the sulphur. It is shown that the extreme physico-chemical environmental conditions envisaged in a model which associates sulphide genesis with rifting may provide a framework wherein inorganic fractionation processes in primary sulphurous fluids may have contributed to a greater extent than currently recognised in producing the measured isotope distribution patterns at Tynagh and Silvermines. It is also noted that if catastrophic sulphide genesis on the scale of the Irish model were an historically recurring global event it might assist towards an explanation of the known isotopic history of the whole world ocean.

Introduction

Of necessity, interpretation of central Irish sulphur isotopic data is critically dependent upon the geological/metallogenic model against which the data are viewed. Following a synoptic review of current thinking on such matters, this note intends to show that the available data for the Tynagh (Boast et al. 1981) and Silvermines (Greig et al. 1971; Coomer & Robinson 1976; Boyce et al. 1983a) ore deposits are in keeping with general expectation of a geological system which involves catastrophic sulphurous fluid injections during rifting as part of its operating mechanism (Deeny 1981a,b, 1982a, 1984).

A consensus is currently emerging concerning the structural background and general geological environment in which central Irish stratiform sulphide deposits were formed. The sulphides were deposited in the vicinity (both lateral and vertical) of exhalative fumaroles (Boyce et al. 1983a) during and immediately following a rifting (Deeny 1982a; Gardiner & McCarthy 1981) or rapid basin subsidence event (Boyce et al. 1983b) which occurred in the central Irish region towards the end of the Courceyan. There is agreement in principle that some or all of these sulphide-exhaling fumaroles were located at fracture intersections, where NE-trending syndepositionally active faults were intersected by basin crosscutting structures. The former

are faults of Caledonoid trend which were re-activated during the Irish Lower Carboniferous (Gardiner & McCarthy 1981; Deeny 1981a,b; Russell & Haszeldine 1984). They have been termed para-axial structures (i.e. parallel to the basin axis – Deeny 1981a,b) and controlled rapid subsidence of the central Irish basin (the Dingle-Shannon basin of Gardiner and McCarthy, 1981) at the end of the Courceyan (Deeny 1981a, 1982a).

There is uncertainty concerning the nature, significance and even the existence of the postulated basin-crosscutting structures. Broadly speaking, two schools of thought exist. One school describes them as 'cryptic N-S geofractures' (Russell & Haszeldine 1984, p.98) and tentatively relates them to E-W directed stresses presumed to have been an early progenitor of the opening of the N. Atlantic which occurred after the intervening (Hercynian) orogeny.

Russell (1978) has suggested that metal-scavenging was effected in the underlying sedimentary pile by downward-excavating hydrothermal cells probably located in fractures of unspecified type/orientation. Sulphides were precipitated at and beneath the contemporaneous seabed, in the former case from hydrothermal fumaroles located at fracture intersections, the sulphur being provided by the presumed local activity of significant concentrations of anaerobic bacteria (Boyce et al. 1983a). A primary sulphur source is acknowledged by adherents of this school for some of the sub-contemporaneous-seabed mineralisation at both Tynagh and Silvermines (Coomer & Robinson 1976, Boast et al. 1981, Boyce et al. 1983a).

Another school argues that a regionally distributed system of NW-oriented fractures exists in Ireland, these fractures possessing a strong mineral association (Horne 1975, Bruck & O'Connor 1980, Deeny 1981a,b, 1982b, 1984) and being both inductively and deductively related to the transverse structures of the Red Sea (Bignell 1975). Deeny (1981a,b, 1982b, 1983, 1984) has suggested that Irish transverse, northwest-trending structures may 'house' Russell's (1978) metal-scavenging convective cells and that these are regionally intersected and tapped by para-axial structures. Deeny (1984) cites the central Irish Waulsortian mudbank

complex (Lees 1961, 1964) as being the contemporaneous seafloor facies manifestation of this exhalative structural network, his model being founded on the hitherto unsubstantiated premise that catastrophic sulphurous fluid injections occurred along para-axial structures during phases of rift activity. According to this model central Irish stratiform sulphide deposits were generated during such rifting phases at sites where sulphur-producing para-axial structures intersected hydrothermal convective cells in their transverse structural 'vessels'.

Sulphur isotope data

It is obvious that the nature of the sulphur source for the sulphides in central Irish ore deposits is of crucial importance in the matter of genetic modelling. Sulphur isotopic data for the Tynagh (Boast et al. 1981) and Silvermines (Coomer & Robinson 1976, Boyce et al. 1983a,b) ore deposits are of some importance in this respect. Because of the nature of the sulphur isotopic fractionation process such data are very open to interpretation. For sulphides generated in any system the distribution of measured isotope ratios is tightly related to the physico-chemical conditions under which fractionation occurred (Ohmoto 1972).

Broadly speaking, the Tynagh and Silvermines data are similar. Sulphides at both deposits display wide-ranging isotope ratios, the bulk of the values falling in the 0- -30‰ (approx.) range (Coomer and Robinson 1976, Boast et al. 1981). At Silvermines much of the obvious feeder-conduit-fill mineralisation displays isotope ratios reasonably tightly centred on the 0‰ value.

Although there is opinion and evidence to the contrary, on both the global stratigraphic (catastrophic rises in seawater isotope ratios – Holser 1977) and local geological levels (proposed catastrophic sulphurous fluid injections related to central Irish rifting – Deeny 1981a,b, 1983, 1984), recent sulphur isotope interpretations have opted for an assumption of reasonably stable physico-chemical environmental conditions for isotopic fractionation during the genesis of the Silvermines/Tynagh ore

deposits. Under such stable conditions the measured data can only be explained in terms of biogenic fractionation at or near the contemporaneous seabed (Boyce et al. 1983a,b, Coomer & Robinson 1976, Boast et al. 1981). As a result these interpretations have been forced to postulate the existence of substantial concentrations of anaerobic bacteria (substantial in view of the tonnages of sulphides generated) in a marine environment which appears to have had a relatively high energy level and to have been well oxygenated (Lees 1961, 1964, Gardiner & McCarthy 1981, Boyce et al. 1983b, Deeny 1982b, 1984). The existence in such an environment of warm brine pools (in themselves representing a rather singular physico-chemical circumstance) as indicated by fluid inclusion studies (Boyce et al. 1983a,b) has been invoked for provision of a possible breeding ground for the (presumably significant) requisite concentrations of anaerobic bacteria. The haloclines of such brine pools are suggested as ecological niches for such organisms (Boyce et al. 1983a).

No interpretation of the isotopic data in the imagined physico-chemical framework of the sulphurous fluid injection hypothesis (Deeny 1981a, 1983, 1984) has yet appeared. In this model we are dealing with proposed rift-related catastrophic injections of hot, primary sulphurous fluids. Depending on the magnitude of the catastrophe (a significant, regionally synchronous event according to the model) and proximity to fluid-injecting para-axial fissures, hiatuses in bottom-water conditions might be expected as follows; i) a sudden decrease in bottom-water oxygen fugacity (O_2 dissolved in seawater being scavenged in the formation of SO_2 and H_2O), ii) a sudden drop in bottom-water pH due to the formation of sulphurous acid and iii) sudden variations in bottom-water temperatures. Since the isotopic fractionation process in question occurred, by definition, in the immediate (lateral or vertical) vicinity of fumaroles *at* para-axial – transverse structure intersections, isotopic fractionation would have taken place where physico-chemical changes were most extensive and extreme. The data must therefore be viewed in terms of possible inorganic fractionation at a variety of temperatures (related to the tem-

perature of the exhalant vs. local cooling in seawater) under probably highly variable fO_2 conditions and at variable low pH's. The total sulphur content of the system would have been relatively speaking very high.

Sulphides generated under such conditions would display wide ranging, light sulphur isotope ratios (Ohmoto 1972), the occurrence of very light values being a probability and related to the local combination of temperature, fO_2 and pH. In this view there is no anomaly in the uniformly positive isotope ratios displayed by barite and both the Tynagh and Silvermines deposits. A seawater sulphur source via non-organic chemical reaction of exhaled barium with seawater sulphate (Coomer & Robinson 1976) is not excluded by the model nor is equilibrium fractionation at higher fO_2 and pH's in the manner suggested by Greig et al. (1971). As regards the several extremely low isotope ratios recorded for sulphides at Silvermines (Boyce et al. 1983a) it should be borne in mind that Ohmoto (1972) has shown that isotope ratios as low as -40% can result by inorganic fractionation at pH 4-6, $\log fO_2 -44$ and $T 150^\circ C$ where the mean isotopic composition of sulphur in the hydrothermal solution is 0% .

It is the purpose of this note merely to redraw attention to the possibilities for inorganic fractionation as outlined by Greig et al. (1971) and to note that the rift model (Deeny 1981a) may provide a framework for extreme physico-chemical environmental conditions and so allow the possibility of significant inorganic isotopic fractionations. Biogenic fractionation mechanisms may not have been as important in central Irish metallogeny as the current literature would suggest.

An added attraction of the catastrophic injection hypothesis is that it may provide an holistic (in view of its complex interrelationships within the geological system represented by the model), rational and intuitively satisfying explanation for the phenomenon of globally synchronous catastrophic rises in ocean water sulphur isotope ratios known to have occurred at various times in Phanerozoic history (Holser 1977). The extreme inorganic fractionation associated with each rifting event would have resulted in the light sulphur isotopes

being 'suddenly' concentrated in sulphides (most of which would have been dispersed and/or eventually oxidised – Deeny 1982b), the heavier isotopes being preferentially incorporated in sulphate and sulphur dioxide (at low fO_2 and pH the heavier isotope would go to the aqueous H_2S and HS^-). For a time at least, seawater sulphur isotope ratios would have risen catastrophically. If the hypothesis is correct then globally synchronous rifting phases are a recurring feature of geological history.

Acknowledgments

The manuscript of this note was submitted to a number of interested parties for comments. Dr. A.M. Boast (BP Research) and Dr. P. Gardiner (Irish Geological Survey) are thanked for their helpful comments. Prof. P. Mohr (University College Galway) is thanked for his editorial annotations; Mr. C. Andrew (Ennex International) and Dr. A. Boyce (Strathclyde University) are owed a considerable debt of gratitude for their diligent and comprehensive critiques. I thank Prof. W.T. Holser (University of Oregon) for his interest in the manuscript and for his helpfully critical and encouraging letter.

References

- Bignell R.D. 1975 Timing, distribution and origin of submarine mineralisation in the Red Sea. *Trans. Instn. Min. Metall. (Sect.B: appl. earth sci.)* 84 B1-6.
- Boast A.M., Coleman M.L., Halls C. 1981 Textural and stable isotopic evidence for the genesis of the Tynagh base metal deposit, Ireland. *Econ. Geol.* 76 27-55.
- Boyce A.J., Coleman M.L., Russell M.J. 1983a Formation of fossil hydrothermal chimneys and mounds from Silvermines, Ireland *Nature* 306 No.5943 545-550.
- Boyce A.J., Anderton R., Russell M.J. 1983b Rapid subsidence and early Carboniferous base metal mineralisation in Ireland. *Trans. Instn. Min. Metall. (Sect.B:appl. earth sci.)* 92 B55-67.
- Bruck P.M., O'Connor P.J. 1980 Major transverse and other linears in the Leinster Granite. *Bull. Geol. Surv. Ireland* 2 349-370.
- Coomer P.G., Robinson B.W. 1976 sulphur and sulphate-oxygen isotopes and the origin of the Silvermines deposits, Ireland. *Mineral Deposita* 11 155-169.
- Deeny D.E. 1981a An Irish Carboniferous metallogenetic model. *Trans Instn. Min. Metall. (Sect.B:appl. earth sci.)* 90 B183-185.
- Deeny D.E. 1981b A postulated Lower Carboniferous Irish rift and possible metallogenetic consequences. In: *Mineral Exploration in Ireland, Progress and Developments 1971-1981*. Brown A.G. ed. *Irish Assoc. Econ. Geol. Wexford conf. 1981* 157-161.
- Deeny D.E. 1982a Further evidence for Devonian-Carboniferous rifting in central Ireland. *Geol. Mijnb.* 61 243-252.
- Deeny D.E. 1982b Addendum to Deeny 1981a *Trans Instn. Min. Metall. (Sect.B:appl. earth sci.)* 91 B109.
- Deeny D.E. 1983 Contributed remarks on Boyce et al. 1983b *Trans Instn. Min. Metall. (Sect.B:appl. earth sci.)* 92 B103-104.
- Deeny D.E. 1984 Downward-excavating hydrothermal convective cells; their surface expression in an Irish Carboniferous metallogenetic model (The central Irish Waulsortian mudbank complex – a sedimentary exhalative facies phenomenon?). In: European Dinantian Environments 1st meeting 1984 Abstracts Volume, *Dept. Earth Sciences, Open University* 1984 148-151.
- Gardiner P., McCarthy I.A.J. 1981 The late Palaeozoic evolution of southern Ireland in the context of tectonic basins and their transatlantic significance. In: J.W. Kerr & A.J. Ferguson (eds): *Geology of the North Atlantic Borderlands – Can. Soc. Pet. Geol.* 7 683-725.
- Greig J.A., Baadsgaard H., Cumming G.L., Folinsbee R.E., Krouse H.R., Ohmoto H., Sasaki A., Smejkal V. 1971 Lead and sulphur isotopes of the Irish base metal mines in Carboniferous carbonate host rocks. *Soc. Min. Geol. Japan Spec. issue* 2 84-92.
- Holser W.T. 1977 Catastrophic chemical events in the history of the ocean. *Nature* 267 403-407.
- Horne R.R. 1975 Possible transverse fault control of base metal mineralisation in Ireland and Britain. *Irish Nat. J.* 18 140-144.
- Lees A. 1961 The Waulsortian 'reefs' of Eire: a carbonate mudbank complex of Lower Carboniferous age. *J. Geol.* 69 101-109.
- Lees A. 1964 The structure and origin of the Waulsortian (Lower Carboniferous) 'reefs' of west central Eire. *R. Soc. Lond. Phil. Trans. Sect.B* 247 No. 740 483-531.
- Ohmoto H. 1972 Systematics of sulphur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.* 67 551-578.
- Russell M.J. 1978 Downward-excavating hydrothermal cells and Irish-type ore deposits: importance of an underlying thick Caledonian prism. *Trans Instn. Min. Metall. (Sect.B:appl. earth sci.)* 87 B168-171.
- Russell M.J., Haszeldine R.S. 1984 Carboniferous basin formation in the central and northern British Isles. In: European Dinantian Environments, 1st, meeting 1984 (Abstracts Volume) *Dept. Earth Sciences, Open University* 97-98.