

Sulphur isotopes in metamorphosed Precambrian Fe-Pb-Zn-Cu sulphides and baryte at Aggeneys and Gamsberg, South Africa

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ABSTRACT. Sulphur isotope ratios in sulphides and baryte from stratabound and stratiform orebodies in a metavolcanic-sedimentary sequence in Namaqualand were found, in part, to be extreme for Precambrian sulphur. Black Mountain, Aggeneys, in the west gave an average for the sulphides of $\delta^{34}\text{S} = +8.9 \pm 3.7\%$ (9 samples), an average for barytes of $+20.6 \pm 4.3\%$ (3 samples). Broken Hill, Aggeneys, in the centre gave an average for the sulphides of $\delta^{34}\text{S} = +19.8 \pm 3.1\%$ (19 samples). Gamsberg, in the east, gave an average for the sulphides of $\delta^{34}\text{S} = +29.2 \pm 1.8\%$ (24 samples), and an average for barytes of $+35.4 \pm 0.2\%$ (2 samples). The $\delta^{34}\text{S}$ values increase eastward. Their range is strongly on the positive side and does not centre around zero. The Gamsberg barytes and most Gamsberg sulphides have more positive $\delta^{34}\text{S}$ values than those reported for other Precambrian sulphides and sulphates. We interpret the above sulphur isotope range as being mainly due to the varying contributions of submarine-exhalative sulphide sulphur with $\delta^{34}\text{S}$ close to zero and bacterially(?) reduced sulphate with strongly positive $\delta^{34}\text{S}$, apparently from evaporites in the east. Metamorphism of amphibolite facies grade has partly isotopically re-equilibrated the ore minerals, as indicated by galena-pyrrhotine and sulphide-baryte isotope temperatures from single specimens, but has not destroyed the primary sulphur isotope range indicating pre-existing sulphate concentrations.

IN the early 1970s, four major Pb-Zn-sulphide deposits were discovered in the Bushmanland area

west of Pofadder, NW Cape Province (fig. 1). They are stratiform deposits and belong to the highly metamorphosed Proterozoic volcano-sedimentary Bushmanland Sequence in the Namaqua Mobile Belt. The aim of this sulphur isotope study has been to obtain information on the source of the sulphur and on the primary conditions of ore formation. The present paper deals with the first results obtained from a series of fifty-seven mineral samples, which already permit some interesting conclusions.

Chadwick (1981) listed the ore reserves of the four deposits as follows (from west to east): Black Mountain, more than 80 million tons with 2.7% Pb, 0.6% Zn, 0.7% Cu; Broken Hill, 38 million tons with 6.35% Pb, 2.87% Zn, 0.45% Cu, 85 g/t Ag; Big Syncline (Aggeneys Mountain), about 100 million tons with 1.0% Pb, 2.5% Zn; Gamsberg, 152.55 million tons with 0.55% Pb, 7.11% Zn.

So far, only Broken Hill is in production. Its dominant economic constituent is galena, and pyrrhotine is the most abundant iron sulphide. The massive sulphide ore varies from 5 to 55% Pb, with local zinc contents as high as 20% (Chadwick, 1981). Wilson (1981) gave the average of the well mineralized massive units within the Broken Hill deposit as 0.98% Cu, 22.3% Pb, 3.8% Zn, and 300 ppm Ag.

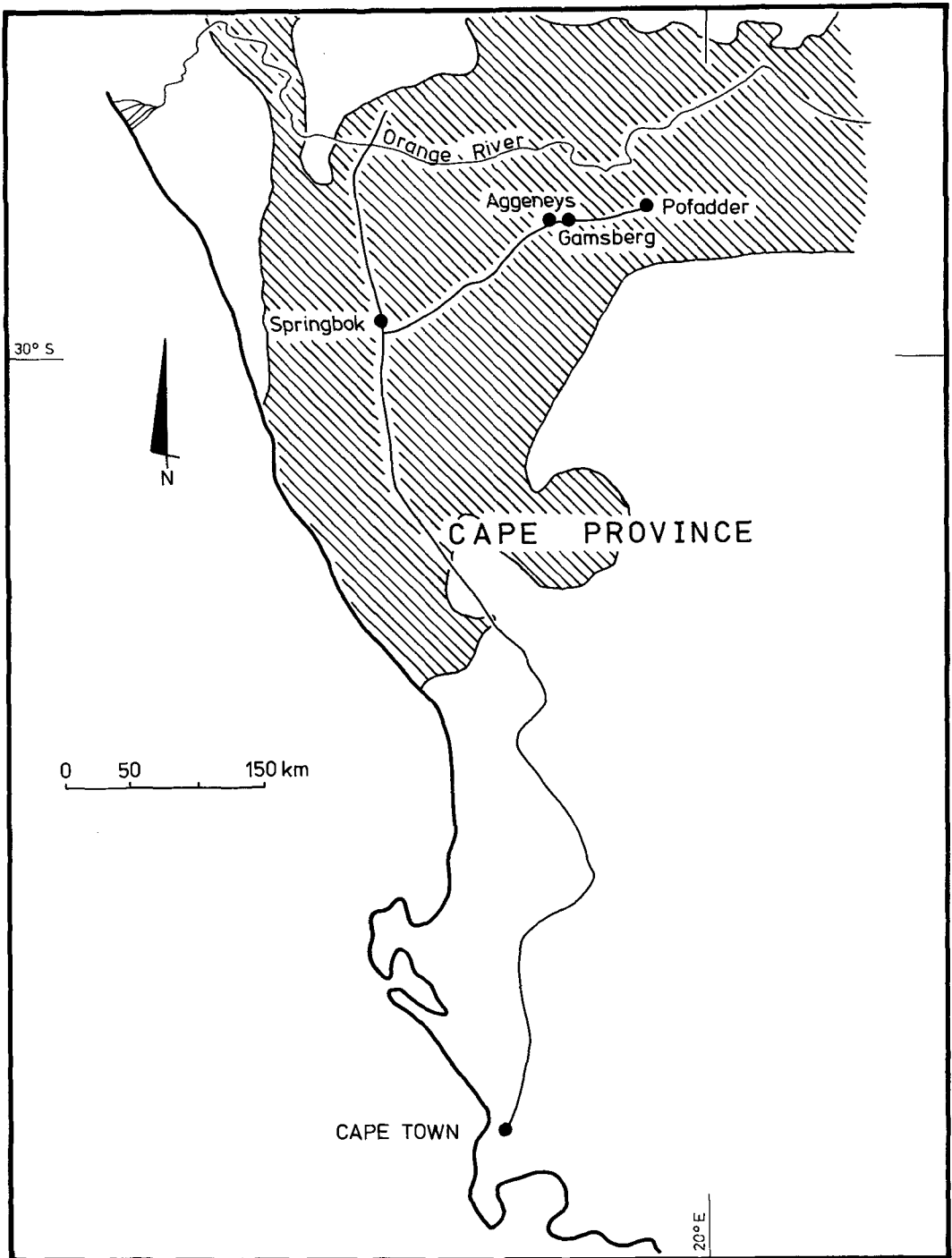


FIG. 1. Locations of Aggeneys and Gamsberg. Ruled: Namaqua-Natal Mobile Belt (1-2 Ga), after Blignault (1981).

Previous work. The three sulphide orebodies in the Aggeneys area, as well as that at Gamsberg some 15 km to the east, are accepted to be stratiform and stratabound deposits and to form part of the Aggeneys Ore Formation (Ryan *et al.*, 1982), equivalent to the Gams Iron Formation (Rozendaal, 1978) which again is part of the Bushmanland Sequence. All rocks and the ore formation in which the sulphides are associated with iron formations, amphibolites, quartzites, and baryte horizons, are highly metamorphosed and repeatedly complexly folded.

First data on the deposits were published in an excursion guide (GSSA, 1975). Stumpfl (1977) gave a few additional details on the Aggeneys ore. The results of the investigation of the three Aggeneys deposits were recently summarized by Ryan *et al.* (1982) and Ryan (1982).

A series of studies has been undertaken on the Gamsberg deposit (Rozendaal, 1976, 1977, 1978, 1980, 1982). From silicate phase assemblages, the maximum temperature during polyphase deformation and metamorphism was deduced as 670 °C, with a maximum pressure of 4.5 kbar. This rather low pressure for garnet-bearing rocks is easily explained by their high Mn contents. Stumpfl (1979) found MnO concentrations from 5 to 40% in garnet and other silicates—pyroxenes and stilpnomelane—from the ore environment. He has shown that at Gamsberg an intense manganese halo around the ores has survived amphibolite-facies metamorphism. Similar Mn haloes have been reported elsewhere e.g. from Tynagh (Russell, 1974); from Broken Hill, NSW (Stanton, 1976); and from Meggen (Gwosdz and Krebs, 1977).

Rozendaal (1980) described the depositional environment for the Gamsberg deposit and accompanying rocks as a relatively shallow, locally restricted basin, with the depositional conditions varying between oxidizing and reducing, resulting in an almost cyclic deposition of oxide-carbonate-sulphide facies in an iron formation. He considered graphite in the ore zone as indicative of the presence of abundant sulphate-reducing organic matter.

Moore (1980) studied massive sillimanite-corundum rocks which occur within the same thin, highly metamorphosed rock sequence as the Aggeneys and Gamsberg orebodies. The sillimanite-rich rocks, already interpreted as metamorphic bauxites by Coetzee (1940), were found by Moore to originate from aluminous clays in a thin continental sequence of red-bed arkoses and shales. To the east these rocks were in contact with evaporitic carbonate-rich beds within a playa or shallow marine environment where a sabkha process developed at the land-sea interface. Moore

considered similar arid weathering conditions as probably also applicable to the formation of the base metal deposits higher in the same sequence.

Ryan *et al.* (1982) suggested that the ores could be assigned to an exhalative-sedimentary model similar to the ferruginous Red Sea deposits, and found many similarities between the Aggeneys deposits and Broken Hill (NSW) in Australia (Stanton, 1976).

Age of the deposits. According to Blignault (1981) the field evidence points towards a 2.0 b.y. age for the Aggeneys-type sediments, but an age of about 1.3–1.4 b.y. cannot be discounted in view of possible erroneous correlations and structural interpretations. Close to the deposits, Reid (1981) determined Sm-Nd ages of (2.01 ± 0.19) to $(2.23 \pm 0.33) \times 10^9$ years for basic amphibolites at Gamsberg; however, lead isotope studies of Aggeneys and Gamsberg sulphides by Köppel (1980) suggested an age of $(1.25 \pm 0.2) \times 10^9$ years. The problem of the age of the Bushmanland metasedimentary sequence and the ore deposits has, therefore, still to be resolved (Barton, 1981).

Determination of sulphur isotope ratios. The sulphur isotope measurements were made at the Stable Isotope Laboratory, Geochemisches Institut, University of Göttingen, using a FINNIGAN MAT 251 mass spectrometer. A special problem in many cases was the separation of pure monomineralic samples from the sulphide intergrowths of the massive ore. Pyrrhotine was separated by means of its magnetic properties, while in all other cases, hand-picking under a binocular microscope was employed. In some cases involving intimate intergrowths, composite samples of unseparated sulphides were measured.

Results. Average values for the sulphur isotope ratios ($\delta^{34}\text{S}$) shown in detail in fig. 2 are as follows:

Black Mountain, Aggeneys, in the west,	
sulphides: $\delta^{34}\text{S} = + 8.9 \pm 3.7\text{‰}$ (9 samples),	
barytes: $\delta^{34}\text{S} = + 20.6 \pm 4.3\text{‰}$ (3 samples);	
Broken Hill, Aggeneys, in the centre,	
sulphides $\delta^{34}\text{S} = + 19.8 \pm 3.1\text{‰}$ (19 samples);	
Big Syncline, Aggeneys, in the centre,	
sulphides: $\delta^{34}\text{S} = + 12.8 \pm 0.7\text{‰}$ (3 samples),	
barytes: $\delta^{34}\text{S} = + 30.2 \pm 0.1\text{‰}$ (2 samples);	
Gamsberg, in the east,	
sulphides: $\delta^{34}\text{S} = + 29.2 \pm 1.8\text{‰}$ (24 samples),	
barytes: $\delta^{34}\text{S} = + 35.4 \pm 0.2\text{‰}$ (2 samples).	

Surprisingly, the $\delta^{34}\text{S}$ values were mostly rather strongly positive, in contrast to most other Precambrian sulphides and sulphates (Monster *et al.*, 1979). However, the scatter of sulphide $\delta^{34}\text{S}$ values within a single deposit was found to be rather small especially for Gamsberg. Sulphur isotope geothermometry for a sulphide-baryte pair (from one

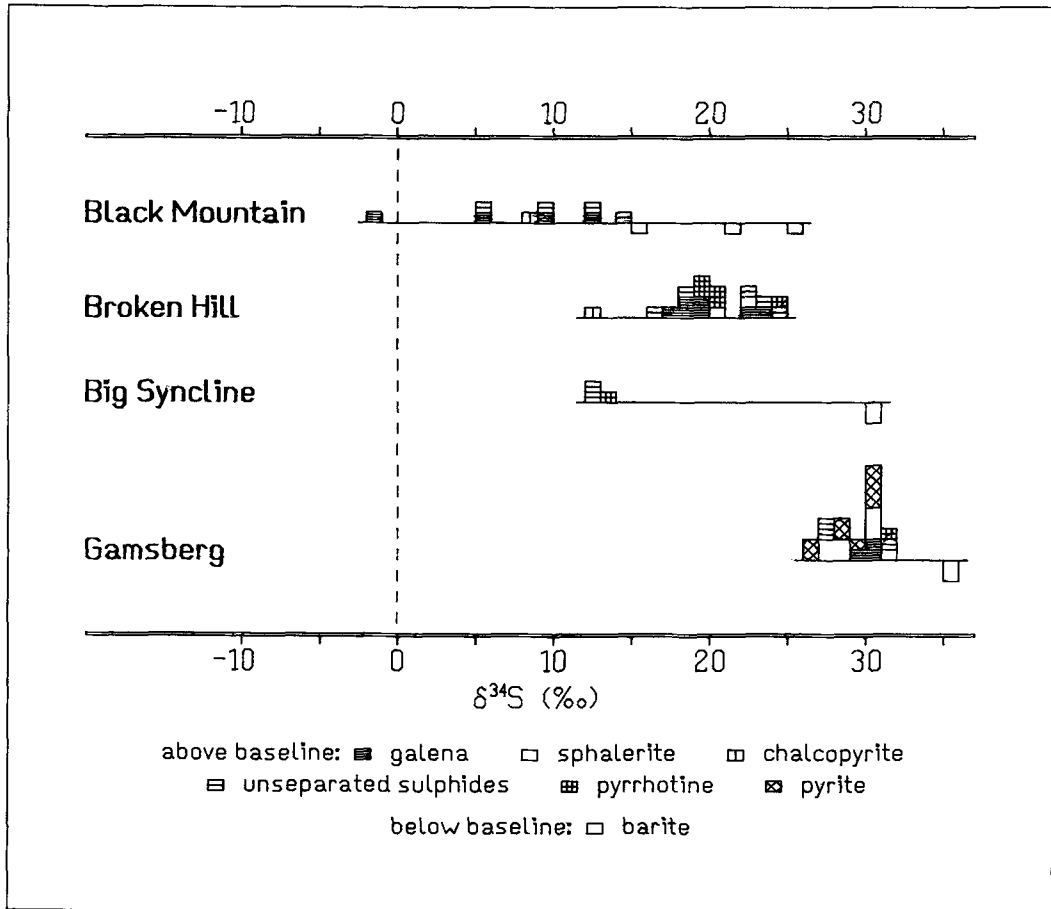


FIG. 2. Sulphur isotope ratios obtained in this study for the Aggeneys-Gamsberg ores.

Black Mountain specimen) gave a temperature of *c.* 700 °C ($\Delta = 9.1\text{‰}$), comparable with the maximum temperature of amphibolite facies metamorphism of 670 °C (Rozendaal, 1978). Sulphide-pair geothermometry (within the same hand specimen in each case) led, in part, to further reasonable temperatures:

Broken Hill, galena-pyrrhotine *c.* 600 °C ($\Delta = 1.1; 1.2; 1.7\text{‰}$),

Broken Hill, galena-sphalerite *c.* 850 °C ($\Delta = 1.0\text{‰}$),

Black Mountain, galena-chalcopyrite *c.* 320 °C ($\Delta = 2.3\text{‰}$).

Considering the low sensitivity of the various geothermometers at high temperatures and the problems of proving equilibrium, the first three of these (*c.* 600–850 °C) apparently indicate metamorphic sulphur isotope equilibration during amphibolite-facies metamorphism.

Regarding variations from deposit to deposit,

there is a definite tendency for the range of sulphide (as well as baryte) $\delta^{34}\text{S}$ to increase from west (Black Mountain) to east (Gamsberg). This tendency, which leads to $\delta^{34}\text{S}$ averages at Gamsberg more positive than any other Precambrian ones listed by Monster *et al.* (1979), is most certainly not accidental but has a genetic significance, especially if one accepts that the stratigraphic position of the deposits, and therefore the results, are comparable. Despite the metamorphic re-equilibration, the *ranges* of $\delta^{34}\text{S}$ indicate that unusual conditions must have prevailed during the primary formation of the sulphides.

Discussion. Starting from a primary (magmatic-exhalative or also 'normal' sedimentary) sulphur source with $\delta^{34}\text{S}$ close to zero, the most probable case during the Precambrian, extreme positive $\delta^{34}\text{S}$ values can only be expected if a fractionation has occurred separating two kinds of sulphur species with strongly contrasting $\delta^{34}\text{S}$ values. The strongest

inorganic S isotope fractionation effects occur in equilibria between sulphide and sulphate at low temperatures. Always δ_{sulphate} is $> \delta_{\text{sulphide}}$. As the difference increases with falling temperature, while the rate of equilibration decreases, the $\Delta_{\text{sulphate-sulphide}}$ rarely exceeds 32‰, corresponding to an equilibrium temperature around 250 °C (Ohmoto and Lasaga, 1983). Under these conditions, a deposit could form with much sulphide of $\delta^{34}\text{S} \approx 0$ and a small amount of sulphate of $\delta^{34}\text{S} \approx +32\%$. However, this process does not lead to isotopically heavy sulphides in a single step.

Sulphate-reducing bacteria can produce similar results even more effectively, with fractionation sometimes reaching as much as $\Delta^{34}\text{S} = 60\%$. Rather large reservoirs of heavy sulphate can form in lagoons and crystallize as evaporites (gypsum/anhydrite). If evaporite sulphate is locally reduced almost completely to sulphide, this may lead to heavy sulphide with a bulk $\delta^{34}\text{S}$ value close to, or identical with, that of the former heavy sulphate. This result is independent of the nature, biogenic or inorganic, of the reduction process. In the case of bacterial sulphate reduction, the primary sulphides formed generally cover a rather broad δ range, which may, however, be obliterated by metamorphic re-equilibration. The observed $\delta^{34}\text{S}$ pattern alone does not permit a clear discrimination between biogenic and inorganic reduction, but the graphite at Gamsberg strongly points towards a biogenic (bacterial) process.

The baryte apparently was precipitated directly from the lagoon or evaporite solutions and thus would indicate the sulphur isotope ratio in the former lagoon sulphate.

The increase in $\delta^{34}\text{S}$ values from west to east apparently indicates two separate sources of sulphur; the variation seems to be a function of the respective contributions of magmatic-exhalative sulphur ($\delta^{34}\text{S} \approx 0\%$) and seawater (evaporite)-derived sulphur ($\delta^{34}\text{S} \approx +30\%$ or more). According to other geological and geochemical criteria discussed elsewhere (Rozendaal, 1982), the Black Mountain deposit in the west formed closest to the magmatic-exhalative source(s) which must have supplied most of the metals and at least some of the sulphur, as indicated by the rather low sulphide $\delta^{34}\text{S}$ values at Black Mountain.

The rather strongly positive $\delta^{34}\text{S}$ values of the sulphides at Broken Hill and especially at Gamsberg in the east (the most sulphur- and graphite-rich of the deposits; Rozendaal, 1982), however, indicate increasing contributions to the east of sulphide sulphur formed by reduction of isotopically heavy evaporite (or lagoon) sulphate. Reduction was probably effected by sulphate-reducing bacteria.

Later metamorphic re-equilibration of sulphur

isotopes is proved by mineral pairs giving reasonable metamorphic temperatures. However, the $\delta^{34}\text{S}$ range which indicates the important contribution of seawater (evaporite)-derived sulphate was not obliterated by metamorphism.

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