

In order to achieve adequate penetration of the resin, this is best done under vacuum.

The specimen and premixed resin ('Araldite' epoxy resin AY103 and hardener HY951, in the proportion 10:1) are separately warmed to 40 °C for about 10 minutes. The resin is then poured over the sample and the whole placed in a vacuum oven which, after about 3 minutes, is evacuated to about 100 mm Hg. With this treatment, air is usually drawn out of the specimen for about 30 seconds. The oven is then brought up to atmospheric pressure to eliminate bubbles formed on the surface of the resin. This sequence is repeated until no further air bubbles are expelled from the specimen: about five evacuation cycles are generally necessary. The epoxy resin tends to boil at pressures less than 100 mm Hg, causing frothing and the occlusion of minute gas bubbles within the specimens, and it is important to evacuate air under very modest vacuum conditions.

*Department of Geology and Mineralogy  
Parks Road, Oxford OX1 3PR*

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R. A. G. HOLLAND  
C. J. BRAY  
E. T. C. SPOONER<sup>1</sup>

<sup>1</sup> Present address: Department of Geology, The University of Toronto, Toronto, Canada.

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## H<sub>2</sub>S-bearing fluid inclusions in baryte from the North Pole deposit, Western Australia

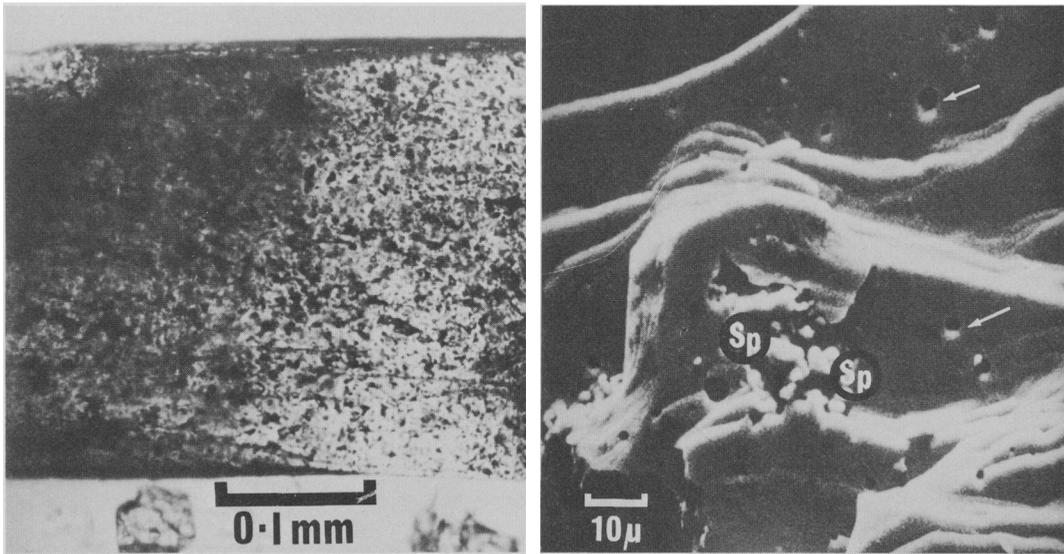
THIS paper reports on the cause of the distinctive odour of H<sub>2</sub>S when certain baryte samples from the North Pole deposit are fractured, crushed, or simply scratched with a steel file or needle.

The deposit, recently described by Dunlop (1976), is located in a sequence of Archean metabasalts and cherts in the eastern portion of the Pilbara Block. Baryte that emits an odour of H<sub>2</sub>S occurs in extensive chert/baryte horizons, which are locally disturbed to form structurally complex zones up to 15 m in width (the B and J orebodies). This baryte is typically dark grey/brown to almost black in colour and coarsely crystalline. In places where the baryte has been remobilized it is white or pale yellow in colour, occurs in veins, and lacks the distinctive odour of H<sub>2</sub>S. A study of representative baryte samples from this deposit using a combination of optical microscopy and mass spectrometry revealed that the H<sub>2</sub>S is a component of the abundant fluid inclusions in these barytes (fig. 1).

The fluid inclusions are usually less than 5 μm in size; too small for conventional heating and freezing stage studies. They are commonly spheroidal or rectangular in shape and occur either in planar or non-planar groupings or as more or less isolated cavities. It is not possible to distinguish between primary and secondary inclusions on the basis of their size, shape, and distribution. Three compositionally different fluid inclusion types were, however, recognized (Table I).

*Type I inclusions* contain an aqueous solution and often a small vapour bubble. The liquid to vapour ratio is highly variable and the inclusions are commonly necked.

*Type II inclusions* usually contain three fluid phases; an aqueous solution and an immiscible CO<sub>2</sub>-rich liquid which, in turn, contains a CO<sub>2</sub>-rich vapour bubble. Less commonly, only two fluid phases are present; aqueous solution and CO<sub>2</sub>-liquid. The amount of aqueous solution within



FIGS. 1 and 2: FIG. 1 (left). Cleavage fragment of 'primary' baryte from the B orebody showing abundant fluid inclusions. FIG. 2 (right). Scanning electron photomicrograph of cleavage fragment of 'primary' baryte from the B orebody showing a cluster of small, rounded sphalerite crystals (Sp) confirmed by Energy Dispersive Analysis. The small holes on the surface (arrowed) are opened fluid inclusions.

TABLE I. Inclusion types present in representative baryte samples from the North Pole deposit

Sample	Location	Fluid inclusion types present
NP 1*	'primary' baryte, B orebody	I, II, III
NP 2	Remobilized baryte, 'B' orebody	I
NP 3*	'primary' baryte, J orebody	I, II, III
NP 4*	Stratiform 'primary' baryte, chert/baryte horizon	I, II, III

\* Odour of  $H_2S$  on crushing; solid inclusions of  $ZnS$  and  $CaCO_3$  present.

these inclusions is variable and ranges from about 70 vol.% to about 10 vol.%.

Type III inclusions consist almost entirely of  $CO_2$ -rich liquid and  $CO_2$ -rich vapour.

In addition to these fluid inclusions, solid inclusions of calcite and sphalerite are also present (fig. 2). They are less common than fluid inclusions, range in size up to about  $50 \mu m$ , and are randomly distributed throughout the host baryte. These solid inclusions are believed to represent solid phases

TABLE II. Abundances of  $H_2S$ ,  $H_2O$ , and  $CO_2$  ( $\pm 5\%$ ) in the inclusion fluids

Sample	Vol. % $H_2O$	Vol. % $CO_2$	ppm $H_2S$ (by volume)
NP 1	80	20	600
NP 2	98	2	13
NP 3	83	17	1300
NP 4	80	20	4100

captured by baryte during its primary growth; in other words they are primary inclusions. This view is substantiated by the absence of such inclusions in the remobilized baryte.

It is clear from the summary in Table I that only those inclusions that contain type II and type III inclusion emit an odour of  $H_2S$  on crushing. It is proposed therefore that  $H_2S$  is a significant component of these two inclusion types.

At first it was thought that the  $CO_2$ -rich phases in type II and type III inclusions were composed predominantly of  $H_2S$ , but subsequent mass spectrographic analysis of the volatiles released on opening the inclusions under high vacuum confirmed the predominance of  $CO_2$  (Table II).

The relatively low levels of  $H_2S$  in 'primary' baryte (600-4100 ppm) may seem surprising. However, type II and type III inclusions account for

about 0.5% of the volume of the baryte. Now, if we assume that the density of the inclusion fluids is about  $1 \text{ g/cm}^3$ , a scratch even as small as  $1 \text{ cm} \times 0.1 \text{ cm} \times 0.1 \text{ cm}$  ( $10^{-2} \text{ cm}^3$  in volume) would release  $5 \times 10^{-5} \text{ cm}^3$  of inclusion fluid. This is equivalent to  $3 \times 10^{-8} \text{ cm}^3$  of  $\text{H}_2\text{S}$  at S.T.P., or about  $0.5 \times 10^{-10} \text{ g}$  for the sample containing the lowest amount of this gas (NP1, 600 ppm). Even this minute quantity can easily be detected by the human nose, which according to Roedder (1972) can detect as little as  $10^{-10} \text{ g}$  in a litre of air, or  $10^{-11} \text{ g}$  in  $10^2 \text{ cm}^3$  of air.

As expected the 'odourless' remobilized baryte contains the lowest proportion of  $\text{H}_2\text{S}$ . It also contains the lowest proportion of  $\text{CO}_2$ . It is not possible to assess whether these two gases are components of type I inclusions or whether they are contained within type II and type III inclusions not readily apparent under the microscope. The former seems more likely.

Several authors (for example, Palache *et al.*, 1951; Dons, 1956; Deer *et al.*, 1963) have also recorded the fetid odour of  $\text{H}_2\text{S}$  when baryte from other localities is heated or rubbed. It is probable that these samples also contain  $\text{H}_2\text{S}$ -bearing inclusions, although it is apparent from this present study that such inclusions need not be rich in  $\text{H}_2\text{S}$ . As little as 600 (by volume) ppm of this gas in inclusion fluids is sufficient to cause this distinctive odour provided the inclusions, as in the case of the North Pole barytes, are present in abundance.

One most useful observation in connection with the origin of the  $\text{H}_2\text{S}$ -bearing type II and type III inclusions is the occasional presence of sphalerite

(and calcite) as captured mineral phases within these two inclusion types. Because sphalerite (and calcite) are considered to be primary inclusions themselves, it follows that at least some of the type II and type III inclusions are also primary. This implies that both free  $\text{H}_2\text{S}$  and sphalerite (reduced sulphur species) were present during the growth of the baryte (oxidized sulphur species) and that the sulphur in these three species is of the same origin. Either  $\text{H}_2\text{S}$  was produced by the reduction of sulphate and reacted with traces of zinc in the baryte-forming fluid, or oxidation of reduced sulphur species ( $\text{H}_2\text{S}$  and  $\text{ZnS}$ ) in a barium-rich fluid resulted in the formation of baryte. Sulphur isotope studies are needed to test the merits of these two alternatives and to investigate the unusual redox conditions prevailing during the formation of baryte from the North Pole deposit.

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A. H. RANKIN

T. J. SHEPHERD

Department of Geology

Imperial College, London SW7 2BP

Geochemical Division, Institute of Geological Sciences  
 64-78 Gray's Inn Road, London WC1X 8NG

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## Clinoptilolite pseudomorphs after calcitic and aragonitic Miocene fossils, Kaipara Harbour, New Zealand

CLINOPTILOLITE, analcime, chabazite, erionite, and phillipsite have been recorded as replacement products of volcanic glass in marine, volcanoclastic-rich beds of the Waitemata Group—an early Miocene sedimentary sequence (Sameshima, 1978). For a number of years, palaeontologists of the Geology Department have recognized that many of the fossil tests collected from one rich

locality of this Group at Bushy Point on the Kaipara Harbour ( $36^\circ 15' \text{ S}$ ,  $174^\circ 13' \text{ E}$ ) are no longer calcareous. Subsequent investigations have shown that most of the specimens in the Departmental fossil collection from this locality are clinoptilolite pseudomorphs, after both calcite and aragonite—the perfection of replacement being very high.