

a small proportion of the chlorine present in the tourmalines could be removed by leaching (table I). This was ascertained by boiling selected samples in distilled water for five hours and then determining the chlorine content of the water. Longer periods, up to three days, of this treatment failed to remove any further chlorine. The high soluble chlorine content found in one sample (26/P) appears to be anomalous and may be the result of contamination of the sample powder. The low soluble chlorine content of the majority of the tourmalines analysed suggests that little, if any, of the total chlorine found is present in fluid or soluble solid inclusions. It seems likely that the chlorine is present in the crystal lattice, possibly in hydroxyl positions.

The tourmalines analysed here are of a restricted range in chemical composition and other varieties may have a very different chlorine content. Also, from our work in progress, it is apparent that the granites of SW. England contain about double the estimated average chlorine for granites and this may have resulted in an abnormal chlorine content in the tourmalines.

*Department of Geology
University College of Wales
Aberystwyth*

R. FUGE
G. M. POWER

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Naturally occurring compositions in the solid-solution series Bi_2S_3 – Sb_2S_3

HAYASE (1955) found a form of bismuthinite in which 36–55 % of the Bi_2S_3 molecule were replaced by Sb_2S_3 ; he named this mineral horobetsuite. It is, however, not yet clear if horobetsuite is a distinct species or only part of a solid-solution series extending from Bi_2S_3 towards Sb_2S_3 . Quantitative electron-probe microanalyses of a number of bismuthinite and stibnite samples have therefore been made in order to establish the range of their mutual solubility in nature.

A Cambridge Geoscan electron-probe microanalyser with a 75° X-ray take-off

angle was employed for the investigation. Metallic Bi and Sb, and pyrite for S, were used as standards. The measured X-ray intensity ratios between specimen and standard were converted into concentration ratios by a method described by Springer (1967).

The analysed bismuthinite specimens came from several localities in Bolivia, from Grube Wenzel (Wolfach, Baden, Germany), and from Villanueva de Cordoba (Spain). The stibnite originated from Brandholz (Fichtelgebirge, Germany), Eidsvold

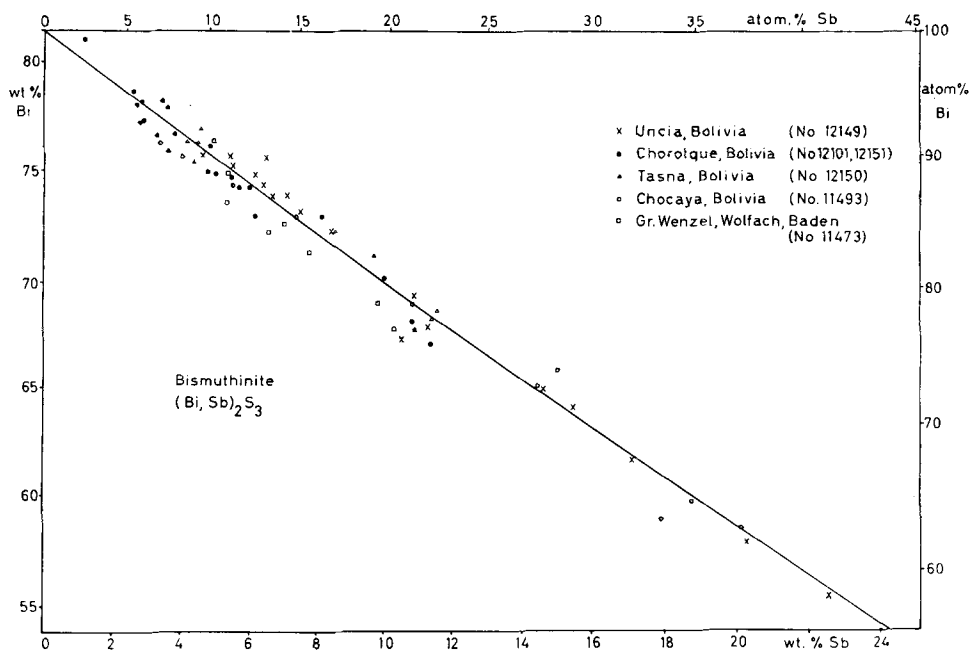


FIG. 1. Plot of Bi against Sb contents of various bismuthinites. The solid line indicates where the experimental determinations should lie assuming perfectly precise measurements and accurate correction procedure.

(Burnett District, Queensland), Barberton (Transvaal), Montluçon (France), Sillian (Lienz, Austria), and Brück (Ahr, Germany). Two to five polished specimens from each locality were studied.

Most of the bismuthinite specimens showed a rather variable composition with differing amounts of Sb. In fig. 1 the measured Bi and Sb contents in some of these are plotted against each other. It is apparent that all degrees of replacement of Bi by Sb up to 42 mol % Sb_2S_3 can occur. Using the information supplied by Hayase (1955) the solid solubility range is documented even up to 55 mol % Sb_2S_3 . On the other hand, all the investigated stibnites contained no elements other than Sb and S, in particular no Bi. Horobetsuite can therefore be considered as the Sb-rich end member in the naturally occurring solid solution series between Bi_2S_3 and Sb_2S_3 . The limit of this miscibility range seems to lie at the composition $(\text{Bi}_{0.45}\text{Sb}_{0.55})_2\text{S}_3$. It is surprising that no minerals with Sb contents intermediate between horobetsuite and

stibnite have been found since such compositions have been obtained artificially in thermal phase diagram studies (Takahashi, 1920).

In addition to the quantitative determinations presented in fig. 1 some full analyses of all the elements present have been made. No significant deviations from the atomic metal:sulphur ratio of 2:3 could be detected.

It is interesting to note that no Cu or Pb was found in any of the bismuthinites. These elements are likely to occur according to Padera (1956) who reported that an isomorphous series exists between aikinite ($\text{Cu}_2\text{S} \cdot 2\text{PbS} \cdot \text{Bi}_2\text{S}_3$) and bismuthinite, leading to the rézbányite group of minerals. This series is thought to arise from the substitution of Bi in Bi_2S_3 by Pb and the simultaneous introduction of a Cu atom for every Bi atom replaced. For the present work microprobe analyses have been made of aikinite from Beresovsk (Ural) and Wittichen (Schwarzwald, Germany), and these led to compositions which were in close agreement with the usual formula for this mineral. Unfortunately no material was available of the other members of the rézbányite group (hammarite, lindströmite, and gladite) to verify their alleged relationship to bismuthinite.

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*Institut für Mineralogie und Lagerstättenlehre
Technische Hochschule Aachen
Germany*

G. SPRINGER

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Growth spirals on baryte

SEAGER (1953) has reported the microstructures on different faces of many crystals including baryte from the Silverband mine, Westmorland, but did not record any spiral on the latter. We examined faces of several forms on many crystals from this mine and have succeeded in observing a few growth spirals on the planer parts of $\{011\}$ faces, along with some growth hillocks. This is the first record of growth spirals on $\{011\}$ faces of natural crystals of baryte.