BaBeF₆, A POSSIBLE UNDISCOVERED MINERAL


The common association of beryllium minerals with fluorite in hydrothermal deposits has suggested that beryllium was carried in solution as the fluoberyllate, BeF₄²⁻, and that beryllium was precipitated when a reduction of the fluoride concentration by the formation of fluorite caused the dissociation of the complex fluorides (Staatz and Griffitts, 1961). Inasmuch as the BeF₄²⁻ ion closely resembles the SO₄²⁻ ion in its chemical and structural properties, we might expect the formation in nature of fluoberyllate analogs of sulfate minerals, some of which are well known laboratory products (Ray, 1931). The cation that seems most likely to form natural fluoberyllates is Ba²⁺, which might be partly replaced by Pb²⁺, as pointed out by Cannas and Rollier (1961). BaBeF₆ probably looks like barite, with which it is isostructural, and is likely to be mistaken for it. These two substances can, fortunately, be distinguished by optical or X-ray examination. I have found no beryllian “barite” myself and hope that publication of its diagnostic properties in this note will facilitate its recognition by others.

BaBeF₆ is readily synthesized over a wide range of pH and temperature merely by adding BaCl₂ to a solution containing fluoride and beryllium. Precipitation from a solution that also contains sulfate yields a single phase containing both anions. Ray (1931) reported that NH₄BeF₄ dissociates into BeF₄ and NH₄Cl in hot solutions, a reaction that may restrict the natural occurrence of fluoberyllates to low or moderate temperature deposits.

The X-ray powder diffraction pattern of BaBeF₆ is distinguishable from that of barite by its slightly larger 2θ angles, because F⁻ is slightly smaller than O²⁻. Indexed reflections of these salts and of one containing approximately equal molecular proportions of SO₄²⁻ and BeF₄²⁻ are shown in Table 1. The progressive decrease in spacings with increasing BeF₄²⁻ content clearly shows the effect of solid solution.

Synthetic BaBeF₆ like BaSO₄ and the intermediate compound, is in granular nearly opaque aggregates of microscopic or submicroscopic crystallites. The refractive index of the fluoberyllate aggregates is low (1.445) reflecting the low molar refractivity of fluorine. The distinct illumination of some crystallites between crossed nicols suggests that the birefringence is rather high—above that of barite.

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<th>mg Barite Synthetic BaSO₄ BaBF₄</th>
<th>Refractive Index</th>
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2. Not determined on the specimen used for determination.
3. Precipitated from solution containing about equal molecular proportions of SO₄ and BF₄⁻.
The minimum requirements for the formation of BaBeF₄ in nature are, of course, an environment containing Ba, Be, and F, but not SO₄, and a low or moderate temperature. Ba and Be are commonly rather well separated geochemically, but they do occur together in a variety of places: in a shallow volcanic environment at Spor Mountain, Utah; in metamorphic rocks at Seal Lake, Labrador (Evans and Desjardins, 1952), Långban, Sweden (Aminoff, 1923), and Franklin, N. J. (Palache, 1935); and in the Vishnevý-Ilmen Mountain alkalic igneous complex (Zhabin and Kazakova, 1960). The two most promising environments in North America are in the classic volcanic epithermal districts of the Basin and Range Province and in the upper Mississippi valley—especially the Kentucky-Illinois fluorospar district, in which all three ingredients have been found (Trace, 1960).

Plutonic rocks, whether igneous or metamorphic, may have formed at too high a temperature to permit the formation of fluoberyllates. Nevertheless, they should not be ignored. Heide’s report (1953) of fluorite, barite, and several beryllium minerals in schlieren in granite at Henneberg, Germany is especially encouraging.

References


