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$BaBeF_4$, A POSSIBLE UNDISCOVERED MINERAL

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The common association of beryllium minerals with fluorite in hydrothermal deposits has suggested that beryllium was carried in solution as the fluoberyllate, BeF_4^{2-}, 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 BeF_4^{2-} ion closely resembles the SO_4^{2-} 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 Ba^{2+}, which might be partly replaced by Pb^{2+}, as pointed out by Cannas and Rollier (1961). $BaBeF_4$ 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.

$BaBeF_4$ is readily synthesized over a wide range of pH and temperature merely by adding $BaCl_2$ 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 NH_4BeF_4 dissociates into BeF_4 and NH_4Cl 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 $BaBeF_4$ is distinguishable from that of barite by its slightly larger 2θ angles, because F^- is slightly smaller than O^{2-}. Indexed reflections of these salts and of one containing approximately equal molecular proportions of SO_4^{2-} and BeF_4^{2-} are shown in Table 1. The progressive decrease in spacings with increasing BeF_4^{2-} content clearly shows the effect of solid solution.

Synthetic $BaBeF_4$ like $BaSO_4$ 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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TABLE 1.—X-RAY POWDER DIFFRACTION AND OPTICAL DATA OF $BaSO_4$, $BaBeF_4$, AND A SALT OF INTERMEDIATE COMPOSITION

hkl	Barite[1]		Synthetic $BaSO_4$[1]		$BaSO_4$—$BaBeF_4$[3]		$BaBeF_4$	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
200	—	—	4.44	17	4.42	22	4.40	34
011	4.48	40	4.34	36	4.34	57	4.23	74
111	3.83	40	3.90	57	3.86	68	3.83	68
201	—	—	3.77	12	3.76	20	3.74	31
002	3.56	40	3.576	31	3.547	27	3.52	15
210	3.43	80	3.442	100	3.437	82	3.380	65
102	3.31	60	3.317	67	3.300	68	3.267	62
211	3.09	80	3.101	97	3.084	93	3.058	81
112	2.85	50	2.834	53	2.814	55	2.780	40
301 }	2.73	50	{ 2.734	16	2.690	38	2.652	34
020 }			{ 2.726	47	2.720	10	2.714	6
212	2.47	20	2.481	14	2.462	12	2.442	3
311	—	—	2.444	2	2.430	5	2.430	9
220	2.33	60	2.322	15	—	—	—	—
103	—	—	2.303	6	2.298	20	2.270	40
302	2.28	20	2.281	7	2.276	25	2.259	37
221	2.21	40	2.209	27	2.186	38	2.168	53
113 }	2.11	100	{ 2.120	80	2.103	95	2.080	19
312 }			{ 2.104	76	2.085	100	2.065	100
410	2.06	40	2.056	23	2.049	30	2.040	37
222	—	—	1.947	<1	—	—	—	—
321	1.93	20	1.930	7	1.914	7	1.893	6
303	1.86	50	1.857	16	1.845	20	1.834	18
004	—	—	1.787	3	1.771	5	1.758	6
031	—	—	1.760	9	—	—	—	—
313	1.75	40	1.754	9	1.738	10	1.719	9
131	—	—	1.726	5 }	1.704	5	1.687	12
501	—	—	1.723	6 }				
230	1.68	50	1.681	7	1.661	15	1.650	12
421	—	—	1.673	14	—	—	—	—
114	—	—	1.669	10	—	—	—	—
231	1.65	40	1.636	8	1.616	5	1.595	9
132	1.594	40	1.593	8	1.574	7	1.566	6
502	—	—	1.590	7	1.579	7	1.561	6
323	1.537	60	1.534	18	1.523	25	1.509	22

Refractive index	Barite	$BaSO_4$	$BaSO_4$—$BaBeF_4$	$BaBeF_4$
$n\alpha$	1.636[2] }			
$n\beta$	1.637[2] }	1.595[2]	1.535	1.445
$n\gamma$	1.648[2] }			

[1] From Swanson, Fuyat, and Urginic (1953, p. 65–66).

[2] Not determined on the specimen used for diffraction.

[3] Precipitated from solution containing about equal molecular proportions of SO_4 and BeF_4.

The minimum requirements for the formation of $BaBeF_4$ in nature are, of course, an environment containing Ba, Be, and F, but not SO_4, 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 Vishnevy-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 fluorspar 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.

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