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## APHTHITALITE FROM KILAUEA<sup>1</sup>

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The mineral apthitalite, a non-hydrated sulfate of potassium and sodium, is one of the rarer of the natural soluble sulfates. It has been reported at Vesuvius,<sup>2</sup> where it is rather common and was first discovered in 1795, at Racalmuto in Sicily,<sup>3</sup> at Douglashall near Stassfurt,<sup>4</sup> and more recently at Searle's Lake, in California,<sup>5</sup> and at Etna.<sup>6</sup> Ponte thinks that it probably occurs also at Stromboli. The composition is undoubtedly variable, but has been commonly (Dana, Groth, etc.) regarded as  $(K, Na)_2SO_4$ , with  $K_2O : Na_2O = 3 : 1$ .

The mineral described in the present paper was obtained by one of us, in September, 1920, from a crevice in a solidified, but still hot, flow of basalt of the eruption of Kilauea, (Hawaiian Islands), which began in December, 1919, at a spot now called Mauna Iki, in the Kau Desert, about 8 kilometers (5 miles) southwest of Halemaumau.<sup>7</sup> The apthitalite coated some of the hotter portions of the walls of a crack in the roof of what was apparently a collapsed lava tunnel. The spot was visited by Dr. Jaggar and Prof. A. L. Dean on 18 July, 1920, when they

<sup>1</sup> Presented at the meeting of the Mineralogical Society of America, December 29, 1920.

<sup>2</sup> Cf. Zambonini, *Mineralogia Vesuviana*, p. 316, 1910.

<sup>3</sup> Vom Rath and Scacchi, *Neues Jahrb. Min. Geol.*, 1875, 620.

<sup>4</sup> H. Bücking, *Z. Kryst. Min.*, 15, 561, 1889. Bücking adopts Hausmann's name, *glaserite*, (1847), which is now commonly used in Germany, altho he admits the priority of Beudant's apthaloze (1832) and Shepard's apthitalite (1835).

<sup>5</sup> W. F. Foshag, *Am. J. Sci.*, [4], 49, 367, 1920.

<sup>6</sup> G. Ponte, *Atti Accad. Lincei*, [5], 28, 362, 1920. The occurrence of apthitalite at Etna was noted by von Waltershausen, *Der Etna*, II, p. 527, 1880.

<sup>7</sup> T. A. Jaggar, *Bull. Haw. Volc. Observ.*, 7, 185, 1919.

found the crack incandescent below, "indicating a temperature not less than 800° C." On the walls of this were "salts subliming from a vaporized condition. These salts appeared bright yellow below, green in an intermediate zone, and blue on the cooler edges. When collected with a stick the salts instantly changed completely to an azure blue color." These salts gave with ammonia a strong reaction for copper, and were considered to be copper sulfate, but the specimens collected by Jaggar and Dean have not as yet been thoroly investigated.<sup>1</sup>

When the specimens studied by us were collected no incandescence was visible, altho the crack was still very hot—so much so that the unprotected hand could not be placed in it for more than a few seconds. At cooler places in the crack, some meters from the apthitalite, the crust consisted chiefly of thenardite, colored slightly blue by copper.

The apthitalite forms small, hexagonal tables, rather poorly developed, from 2 to 5 mm. in diameter, and a millimeter or less in thickness. They are rather firmly adherent to the lava by a thin layer of what appears to be the same material. The tables are of a dull white color, with a very slightly bluish tinge; this, however, is not so pronounced as when the mineral was first collected. The tables are coated and are intergrown, to the extent of about 5 per cent., with an apparently colorless, unidentifiable salt ( $\alpha = 1.55$ ,  $\gamma = 1.585$ ). The apthitalite is uniaxial. Its optical properties are given in the table below, together with those of related minerals.

TABLE I. OPTICAL PROPERTIES OF APHTHITALITES

	K <sub>2</sub> O : Na <sub>2</sub> O	$\alpha$	$\beta$	$\gamma$	
Arcanite . . . . .	(K <sub>2</sub> SO <sub>4</sub> )	1.493	1.494	1.497	Artificial
Apthitalite . . . . .	ca. 3 : 1	1.490		1.496	Searle's Lake
Apthitalite . . . . .	ca. 1 : 1.5	1.487		1.492	Kilauea
Thenardite . . . . .	(Na <sub>2</sub> SO <sub>4</sub> )	1.471	1.477	1.484	Artificial

The optical similarities are notable; but even more noteworthy are the crystallographic similarities between arcanite (orthorhombic) and apthitalite (rhombohedral). The positions of the simple forms (001), (111), (021), (110), (100), and (010) of arcanite coincide, within  $\pm 5'$ , with the base, unit rhombohedron, and prism, of certain apthitalites; furthermore the positive acute bisectrix of arcanite corresponds to the positive

<sup>1</sup> Jaggar, *Bull. Haw. Volc. Observ.*, 8, 84 and fig. 2, 1920.

optic axis of apththitalite.<sup>1</sup> The reported inversions of potassium sulfate<sup>2</sup> and sodium sulfate<sup>3</sup> at about 600° and 200° respectively to uniaxial (probably hexagonal) forms are of interest in this connection. It would appear to be probable that both salts are isodimorphous, the hexagonal form being that of the higher temperature.

An analysis (by H. S. W.) gave the following results: SO<sub>3</sub> 51.50, Cl 0.03, K<sub>2</sub>O 23.72, Na<sub>2</sub>O 22.76, CaO 0.39, MgO none, CuO 0.46, H<sub>2</sub>O 0.25, insol. 0.76, sum 99.87%. The composition, calculated from these data, is given below, with analyses of the mineral from other localities. The references have been given above.

TABLE II. ANALYSES OF APHTHITALITE.

	Kilauea	Searle's Lake	Douglas-hall	Etna	Vesuvius	Vesuvius
K <sub>2</sub> SO <sub>4</sub> .....	43.88	72.37	66.5	38.3	70.39	50.35
Na <sub>2</sub> SO <sub>4</sub> .....	52.12	18.38	22.0	58.9	26.91	43.97
CaSO <sub>4</sub> .....	0.95	.....	.....	none	1.46	4.23
CuSO <sub>4</sub> .....	0.94	.....	.....	2.8	.....	.....
PbSO <sub>4</sub> .....	none	.....	.....	.....	.....	1.25
NaCl.....	trace	7.87	10.1	.....	.....	.....
SO <sub>3</sub> (excess) ...	0.94	.....	.....	trace	.....	.....
Cl.....	0.03	.....	.....	trace	.....	.....
H <sub>2</sub> O.....	0.25	0.10	1.0	.....	.....	.....
Insoluble.....	0.76	.....	0.4	.....	0.81	.....
	99.87	100.04	100.0	100.0	99.57	99.80

In the Kilauea apththitalite no trace of lead could be detected, altho this seems to be usually present in that from Vesuvius. Palmierite, a hexagonal sulfate of lead and potassium, was found by Lacroix in crevices of the lava of 1906, and has been more recently investigated by Zambonini,<sup>4</sup> who shows that it is apparently isomorphous with apththitalite. The occurrence of lead in the apththitalite of the highly potassic lavas of Vesuvius, while it is not present in the sodi-calcic ones of Etna and Kilauea, is a point to be noted.

The insoluble matter in the Kilauea salt was mostly (0.51)

<sup>1</sup> Zambonini (*op. cit.*, p. 318) observed a slight biaxiality in some Vesuvian apththitalites.

<sup>2</sup> Groth, *Chem. Kryst.*, II, p. 3221, 1908.

<sup>3</sup> Cf. Mügge, *Neues Jahrb. Min. Geol.*, 1884, II, 3.

<sup>4</sup> Zambonini, *Mineralogia Vesuviana*, p. 323.

volcanic ash or fragments of scoria, with a smaller amount (0.25) of what appeared to be a yellow basic ferric sulfate. It was impossible to free the material for analysis from the slight amount of admixed salt with a higher refractive index, noted above. After allowing for such physical impurities in this and other analyses, the composition of apththalite is obviously quite variable. Indeed, some of the Vesuvius specimens analyzed by Casoria seem to be acid sulfates, at least in part, and, as pointed out by Zambonini, can scarcely be considered to be apththalite.<sup>1</sup>

In view of this variability in composition, the question arises as to the constitution of apththalite—whether it is a mixture or solid solution of the two sulfates, or whether it represents, as is commonly supposed (Bücking, Groth, etc.), a double salt,  $3K_2SO_4 \cdot Na_2SO_4$ . Van't Hoff<sup>2</sup> found that sodium and potassium sulfates, under certain conditions, at a temperature of about 60°, form solid solutions, in which the proportion of potassium sulfate varies from about 62 to 77 per cent. Some of the occurrences of apththalite, such as those from Searle's Lake and Douglasshall, and some from Vesuvius, correspond to these solid solutions; altho those from Vesuvius were undoubtedly formed at much higher temperatures. On the other hand, the analysis by Ponte of the Etna mineral, and that of the Kilauea specimen, show a sodium content that is considerably greater than that found by Van't Hoff at 60°, and thus raise the question as to the character of these solid solutions at higher temperatures. The chemical character of the lavas from which they are derived, a matter mentioned above, is also a factor to be taken into consideration.

The crystallographic and optical properties of the more highly potassic members of the series are known, but the more sodic members need further study. Jaeger<sup>3</sup> found that the rhombohedral angle increased with the sodium content; and the refractive indices of the highly sodic Hawaiian crystals are the lowest yet observed.

<sup>1</sup> Casoria, (cited by Zambonini), determined copper in several specimens; and in one he found small amounts of Mg, Mn, Cu, Zn, Mo, Co, and Bi. The actuality of the presence of the last four may, possibly, be regarded as doubtful.

<sup>2</sup> Van't Hoff and Barschall, *Sitzb. preuss. Akad. Wiss.*, 1903, 359-371.

<sup>3</sup> In Van't Hoff and Barschall, *op. cit.*

A word may be said in regard to the copper content of the Kilauea apthitalite. The decidedly bluish color that the salt showed when first collected has gradually faded out, until now (January, 1921) it is almost colorless. Heating to about 300° partly restores the color, which fades again in a few days. The presence of acid sulfates may partly control these color changes. Anhydrous copper sulfate fuses with apthitalite mixtures of varying composition to form mix-crystals<sup>1</sup> varying in color according to the proportions of potash and soda, as well as the amount of copper. The colors have remained permanent for some weeks.

Anhydrous copper sulfate, crystallized from hot sulfuric acid, forms thick, lozenge-shaped or hexagonal tables, with bounding angles of sensibly 60°. Optically the symmetry is orthorhombic, altho the optical characteristics are not entirely clear because of an hour-glass twinning structure seen thru the edges of some grains:  $\beta = 1.72$ , and  $\gamma - \alpha = 0.02$ . A close crystallographic relationship to apthitalite and the alkali sulfates is thus indicated.

The reference books (Abegg and Gmelin-Kraut) state that anhydrous copper sulfate is colorless or slightly bluish gray. The grayish white color of the pulverulent salt produced by heating the pentahydrate is much deepened by wetting with a liquid of similar refractive index; so that crystals of megascopic size must be distinctly colored, probably dull greenish blue.

As to the mode of formation of apthitalite, Ponte suggests that, at Etna, alkali chlorides were first formed, and that these were changed to sulfates when the fumarole temperature had decreased to about 500°, and sulfur trioxide had begun to be evolved. At Kilauea, on the other hand, hydrochloric acid and chlorides are present in but very small amount, while SO<sub>2</sub> and SO<sub>3</sub>, as well as S, are abundant.<sup>2</sup> It may therefore be suggested that, at Kilauea (and possibly also at Etna) the alkalies and copper were volatilized as sulfides, in the gases escaping from the lava, and that the sulfates were formed and deposited where these gases were oxidized by contact with the air.

<sup>1</sup> Copper sulfate increases the refractive indices to at least  $\alpha = 1.505$ ,  $\beta = 1.545$ ,  $\gamma = 1.580$ , for crystals that are deep green or bluish green, and which contain about 30 per cent of copper sulfate.

<sup>2</sup> Day and Shepherd, *Bull. Geol. Soc. Am.*, 24, 588, 1913; Shepherd, *Bull. Haw. Volc. Observ.*, 7, 94, 1919.