REEXAMINATION OF SPHENE (TITANITE)[1]

HOWARD W. JAFFE[2]

ABSTRACT

Sphene (titanite) invariably contains a minor amount of fluorine, as well as varying amounts of R_2O_3. R includes Fe, Al, Y and Ce. On the basis of similarities of ionic radii, trivalent Cr and quinquevalent Cb may be expected to proxy for quadrivalent Ti. An occurrence of a chromiferous sphene from California is described. The presence of Cb in sphene is verified.

GENERAL

A portion of the data included in this paper was originally incorporated into a manuscript completed in July 1946. Shortly thereafter some additional data on sphene was obtained and necessitated a revision of and an addition to the original manuscript. Upon completion of this second manuscript, it was learned that Th. G. Sahama had been engaged in a similar study in Helsinki, Finland, and had published a paper, "On the Chemistry of the Mineral Titanite," in the *Bulletin de la Commission Geologique de Finlande*, N:o 138, 1946. Although this paper was not available to American readers until very recently, Dr. Sahama's priority in this study is apparent. Consequently, a section on the isomorphous replacements in sphene has been deleted from the present paper in deference to Sahama's very thorough treatment of the subject.

Although several of the writer's findings are similar to those of Sahama, the studies were made of sphenes and keilhauites from different localities than those described by him. The six sphenes described by Sahama are all from Finnish or Russian localities, whereas the sixteen sphenes described by the present writer are representative of a more world-wide distribution of this mineral. The significance of two independent investigations of different samples of sphene leading to similar analytical results and theoretical conclusions is apparent.

FLUORINE IN SPHENE

During a routine visual spectroscopic examination of sphene, it was observed that the mineral contained fluorine. After microscopic examination showed the sample to be homogeneous, sixteen additional samples of sphene were examined in a like manner. All were found to contain fluorine in minor amounts. Most of the samples were furnished through

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[2] Chemist-Petrographer, Metallurgical Branch, College Park Division, Bureau of Mines, College Park, Maryland.

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A very rapid and an exceedingly sensitive qualitative method for detecting fluorine in minerals is that of visual arc spectroscopy. This method was described by Papish, Hoag and Snee (1930) and more recently by Peterson, Kauffman and Jaffe (1947). Fluorine may be readily detected spectroscopically, provided the sample contains calcium. When both elements are present and the sample is subjected to arc excitation, visual observation of the calcium fluoride band serves for the detection of fluorine. The band has its maximum or head at 5291 Å and fades toward the red or long wavelength portion of the spectrum. If the mineral does not contain calcium, any pure salt of calcium may be added. In such instances the salt should first be examined spectroscopically in order to determine that fluorine is not present as an impurity. Recent studies indicate that under normal operating conditions, the visual method is more sensitive than the photographic plate, as regards the detection of calcium fluoride. Papish, Hoag and Snee (1930) state that the calcium fluoride band cannot be detected in the arc spectrum (presumably the spectrogram) of topaz without the addition of a calcium salt. The writer recently examined samples of topaz from Nigeria, Brazil, Connecticut, Virginia and North Carolina and was able to detect the calcium fluoride band in all five samples by visual spectroscopic examination and without the addition of a calcium salt. Similarly, the band was observed in samples of amblygonite, muscovite, biotite, and wavellite. Apparently a small amount of calcium is present as an impurity in all of these minerals. Fluorine in minerals may be detected by this method in concentrations of

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quadrivalent Ti (0.64 Å) may be cited in support of Sahama's calcula-

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F)$_5$, where X = Y, Ce, Na, Mn, Sr, (Ba) and Z = Fe, Al, Cr, Cb, (Ta), V, Mg.

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sphene is questionable. Mellor (1930) notes that sphene is not easily synthesized but lists several investigators who claim to have done so. The possibility exists that the constituents used in the syntheses contained a minor amount of fluorine as an impurity.

Sphene occurs in a wide variety of rocks and the presence of fluorine is not necessarily attributed to pegmatitic activity. It is found in igneous and metamorphic rocks and to a lesser extent as a detrital mineral. Host rocks include syenite, nepheline syenites, phonolite, monzonite, granite, talc schist, mica slate, tactite, skarn, metamorphosed limestone, chlorite schist and amphibolite. Fluorine was detected in samples of sphene occurring in syenite (#15—Table 3); in tactite (#13—Table 3); in chlorite schist (#5—Table 3); and in a detrital heavy mineral sand (#12—Table 3).

R_2O_3 IN SPHENE

Sphene has long been known to contain varying amounts of R_2O_3 with R = Fe, Al, Y and Ce replacing calcium and titanium. Where the substitution becomes significant, the varietal names kielhauite and yttrotitanite are sometimes used. In recent years, it has been shown that sphene and keilhauite have virtually identical *x*-ray diffraction patterns (Young, 1938, and Kauffman and Jaffe, 1946) although the axial angles and refractive indices may show slight to moderate variation. According to Goldschmidt (1945) and others, large-scale isomorphous substitution in minerals may take place most reaily where the pairs of ions involved have similar ionic radii. For a thorough study of the isomorphous mixtures encountered in sphene, the reader is referred to the very recent paper by Sahama (1946). In brief review we find that Ca^{++} and Y^{+++} both have ionic radii of 1.06 Å. and might be expected to replace one another in sphene. Similarly, Fe^{+++} and Al^{+++} have ionic radii of 0.67 Å. and 0.57 Å., respectively, and may proxy for Ti^{++++}, which has an ionic radius of 0.64 Å. Sahama notes the following replacements found in sphene.

> "Calcium: Na, Rare Earths, Mn, Sr, (Ba).
> Titanium: Al, Fe (ferric and ferrous), Mg, Nb, (Ta), V, (Cr).
> Oxygen: OH, F, (Cl?)."

Chromium, placed in parentheses, was reported in two of his six analyses; 0.01 per cent Cr_2O_3 in Analysis 2 and 0.02 per cent in Analysis 3. He calculates that if the abundance relation of titanium to chromium in the sphene lattice was the same as in the igneous rocks in average, this mineral would contain as much as 1.6 per cent Cr_2O_3. Sahama concludes that, in spite of the small number of determinations, this figure is at best a theoretical value and apparently is high.

An unusual instance of the substitution of trivalent Cr (0.64 Å) for quadrivalent Ti (0.64 Å) may be cited in support of Sahama's calculations. A sample of sphene in a tactite recently submitted to the Eastern Experiment Station, College Park, Maryland, has a Cr_2O_3 content of 0.3–0.8 per cent. The sample was sent by J. M. Musgrave of Pasadena, California, who states that it occurs in "the southern California desert area." Further field information was not given.

The tactite contains several small grass-green crystals of chromiferous sphene. These have an average grain diameter of 0.5 mm. and are imbedded in a matrix of buff idocrase and gray-green diopside. Several grains of deep emerald green uvarovite are present. These show a maximum size development of 10 mm.

In plane-polarized light, the sphene shows a marked pleochroism, with X colorless, Y pale yellow-green, and Z grass-green. The intermediate index is 1.91 and the birefringence equal to 0.12. The mineral is optically positive with 2V equal to approximately 35°. Dispersion is strong with $r>v$.

Not enough pure material could be selected for a quantitative chemical analysis. Spectrographic analysis, however, shows that the Cr_2O_3 content lies in the range of 0.3 to 0.8 per cent. An *x*-ray powder diffraction pattern obtained with Cu radiation proved to be identical with that of normal sphene.

COLUMBIUM IN SPHENE

An additional minor element found in some samples of sphene is columbium. Eight of the sixteen samples examined spectroscopically contained this element. Quinquevalent Cb having an ionic radius of 0.69 Å should be expected to substitute for quadrivalent Ti with a radius of 0.64 Å. Four of these samples were analyzed spectrographically. The results are given in Table 2.

TABLE 2. COLUMBIUM CONTENT OF SPHENE (SPECTROGRAPHIC)

Locality	Cb_2O_5
1. Bancroft, Ontario	0.1 -1.0
2. Midongy, Madagascar	0.05-0.5
3. S. W. Africa (Kahn Mine)	0.1 -1.0
4. Arendal, Norway	0.1 -1.0

CONCLUSIONS

As pointed out by Young (1938) and recently emphasized by Sahama (1946), many analyses of sphene are in the neighborhood of 50 years old and in many of these only the three constituents, CaO, TiO_2 and SiO_2 were determined. As is shown in Table 3, ferric iron, alumina and fluorine are commonly present in sphene and frequently are not reported by analysts. In the light of recent studies, it appears that the generally accepted but old formula, $CaTiSi_2O_5$, needs revision. Accordingly the following more inclusive formula is offered for sphene: (Ca, X) (Ti, Z) Si_2 (O, OH,

TABLE 3. VISUAL SPECTROSCOPIC ANALYSES OF SPHENE

Locality	CaO	TiO_2	SiO_2	F	Fe_2O_3	Al_2O_3	Cb_2O_5	R.E.*	Cr_2O_3
1. Delaware Co., Pa. (N.M. 92843)	M	M	M	m	m	m	—	—	—
2. North Carolina (N.M. 48811)	M	M	M	m	m	m	—	—	—
3. Ontario (N.M. 97487)	M	M	M	m	m	m	—	—	—
4. Kola, U.S.S.R. (N.M. 103300)	M	M	M	m	m	m	m	m	—
5. Washington, D. C. (N.M. 45848)	M	M	M	m	m	m	—	—	—
6. Askero, Norway (N.M. R7134)	M	M	M	m	m	m	m	m	—
7. Arendal, Norway (N.M. 49019)—var. keilhauite	M	M	M	m	m	m	m	m-M	—
8. Natural Bridge, N. Y. (N.M. C3921)	M	M	M	m	m	m	—	—	—
9. Midongy, Madagascar (H.M. 88743)	M	M	M	m	m	m	m	m	—
10. Arendal, Norway (H.M. 87737)—var. keilhauite	M	M	M	m	m	m	m	m-M	—
11. S. W. Africa (Kahn Mine)** (H.M. 89494)—var. keilhauite	M	M	M	m	m	m	m	m	—
12. El Dorado Co., Calif. (C.P. A209)	M	M	M	m	m	m	—	—	—
13. S. California (C.P. A209-*a*)	M	M	M	m	m	m	—	—	m
14. Kragero, Norway (C.P. A208)	M	M	M	m	m	m	m	m	—
15. Bancroft, Ontario (C.P. A208-*a*)	M	M	M	m	m	m	m	m	—
16. N.Y. (C.P. 323)—var. yttrotitanite	M	M	M	m	m	m	—	m	—

* R.E. = Rare Earths, mostly Y_2O_3 and Ce_2O_3 N.M. = National Museum
M = Major constituent H.M. = Harvard Museum
m = Minor constituent C.P. = College Park Petrographic Lab.
** Contains an opaque Cu mineral.

F)$_5$, where X = Y, Ce, Na, Mn, Sr, (Ba) and Z = Fe, Al, Cr, Cb, (Ta), V, Mg.

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