

SHORT COMMUNICATIONS

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A tantalum-rich variety of sphene

NIObIUM and tantalum have long been recognized as important minor constituents of sphenes. Since these elements have ionic radii of 0.69 and 0.68 Å respectively their substitution for titanium (0.68 Å) in the structure is not unexpected, but no reliable reports exist of sphenes containing more than 2 % ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$). One of the highest concentrations of these elements was noted by Sahama (1946) in a large zoned sphene crystal from Nuolainniemi, Impilahti, Finland, the altered part of which contained 3.3 % Nb_2O_5 and 2.9 % Ta_2O_5 . The crystal, however, contained numerous inclusions of a mineral thought to be wiikite, a metamict niobotantalate of Ti, the rare earths, Ca, and U, which casts some doubt on the analysis. A sphene from the Kola Peninsula has been reported by Burova (in Fersman and Bohnstedt, 1937) as containing 1.87 % ($\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$).

We have recently obtained further information on this subject during an examination of the type specimen of strüverite (spec. no. BM. 1906, 123). This strüverite occurred as small black crystalline masses embedded in feldspar and quartz from the pegmatite at Craveggia, Piemonte, Italy, and was examined originally by Prior and Zambonini (1908). For the purpose of the present investigation a small, poorly polished fragment was dissolved out of Prior's resin mount and re-embedded in a modern resin. When the fragment had been polished several grey intergrown inclusions were observed in the strüverite. These had not been reported in the earlier work.

The elements present in the grey inclusions were determined by running complete Bragg angle scans with the electron probe and subsequently carrying out quantitative analyses of this phase and the strüverite. Pure metal standards were used for all the elements determined except calcium, silicon, aluminium, and sodium for which analysed wollastonite, olivine, corundum, and jadeite respectively were used. The analyses were made at an accelerating potential of 20 KV using a Geoscan microanalyser. After correcting the counts obtained for instrument dead time and subtracting the continuous background, the measured concentrations were corrected for effects arising from X-ray absorption, secondary fluorescence, and average atomic number differences between the specimen and standards, using the BM-IC-NPL computer programme (Mason *et al.*, 1969). The analyses are given in Table I.

The grey inclusions in the strüverite were found to be a silicate of titanium, tantalum, calcium, and aluminium with minor amounts of niobium, iron, sodium, and manganese. It was at first thought to be the tantalum analogue of fersmanite, $(\text{Na,Ca})_2(\text{Ti,Nb})\text{Si}(\text{O,F})_6$ (Starynkevich-Borneman, 1936), but an X-ray powder photograph gave lines that identified it as a sphene. The composition of an ideal sphene is given for comparison purposes in Table I (b). The strüverite analysis (c) can be compared

TABLE I. *Electron-probe analyses of tantalian sphene and of strüverite*

	(a)	(b)	(c)		Numbers of ions on the basis of 20 oxygens	
					(a)	(b)
SiO ₂	26.9	30.65	—	Si	3.87	4.00
Al ₂ O ₃	5.1	—	—	Al	0.87	—
TiO ₂	22.2	40.75	47.8	Ti	2.40	4.00
Nb ₂ O ₅	2.9	—	6.5	Nb	0.19	—
Ta ₂ O ₅	16.0	—	35.5	Ta	0.63	—
SnO ₂	0.1	—	0.3	Sn	0.01	—
FeO	0.9	—	9.2	Fe ²⁺	0.10	—
MnO	0.05	—	0.1	Mn	0.01	—
Na ₂ O	0.3	—	—	Na	0.10	—
CaO	25.6	28.60	—	Ca	3.95	4.00
	100.1	100.0	99.4			

(a) BM. 1906, 123 grey inclusions in strüverite.

(b) Theoretical sphene.

(c) BM. 1906, 123 strüverite.

TABLE II. *Indexed powder data for sphene and tantalian sphene*

1. PDF card 11-142 sphene.

2. BM. 1906, 123, grey inclusions. Lines for which intensities could not be estimated because of the coincidence of strüverite (rutile) lines, also present in the powder, are indicated by +.

<i>hkl</i>	1		2		<i>hkl</i>	1		2	
	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>		<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>
$\bar{1}11$	30	4.93	m	4.93	240	10	1.725	—	—
$111, 002$	100	3.233	ms	3.235	$\bar{2}24$	30	1.703	+	1.705
$\bar{2}02$	90	2.989	m	2.992	$\bar{3}33$	40	1.643	+	1.641
200	5	2.841	—	—	151, 241	20	1.554	vw	1.557
$\bar{2}\bar{2}\bar{1}, 022$	90	2.595	mb	2.598	043, $\bar{1}34$	10	1.527	vwv	1.527
$\bar{1}\bar{1}3, 220$	5	2.362	—	—	133	40	1.494	—	—
$112, \bar{1}32$	30	2.273	w	2.275	400	40	1.418	w	1.419
131	5	2.225	—	—		20	1.409	vwv	1.408
$\bar{3}12$	20	2.101	vwv	2.106		20	1.344	vwv	1.344
$\bar{3}11$	40	2.058	mw	2.062		20	1.306	vwv	1.302
221	10	1.972	—	—		10	1.275	vwv	1.274
$\bar{3}13$	10	1.945	—	—		5	1.227	—	—
$\bar{2}04, 310$	5	1.848	—	—		10	1.132	—	—
042, $\bar{2}41$	10	1.802	vw	1.800		5	1.117	—	—
$\bar{3}32$	20	1.741	vw	1.743		10	1.107	+	1.106

with Prior and Zambonini's (1908) analysis and it is found that (c) falls nearer rutile in the tapiolite-rutile series ($\text{FeTa}_2\text{O}_6\text{-TiO}_2$) than the original analysis. Apart from 0.51 % CaO their analysis shows no evidence of admixture with a mineral with a composition corresponding to the grey inclusions.

Considering that almost half the sites of quadrivalent titanium have been replaced by quinquevalent tantalum, the X-ray powder data for these inclusions compares remarkably closely with the reference data for normal sphene given on PDF card 11-142 (Table II). Had the mineral been related to fersmanite (PDF card 14-27a) its pattern would have been completely different.

Optical data could not be obtained for the sphene owing to the limited amount of material available and the fact that the small inclusions are intimately intergrown with opaque strüverite. However, from the chemical data it can be concluded that the sphene has crystallized with appreciable tantalum, niobium, and aluminium occupying titanium sites. This substitution has not been accompanied by any significant replacement of calcium by sodium (or any other element) contrary to Sahama's (1946) suggestion that titanium replacement by niobium or tantalum is accompanied by a simultaneous replacement of calcium by sodium.

Since there was no experimental evidence to the contrary Sahama concluded that, despite the lack of any structural limitations, tantalum and niobium do not enter into minerals with the sphene structure as major components, but when present in sufficient concentration, as in certain pegmatites, tend to crystallize as oxide minerals such as pyrochlore. However, in the mineral described, almost half the available titanium sites in the sphene are occupied by tantalum, niobium, and aluminium, showing that this statement needs to be modified, and that tantalian sphene does in fact exist.

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