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Niobian Sphene from the McDonald Pegmatite Mine, Bancroft, Ontario, Canada: Consideration of Substitutions

카나다 온타리오 밴크로프트의 맥도날드 페그마타이트 광산에서 산출된 Nb Sphene: 원소 치환에 관한 고찰

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ABSTRACT: Sphene from the McDonald pegmatite mine near Bancroft, Ontario, Canada was analyzed using EPMA. It contains 4.3 to 6.3 weight percent of Nb_2O_5 with an average formula $Ca_{1.02}(Ti_{0.62}Al_{0.22}Nb_{0.07}Fe_{0.06}Ta_{0.01})Si_{0.99}(O_{4.85}F_{0.16})$. Three types of subtitutions are possible; 1) $2Ti^{4+} = (Nb, Ta)^{5+} + (Al, Fe^{3+})$, 2) $Ti + O = (Al, Fe^{3+}) + (F, OH)$,and 3) $2Ti + O = Fe^{2+} + (Nb, Ta)^{5+} + (F, OH)$.

Two different schemes of substitutions for balancing the analysis are considered when the iron is either all ferric or all ferrous. Assuming stoichiometry for Ca and Si, a general formula derived from the two different schemes is $Ca(Ti_{0.64}Al_{0.22}Fe^{3+}_{0.06-x}Fe^{2+}_{x}Nb_{0.07}Ta_{0.01})SiO_{4.80-x}F_{0.16}(OH)_{0.04+x}$.

요약 : 카나다 온타리오주 Bancroft 부근 McDonald pegmatite 광산에서 산출된 sphene에 대한 EPMA 분석결과 4.3 내지 6.3 중량 퍼센트의 Nb_2O_5가 검출되었다. 분석치로부터 계산된 평균 화학식은 $Ca_{1.02}(Ti_{0.62}\ Al_{0.22}\ Nb_{0.07}\ Fe_{0.06}\ Ta_{0.01})Si_{0.99}(O_{4.85}\ F_{0.16})$이다. 이 화학식에는 세 종류의 원소치환이 가능하다; 1) $2Ti^{4+} = (Nb, Ta)^{5+} + (Al, Fe^{3+})$, 2) $Ti + O = (Al, Fe^{3+}) + (F, OH)$ 그리고 3) $2Ti + O = Fe^{2+} + (Nb, Ta)^{5+} + (F, OH)$.

분석치의 원자가 균형을 맞추기 위해 두개의 다른 방법, 즉 철이 모두 +3가인 경우와 모두 +2가인 경우가 고려되었다. Ca와 Si가 stoichiometry에 맞는 경우 이들 두개의 방법으로부터 얻어지는 일반적인 화학식은 $Ca(Ti_{0.64}\ Al_{0.22}\ Fe^{3+}_{0.06-X}\ Fe^{2+}_{X}\ Nb_{0.07}\ Ta_{0.01})\ SiO_{4.80-X}\ F_{0.16}(OH)_{0.04+X}$이다.

INTRODUCTION

Niobium is often found in sphene ($CaTiSiO_4$) as a minor constituent. Sahama(1946) analyzed 3.3% of Nb_2O_5 in sphene from the altered part of a large zoned sphene crystal from Nuolainniemi, Impilahti, Finalnd. Most of the niobian sphene analyzed, however, contain less than 2% of Nb_2O_5. Clark(1974) reported 2.9% Nb_2O_5 along with 16.0% Ta_2O_5 in sphene from inclusions of sphene intergrown in struverite and Paul *et al.*(1981) recently reported an analysis of sphene with unusually high content of Nb_2O_5 (6.5 wt.%) and Ta_2O_5(3.7 wt.%) from a pegmatite in southeastern Manitoba, Canada.

Malayaite, $CaSnSiO_5$, occurs as a limited solid solution(Tachenouchi, 1971) with sphene($CaTiSiO_5$). Not only Sn, but also many other minor elements substitute into sphene. Sr, Ba and Na as alkaline earths and alkali elements, and Ce, Nd, and Y among rare earth elements(REE) are common substituents for Ca in sphene. Mn(Roy, 1974) Th, U, and radiogenic Pb(Higgins and Ribbe, 1976) are also reported. Ti is mostly substituted by Al and Fe^{3+} with compensating OH for O. Minor or trace amounts of Cr, Fe^{2+}, Cu, Mg, Zr^{4+}, and V^{5+}, as well as Nb and Ta, also substitute for Ti.

Wedge-shaped dark brown crystals of sphene are well developed in pink calcite and quartz pegmatite at the McDonald mine, at Bancroft, Ontario. The crystals range from microscopic sizes(~1 mm) to over 10 cm across. Careful examinations of a hand specimen also reveal the presence of elsworthite(pyrochlore). Small grains of albite and inhomogeneous Ti, Nb oxide (struverite?) were identified during the study of energy dispersive spectra. The Ti, Nb oxide was not analyzed due to extreme variation in the composition. The purpose of this paper is to introduce the occurence of sphene with unusually high content of Nb and to estimate substitutions without analyzing for Fe^{2+}, Fe^{3+} and H_2O.

EXPERIMENTAL

The sphene was analyzed using wavelength dispersive method on an ARL-EMX electron microprobe at the University of Michigan (Table 1). The analyses, each averaged from counts of three spots were taken from two different grains; Nos. 1-8 from one grain and 9-10 from the other. As indicated by the standard deviations in the table, little compositional variation was detected within a grain or between the grains during the wavelength dispersive analysis. No other minor substituents than those analyzed were detected in the energy dispersive spectral analysis.

The standards for electron microprobe analyses were synthetic sphene for Si, Ca, and Ti; synthetic Nb_2O_5 for Nb; Thetford grossular for Al; Marjahaliti olivine for Fe; Irving kaersutite for Na; fluorapatite for F; chlorapatite for Cl; and microlite for Ta. Analysis was conducted at 15 KV with 150 μA beam current and 0.005-0.01 μA sample current conditions. The data collected on the EPMA then processed using a computer program EMPADR for further reduction (ZAF correction, etc.)

DISCUSSION

Table 2 shows the number of ions normalized from the anlyses based on 3 total cations. The value for each atom was averaged from 10 analyses in the last column of Table 2. The average formula from the 10 analyses is $Ca_{1.02}(Tl_{.62}\ Al_{.22}\ Nb_{.07}\ Fe_{.06}\ Ta_{.01})_{.98}\ Si_{.99}\ (O_{4.85}\ F_{.16})_{5.01}$. The total charge balance is slightly off (total cation, +9.72 when ferric iron is assumed and total anion, −9.86) probably due in part to the substitution of hydroxyl ions for oxygen. The substitution of OH becomes more significant if the iron is all ferrous. Fe can occur as either +3 or +2 valence state and the both have been frequently reported in the analyses of sphene.

A series of substitutions can be considered to account for the associated substituents in the analyses and for charge balances:

$$2Ti = (Nb, Ta)^{5+} + (Al, Fe^{3+}) \quad (1)$$

Table 1. 10 Analyses of Nb-Sphene.*

Oxides	1	2	3	4	5	6	7	8	9	10	Ave.
SiO_2	30.99	30.83	30.55	31.20	29.20	30.15	30.47	30.56	30.74	30.64	30.53(66)&
TiO_2	24.99	25.69	25.18	25.14	25.36	25.58	25.16	25.48	24.99	25.45	25.30(25)
Nb_2O_5	4.42	5.12	5.37	5.33	5.36	4.94	4.27	4.89	6.19	5.70	5.16(57)
Ta_2O_5	.49	1.33	.92	.88	1.20	.98	.69	1.01	.89	.67	.91(25)
Al_2O_3	5.53	5.61	5.45	5.34	5.77	5.58	6.06	6.04	5.76	5.66	5.68(23)
FeO@	2.15	2.17	2.27	2.16	2.16	2.14	2.27	2.20	2.13	2.12	2.18(05)
CaO	29.91	29.60	29.72	29.55	28.75	29.58	28.98	29.37	29.10	29.46	29.40(36)
Na_2O	.08	.07	.04	.06	.08	.05	.03	.05	.09	.09	.06(02)
F_2#$	.91	.85	.90	.87	.92	.90	.99	.97	.81	.85	.90(06)
$Cl_2$$	.02	.01	.00	.02	.00	.00	.00	.00	.00	.03	.01(01)
Total	99.49	101.28	100.40	100.55	98.80	99.90	98.92	100.57	100.70	100.67	100.13(82)

* 15 KV, 150μA beam current and 0.005-0.01 μA sample current were used.
& Standard deviations in paranthesis.
@ Total iron as FeO.
# Pulse height analysis was used to locate the peak.
$ 0 = 2 (F, Cl).

Table 2. No. of Atoms in Nb-Sphene.*

Atoms	1	2	3	4	5	6	7	8	9	10	Ave.	
Ca	1.04	1.02	1.03	1.03	1.02	1.03	1.02	1.02	1.01	1.02	1.02	
Na	.00	.00	.00	.00	.00	.00	.00	.00	.01	.01	.00	
Ti	.61	.62	.61	.61	.63	.63	.62	.62	.61	.62	.62	
Al	.21	.21	.21	.20	.23	.21	.23	.23	.22	.22	.22	
Fe	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.06	.98
Nb	.06	.07	.08	.08	.08	.07	.06	.07	.09	.08	.07	
Ta	.00	.01	.01	.01	.01	.01	.01	.01	.01	.01	.01	
Si	1.01	.99	.99	1.01	.97	.98	1.00	.99	1.00	.99	.99	
F	.16	.15	.16	.15	.17	.16	.18	.17	.14	.15	.16	
Cl	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	
O	4.83	4.85	4.84	4.85	4.85	4.84	4.84	4.84	4.86	4.86	4.85	

* Analyses in Table 1 are normalized based on 3 total cations.

$Ti + O = (Al, Fe^{3+}) + (F, OH)$. . . . .(2)
$2Ti + O = Fe^{2+} + (Nb, Ta)^{5+} + (F, OH)$. . . .(3)

The contributions of each substitution in the formula above may be counted for the both valence states of iron:

1) for all Fe^{+3}

$.08\ [2Ti = (Nb, Ta) + (Al, Fe^{3+})]$
$.16\ [Ti + O = (Al, Fe^{3+}) + F]$
$.04\ [Ti + O = (Al, Fe^{3+}) + OH]$

$Ti_{.36} + O_{.20} = (Nb, Ta)_{.08} + (Al, Fe^{3+})_{.28} + F_{.16} + (OH)_{.04}$

2) for all Fe^{2+}

$.06\ [2Ti + O = Fe^{2+} + (Nb, Ta) + (F, OH)]$
$.02\ [2Ti = (Nb, Ta) + Al]$
$.20\ [Ti + O = Al + (F, OH)]$

$Ti_{.36} + O_{.26} = (Nb, Ta)_{.08} + Al_{.22} + Fe^{2+}_{.06} + F_{.16} + (OH)_{.10}$

From the basis of the substitutions discussed above, the ideal formula when stoichiometric Ca and Si are assumed and when the number of niobium ion is slightly modified, is; for Fe^{3+} end-member, $Ca(Ti_{.64}\ Al_{.22}\ Fe^{3+}{}_{.06}\ Nb_{.07}\ Ta_{.01})SiO_{4.80}\ F_{.16}(OH)_{.04}$ and for Fe^{2+} end-member, $Ca(Ti_{.64}\ Al_{.22}\ Fe^{2+}_{.06}\ Nb_{.07}\ Ta_{.01})SiO_{4.74}\ F_{.16}(OH)_{.10}$. The both formula exactly charge balance and an intermediate distribution of Fe^{3+} and Fe^{2+} can be expressed as $Ca(Ti_{.64}\ Al_{.22}\ Fe^{3+}_{.06-x}\ Fe^{2+}_{x}\ Ta_{.01})SiO_{4.80-x}F_{.16}(OH)_{.04+x}$ where $x \leqslant .06$.

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