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RARE EARTHS IN MINERALS OF THE JOAQUINITE GROUP

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ABSTRACT

An apparently new rare-earth mineral of the joaquinite group occurs in nephelin-syenite pegmatites of Ilimaussaq alkaline massif (S. Greenland). Optical and X-ray properties are the same, as for standard joaquinite $NaBaTi_3Si_4O_{15}$ from California, but the chemical analysis is quite different: SiO_2 33.82, Nb_2O_5 2.31, TiO_2 9.20, Fe_2O_3 0.39, FeO 4.78, MnO 0.70, ThO_2 0.38, RE_2O_3 22.59, BaO 21.46, (Ca, Sr)O 0.03, Na_2O 2.41, K_2O 0.22, H_2O 1.50, F 0.38, $-O=F_2-0.16$, sum 100.01. The formula is $NaBa_2Fe^{2+}Ce_2Ti_2Si_8O_{26}(OH)$ $(Z=4)$. Semiquantitative analyses of California joaquinite also showed the presence of considerable rare earths.

INTRODUCTION

During summer field work (1964) in the expedition of the Greenland Geological Survey, headed by H. Sørensen, in the Ilimaussaq alkaline massif (S. Greenland), E. I. Semenov found an unknown mineral of composition $NaBa_2FeCe_2Ti_2Si_8O_{26}(OH)$ containing 23% RE_2O_3 in the nepheline syenite pegmatites. At present no barium-titanium silicate minerals containing rare earths are known. However, the Soviet Commission on New Minerals observed the similarity of unit cell dimensions and optical affinities of this mineral with joaquinite, $NaBa(Ti,Fe)_3Si_4O_{15}$, for which the content of rare earths was not shown in analyses. Therefore both minerals were studied.

Joaquinite has been described from San Benito County, California (Palache and Foshag, 1932), and from Seal Lake, Quebec, Canada (Bell, 1963). One California specimen (No. 1) is from Ward's collection; No. 2 is from Dr. Brian Mason, National Museum, Washington (USNM No. 103055); and the Canadian specimen was donated to us by Dr. E. H. Nickel, Department of Mines and Technical Surveys, Ottawa, Canada.

OCCURRENCE

In San Benito County, California, joaquinite occurs in natrolite veins with neptunite and benitoite. These veins transect glaucophane schists which contain 0.023% RE of the yttrium-cerium group: $La_{12.9}Ce_{33.5}Pr_{3.1}Nd_{12.9}Sm_{3.0}Gd_{3.9}Dy_{3.1}Er_{2.4}Yb_{2.2}Y_{23.2}$. Vesuvianite with 16.7% Ce_2O_3 was recently found near a benitoite mine shaft in high-temperature veins with garnet and perovskite (Murdoch and Ingram, 1966). At Seal Lake, Quebec, joaquinite occurs in fenitized gneisses and

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alkaline syenites together with aegirine, barylite, eudidymite, and neptunite.

The following is a detailed description of our "apparently" new rare earth mineral of the joaquinite group from Southern Greenland. In the northwest part of the Ilimaussaq alkaline massif, on the right bank of the Narssaq River at the foot of Kuanefield Mountain, a mineral occurs in nepheline-sodalite syenitic pegmatites. A pegmatite lens 4×7 meters in size occurs at the contact between gneissic nepheline syenite (lujavarite) and parent poikilitic sodalite syenite (naujaite). The pegmatite border zone is melanocratic, consisting of aegirine and microcline and its central part is leucocratic natrolite-analcime. The joaquinite-type rare-earth mineral occurs in the intermediate zone, which also contains riebeckite, analcime, sodalite, and steenstrupine. Pistachio-green ochres of rabdophane are products of weathering of this mineral or steenstrupine.

General Physical and Chemical Properties

The weight of joaquinite from specimen (No. 1) is 2.5 mg, (No. 2) is 12.4 mg, and (No. 3) is 1.0 mg. By means of chemical analyses and chromatography, YU. A. Balashov established the presence and content of individual rare-earth elements in all these specimens (Tables 1 and 2). Semiquantitative analyses of the smallest specimens (Nos. 1 and 3) showed about 15% RE_2O_3. More exact determinations in the largest specimen (No. 2) indicated 11.5% TR_2O_3 (and also presence of Ca and Sr). Thus joaquinite from California and Quebec contain rare earths, but their amount is half of the content of rare earths occurring in the Greenland specimen. Also other substantial differences appear to exist in the content of (Ca, Sr)O, TiO_2, and other elements and hence, in chemical affinities of these minerals (Table 1).

The mineral from Greenland (and from Canada?) with the highest quantity of rare earths (and niobium) has maximum volume (2280 Å^3) and dimensions of unit cell (especially, $b=10.54$). The California mineral with a lower content of rare earths has a volume (2232 Å^3) and $b=10.465$ Å (Bell, 1963).

Apparently we have not one joaquinite, but different minerals of the joaquinite group. But this problem can be completely solved only by a new complete chemical analysis of the California-type mineral, since its first analysis (by W. F. Foshag) was incorrect. The establishment of rare-earth content in the California joaquinite shows the existence of a new type of rare-earth concentrations, in hydrothermal deposits, genetically connected with harzburgites (serpentinites, glaucophane-, jadeite-albite rocks), which are known also in the USSR in western Sayan, northern Urals, Kamchatka, and central Kazahstan.

TABLE 1. COMPOSITION AND CHARACTERISTICS OF MINERALS OF THE JOAQUINITE GROUP

	Greenland	California			Quebec
			Specimen No. 1	Specimen No. 2	
SiO_2	33.82	36.4			
Nb_2O_5	2.31	—			
TiO_2	9.20	30.5			
RE_2O_3	22.59	—	15.0	11.5	15.0
FeO	4.78	3.5			
(Ca,Sr)O	0.03	—		8.1	
BaO	21.46	24.7	18.0	18.1	
Na_2O	2.41	4.6			
H_2O	1.50	—			
Others	1.91[1]	0.3(MgO)			
Total	100.01	100.0			
Analyst:	M. E. Kazakova	W. F. Foshag	YU. A. Balashov		

[1] ThO_2 0.38, MnO 0.70, K_2O 0.22, Fe_2O_3 0.39, $F=0.38-O=F_2$ 0.16.

	Greenland	California		Quebec
			Specimen No. 1	
Specific Gravity	4.1	3.89	—	—
γ	1.797	1.823		1.80
α	1.754	1.748		1.752
$2V$	+40°	+50°		—
a in Å	9.680	9.61	9.688	9.699
b	10.539	10.45	10.522	10.533
c	22.345	22.40	22.283	22.33
	V. I. Bukin	Palache	V. I. Bukin	V. I. Bukin

TABLE 2. COMPOSITION OF RARE EARTHS IN MINERALS OF THE JOAQUINITE GROUP

	La	Ce	Pr	Nd	Sm	Gd	Dy	Er	Y
California									
No. 1	24.0	45.5	6.5	21.3	1.0	—	—	—	1.7
No. 2	20.3	48.8	5.1	18.3	3.5	2.4	1.0	0.6	—
Quebec	39.0	44.0	—	17.0					
Greenland	44.5	41.6	4.4	9.5					

Mineral of the Joaquinite Group from Greenland—Physical and Optical Properties

Greenland joaquinite forms banded gneissic and irregular masses up to 4×3×1 cm in size, which consist of tiny bent flakes one millimeter in length. The mineral is clear-brown with silky luster. Its specific gravity of 4.1 was determined by hydrostatic weighing. The micro-hardness (measured by J. A. Pudovkina with the instrument PMT-3) is 350–430 kg/mm^2, which nearly corresponds to a hardness of 4.9–5.3 on the Mohs scale. The DTA curve of the mineral (Fig. 1) has a strong endothermal reaction of melting at 1040°C and a small reaction at 770°C (release of water?).

Table 3. Chemical Composition of the Joaquinite-Group Mineral from Greenland

Component	Weight Percent	Atomic Proportions	Grouping
SiO_2	33.82	0.564	0.071 8.00
Nb_2O_5	2.31	0.017	0.137=1.93
TiO_2	9.20	0.115	
Fe_2O_3	0.39	0.005	
			0.077=1.08
FeO	4.78	0.067	
MnO	0.70	0.010	
ThO_2	0.38	0.002	
			0.140=1.99
RE_2O_3	22.59	0.138	
BaO	21.46	0.140	1.99
(Ca,Sr)O	0.03	—	
Na_2O	2.41	0.078	
			0.083
K_2O	0.22	0.005	
H_2O	1.50	0.167	
F	0.38	0.022	
$-O=F_2$	0.16		
Sum	100.01	—	

The mineral is optically biaxial positive with $2V=40°$. Indices are $\alpha=1.754$; $\beta=1.760$; $\gamma=1.797$; $c=\gamma$. Elongated sections have bright interference colors and strong pleochroism in yellow-green, $\gamma>\alpha$. Sections perpendicular to the c-axis have weak birefringence and no pleochroism. In the plane of cleavage (001) there are two nearly perpendicular systems of cracks, with diagonal extinction.

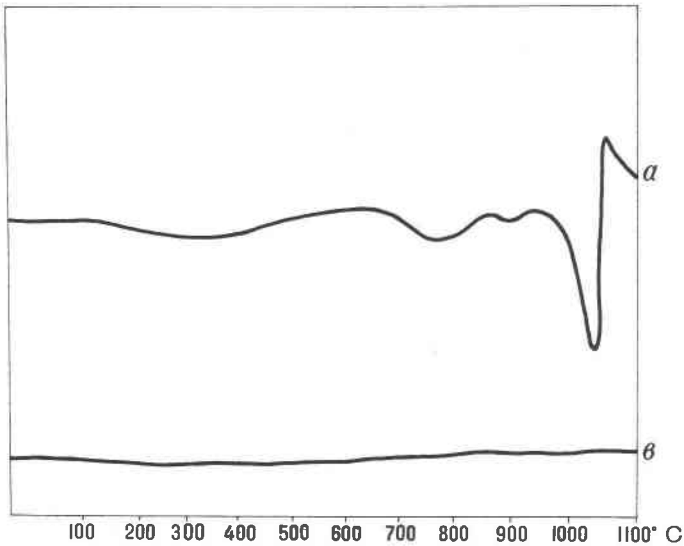

FIG. 1. Curves of (a) DTA and (b) TGA for joaquinite-group mineral from Greenland.

INFRARED AND X-RAY DATA

M. V. Achmanova obtained an absorption curve in the region 400–4000 cm^{-1} on a Zeiss UR -10 spectrometer (Fig. 2), which is quite distinct and rather characteristic for chain- or ribbon-silicates.

The absorption in the area of 900–1100 cm^{-1}, where usually there are

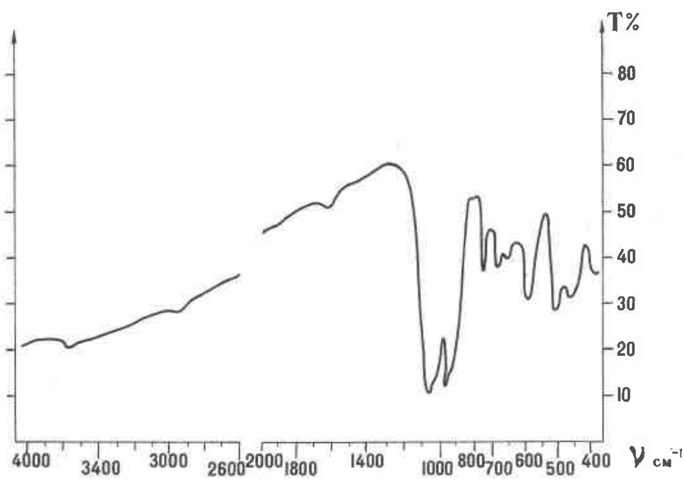

FIG. 2. Infrared absorption for the joaquinite-group mineral from Greenland.

stretching vibrations of the bond Si-O, as in this case, is characteristic for silicates having in their structure SiO_4-tetrahedrons, connected in chains or ribbons (Table 4 and Fig. 2). This is confirmed by the presence in the IR-spectrum of the sharp, narrow region at 730 cm^{-1}, which apparently concerns the symmetric vibrations of chains or ribbon polyradicals.

In the IR-spectrum of the Greenland mineral there is a weak absorption of molecular water from 3600–3400 cm^{-1} and a minimum of absorption at 1620 cm^{-1}. The IR-spectrum of this mineral, is closely related to

TABLE 4. ABSORPTION MAXIMA OF THE JOAQUINITE-GROUP MINERAL FROM GREENLAND

No.	Frequency in cm^{-1}		Interpretation
1	3600–3400	vw	ν H_2O
2	1620	w	δ H_2O
3	1040	st	
4	1000	sr	as ν SiO_4—group, combined in chains or bonds
5	935	st	
6	915	w	
7	930	m, sp	s ν SiO_4—groups, combined in chains or bonds
8	680	w	
9	650	w	
10	590	st	as sδ SiO_4, Me-O
11	500	m	
12	470	m	

Explanation: st—strong, w—weak, m—moderate, sp—sharp, sr—shoulder, vw—very weak. Me—metal, ν—stretching vibration, s—symmetric, as—asymmetric.

those of aegirine, jadeite, aenigmatite, and rhodonite, and is similar also to the absorption spectrum of benitoite.

From single-crystal x-ray diffraction examination, V. I. Bukin established the following parameters: $a=9.680\pm0.005$; $b=10.539\pm0.010$; $c=22.345\pm0.010$; $a:b:c=0.919:1:2.120$; $V=2280$ Å^3. This is the same as for the Canadian joaquinite (Bell, 1963). The most probable space group is $D_{2h}^{17}=Cmcm$, but may be also $C_{2v}^{12}=Cmc2$, and $C_{2v}^{16}=Ama2$. X-ray powder data (Table 5) for the Greenland mineral is similar to those given for the California mineral, but the former has more intensive lines (001) owing to its better layered textures.

Chemical analysis (Table 3) led to the formula $NaBa_2Fe^{2+}Ce_2Ti_2Si_8O_{26}(OH)$ with molecular weight 1377. Then $Z=4$. Another way of writing

TABLE 5. X-RAY DIFFRACTION POWDER PATTERN OF THE JOAQUINITE-GROUP MINERAL FROM GREENLAND

No.	I	*hkl*	d(meas), Å	d(calc), Å	No.	I	*hkl*	d(meas), Å	d(calc), Å
1	0.9	110	7.09	7.13	27	2.0	047		2.031
2	1.0	111	6.81	6.79			406	2.028	2.029
3	67.5	004	5.58	5.59			2.0.10		2.028
4	2.0	200	4.82	4.84			152		2.026
		022		4.77	28	3.1	1.1.11	1.956	1.956
5	4.2	202	4.44	4.44			0.2.11		1.895
6	1.5	023	4.30	4.30	29	2.8	2.2.10	1.895	1.893
7	2.5	024	3.79	3.83			426		1.893
		115		3.78	30	3.5	247	1.872	1.873
8	3.5	006	3.72	3.72			155		1.870
9	1.0	204	3.66	3.66	31	2.2	427	1.807	1.811
10	1.2	220	3.55	3.56			049		1.807
11	3.5	130	3.30	3.30	32	1.0	441	1.775	1.776
12	4.2	311	3.05	3.06	33	2.8	2.0.12	1.738	1.738
		026		3.04			062		1.736
13	8.8	224	3.00	3.00	34	3.0	1.1.13	1.672	1.671
14	17.0	206	2.95	2.95			260		1.651
15	10.5	117	2.91	2.91	35	1.9	2.2.12	1.647	1.650
		313		2.85			261		1.647
16	100.0	008	2.80	2.79	36	1.5	517	1.634	1.635
		225		2.79	37	12.8	0.0.14	1.596	1.596
17	3.5	041	2.613	2.614			602		1.596
18	2.0	028	2.467	2.468	38	1.9	604	1.549	1.549
19	5.8	400	2.418	2.420	39	1.9	622	1.526	1.528
		208		2.420			0.2.14		1.527
20	0.9	330	2.375	2.376	40	1.0	2.0.14	1.515	1.515
		045		2.269	41	1.0	3.1.13	1.501	1.501
21	2.2	242	2.267	2.266	42	1.0	171	1.487	1.486
		333		2.264			624		1.486
22	7.5	0.0.10	2.232	2.234	43	0.8	606	1.478	1.480
23	4.5	404	2.217	2.222			172		1.475
		317		2.218	44	0.8	4.0.12	1.458	1.460
24	1.0	422	2.155	2.158			2.2.14		1.457
		046		2.151	45	1.1	0.4.13	1.442	1.441
25	1.2	138	2.133	2.132	46	0.8	552		1.414
		150		2.059			462	1.412	1.410
26	1.2	0.2.10	2.054	2.057	47	7.2	0.0.16	1.397	1.396
		151		2.051					

the formula might be $(Na,Ba,Ce,Fe,Ti)_8\ Si_8O_{25}(OH,F)_3 = A_2Si_2O_7$. Titanium is isomorphically substituted by niobium; iron by manganese and rare earths by thorium.

Besides the above described mineral, we found in the same pegmatite of Narssaq River a colorless mineral of the joaquinite group which differs in its low indices of refraction (1.65) and in its unit cell dimensions $a = 9.657$, $b = 10.508$, $c = 22.334$ Å, especially on b. The tiny plates of this mineral occur very rarely in vugs of natrolite. Apparently it contains the minimum quantity of RE and (Fe,Ti).

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