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SPHENE, PEROVSKITE AND COEXISTING Fe-Ti OXIDE MINERALS

A. L. SMITH,[1] *Department of Geology and Geophysics, University of California, Berkeley, California 94720.*

ABSTRACT

Analytical data on perovskite, sphene and their coexisting Fe-Ti oxides are given. Sphene contains high ZrO_2 (up to 3.6%), less Nb_2O_5 and small amounts of F. Perovskite is rich in the rare earths (up to 7.4%), strontium, sodium and niobium. On average, sphene has 8.2 wt. % minor element substitution and perovskite 10.8 wt. %. The coexisting titanomagnetites have less than 45% Fe_2TiO_4, but may be relatively magnesian (up to 7.0%).

INTRODUCTION

The coexistence of perovskite and sphene in a rare group of nephelinite lavas (Tilley, 1953) instigated the companion study of silica activity in igneous rocks (Carmichael *et al.*, 1970). These same lavas provide the basis of this report on the paragenesis and composition of these two minerals and their coexisting iron-titanium oxides. Verhoogen (1962) has suggested that in natural liquids with a high f_{O_2}, sphene will take the place of ilmenite, and the coexisting titanomagnetite will be depleted in titanium. It was also suggested that low silica activity would encourage the precipitation of a Ti-rich pyroxene (with concomitant enrichment in Al_2O_3) and of course perovskite at the expense of Ti-rich oxide minerals.

RESULTS

The rocks in which the analyzed minerals occur are, with one exception, all lavas and may be divided into three groups. These are (Table 1):

a) Lavas which contain microphenocrysts of sphene.
b) Lavas, except for a monticellite peridotite, which contain microphenocrysts of perovskite. Perovskite is found with various combinations of augite, olivine, phlogopite, melilite, nepheline, kalsilite and leucite (Table 1).
c) Lavas which contain both sphene and perovskite. These are etindites (Tilley, 1953) which contain titanaugite zoned towards acmite, titanomagnetite, nepheline, interstitial leucite and early crystallization perovskite with sphene in the groundmass.

All the mineral analyses were made with an ARL electronprobe using mineral standards and computer techniques which by now must be standard.

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[1] Present address: Department of Geology, University of Puerto Rico, Mayaguez, Puerto Rico 00708.

TABLE 1. MINERAL ASSEMBLAGES OF SPHENE AND PEROVSKITE VOLCANICS

	1	2	3	4	5	6	7	8	9	10	11	12
Magnetite			×	×	×	×	×	×	×	×	×	×
Ilmenite			×					×				
Spinel					×	×						
Sphene	×	×	×	×						×	×	×
Perovskite					×	×	×	×	×	×	×	×
Olivine					×	×		×	×			
Monticellite					×							
Pyroxene	×	×	×	×			×	×	×	×	×	×
Biotite			×									
Phlogopite					×		×	×	×			
Hornblende			×									
Nepheline	×	×					×	×	×	×	×	×
Kalsilite							×		×			
Leucite								×		×	×	×
Sanidine			×	×								
Plagioclase			×	×								
Melilite						×	×					

Key to specimen localities

1.	Nephelinite, Lemagrut volcano, Tanzania	(479-2)[a]
2.	Nephelinite, Shombole volcano (N. end of Lake Natron), Kenya	(479-4)[a]
3.	Porphyritic trachytic pitchstone, Murat, Cantal, France	(3811)[a]
4.	Trachyte, Tristan da Cunha (Carmichael, 1965)	(439)[a]
5.	Monticellite peridotite, Haystack Butte, Montana, U. S. A.	(767-226)
6.	Melilitite, Dwinberg, near Wartenberg, Czechoslovakia	(94-3)[a]
7.	Melilite-nephelinite, inner wall of upper crater, Nyiragongo, Congo	(20424)[a]
8.	Ugandite, Katwe volcanic field, Uganda	(U-50)
9.	Mafurite, Katwe volcanic field, Uganda	(U-56)
10.	Nephelinite, Mt. Etinde, W. Africa (Tilley, 1953)	(61156)[b]
11.	Nephelinite, Mt. Etinde, W. Africa	(61157)[b]
12.	Nephelinite, Mt. Etinde, W. Africa	(61169)[b]

[a] These specimens are in the petrographic collection at Berkeley.

[b] These specimens obtained from the petrographic collection at Cambridge University, England.

The sphene analyses are given in Table 2 and those of perovskite in Table 3. As may be seen, there is extensive substitution of the minor elements, which, on average, amount to 8.2 percent of sphene and 10.8 percent of perovskite. The sphene analyses are notable for their high contents of ZrO_2 (up to 3.6%), rather less niobium, together with definite but small amounts of F, but only little alkali. The rare-earths in sphene are seldom as high as in the perovskites, which when they coexist with sphene (Table 3, Nos. 10, 11 and 12) are relatively enriched in the rare earths, strontium, sodium and niobium, and depleted in F and Zr.

TABLE 2. MICROPROBE ANALYSES OF SPHENE

	1[a]	2	3	4	10	11	12	Average
SiO_2	30.2	30.9	29.4	29.6	30.3	29.7	29.5	29.9
TiO_2	36.1	36.4	34.7	34.2	33.2	33.2	32.5	34.3
Al_2O_3	1.0	[b]	0.04	0.05	1.0	1.0	0.8	0.6
R. E.	0.9	0.8	2.8	3.7	1.2	1.0	0.7	1.6
FeO[c]	1.9	2.1	2.0	2.1	2.5	2.3	2.4	2.2
MnO	0.03	[b]	0.2	0.01	0.05	0.06	0.07	0.07
CaO	27.5	26.7	25.1	26.2	25.3	26.2	25.8	26.1
SrO	0.3	0.3	0.09	0.08	1.0	0.6	0.9	0.5
Na_2O	0.09	0.11	0.07	0.06	0.2	0.08	0.2	0.12
K_2O	0.03	0.03	0.07	0.05	0.04	0.07	0.05	0.05
ZrO_2	0.5	0.4	1.3	1.5	2.2	2.4	3.6	1.7
Nb_2O_5	0.5	0.4	0.7	1.2	1.4	0.8	1.2	0.9
Y_2O_3	0.07	0.08	0.4	0.2	0.09	0.09	0.09	0.15
F	0.3	0.2	0.2	0.1	0.3	0.4	0.4	0.3
Total	99.4	98.4	97.1	99.1	98.8	97.9	98.2	98.5
La_2O_3	0.1	0.1	0.4	0.6	0.2	0.2	0.1	
Ce_2O_3	0.3	0.2	1.1	1.3	0.4	0.3	0.2	
Pr_2O_3	0.1	0.1	trace	0.3	0.1	0.1	0.1	
Nd_2O_3	0.2	0.2	1.2	0.9	0.2	0.2	0.1	
Sm_2O_3	0.1	0.1	trace	0.2	0.1	0.1	0.1	
Eu_2O_3	trace	trace	0.1	0.1	0.1	trace	trace	
Gd_2O_3	0.1	0.1	[b]	0.3	0.1	0.1	0.1	

[a] For key to localities see Table 2.

[b] Below limit of detection (0.02%). MgO below limit in all cases.

[c] Total iron reported as FeO.

The analyses of one-phase iron-titanium oxides are given in Table 4. All the titanomagnetites have less than 45 percent of the ulvospinel component, and as ilmenite is absent in all but two rocks (Table 1), these data tend to support Verhoogen's contention noted above. This relative paucity of the titanium component can be seen particularly in comparison to the titanium-rich oxide minerals of a tholeiitic series (Carmichael, 1967). In the etindites, titanaugite encloses small grains of titanomagnetite which are highly magnesian (Table 4, 11A) whereas the Fe-Ti oxide phenocrysts and the corresponding groundmass phase are depleted in both Mg and Al.

Yagi and Onuma (1969) studied the system diopside-akermannite-nepheline-$CaTiAl_2O_6$ in which the diopsidic pyroxene incorporated 4 percent TiO_2 before perovskite precipitated. In the etindites, the titanaugite contains up to 5 percent TiO_2 and is also accompanied by perovskite,

TABLE 3. MICROPROBE ANALYSES OF PEROVSKITE

	5[a]	6	7	8	9	10	11	12	Average
SiO_2	0.05	0.15	0.03	0.05	0.05	0.03	0.04	0.09	0.06
TiO_2	53.0	53.6	53.6	54.4	53.7	53.1	52.3	52.7	53.3
Al_2O_3	[b]	0.9	[b]	0.2	0.2	0.3	0.4	0.3	0.3
R. E.	5.7	2.8	6.4	3.7	4.1	7.4	7.4	7.0	5.6
FeO[c]	2.0	1.9	1.7	1.1	1.2	1.4	2.7	1.5	1.7
MnO	[b]	0.03	0.04	0.04	0.03	0.06	0.06	0.07	0.04
CaO	35.7	38.2	35.3	36.7	36.6	35.2	32.3	34.7	35.6
SrO	1.3	0.5	0.8	0.8	0.6	1.1	1.2	1.0	0.9
Na_2O	0.4	0.3	0.7	0.4	0.4	0.7	0.8	0.7	0.6
K_2O	0.09	0.08	0.11	0.08	0.04	0.05	0.05	0.04	0.07
ZrO_2	0.4	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.2
Nb_2O_5	1.1	0.8	1.4	0.6	0.5	1.4	1.5	1.4	1.1
Y_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
F	0.05	0.3	0.1	0.1	0.1	[b]	[b]	0.1	0.1
Total	99.9	99.9	100.5	98.4	97.7	101.0	99.1	99.9	99.7
La_2O_3	1.2	0.5	1.2	0.6	0.7	1.3	1.4	1.3	
Ce_2O_3	2.0	1.0	2.5	1.4	1.6	2.9	2.8	2.7	
Pr_2O_3	0.5	0.2	0.5	0.3	0.3	0.6	0.6	0.5	
Nd_2O_3	1.4	0.7	1.6	1.0	1.1	1.9	1.9	1.9	
Sm_2O_3	0.2	0.1	0.2	0.1	0.1	0.2	0.2	0.2	
Eu_2O_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
Gd_2O_3	0.3	0.2	0.3	0.2	0.2	0.4	0.4	0.3	

[a] For key to localities see Table 1.
[b] Below limit of detection (0.02%). MgO below limit in all cases.
[c] Total iron reported as FeO.

sphene and titanomagnetite.

As coexisting titanomagnetite and ilmenite are rare or absent (characteristically) in sphene and perovskite assemblages, it is impossible to use the oxygen geobarometer of Buddington and Lindsley (1964) to estimate oxygen fugacity. However, one of the contrasts between sphene and perovskite is that the latter may occur with olivine and titanomagnetite (Table 1) and hence equilibrate with oxygen fugacities near those of the synthetic fayalite-magnetite-quartz assemblage, while the former, in association with titanomagnetite, but not olivine, requires relatively high oxygen fugacities (Verhoogen, 1962; Carmichael and Nicholls, 1967). The distinction between sphene and perovskite assemblages therefore lies not only in silica activity but also in f_{O_2}, or their interdependence, which underscores the conclusion in the companion paper (Carmichael *et al.*, 1970).

TABLE 4. ANALYSES OF ONE-PHASE IRON-TITANIUM OXIDES AND CHROME-BEARING SPINELS
(A—titanomagnetite; B—ilmenite; C—chromespinel)

	3A[a]	3B[b]	4A	5A	5C	6A	6C	7A		11A		
	Phenocrysts	Phenocrysts	Phenocrysts	Phenocrysts	Phenocrysts	Phenocrysts	Phenocrysts	Phenocrysts	Groundmass	Inclusions	Phenocrysts	Groundmass
TiO_2	11.9	40.9	12.5	9.1	2.9	8.8	1.3	14.0	12.0	15.3	15.6	12.8
MnO	1.18	0.72	2.92	0.56	0.43	0.63	0.13	1.62	2.20	0.98	1.41	1.57
MgO	2.73	3.79	0.60	5.7	10.6	7.0	22.3	2.08	2.30	5.64	1.41	0.24
ZnO	0.15	—[c]	0.96	0.05	0.16	—[c]	—[c]	0.66	0.72	0.10	0.16	0.20
Al_2O_3	3.08	0.36	0.67	1.88	8.6	8.7	46.1	1.54	0.15	4.53	1.67	0.44
Cr_2O_3	—[c]	—[c]	0.18	0.93	48.6	0.36	12.9	0.20	0.19	0.04	0.06	0.02
V_2O_3	0.45	0.07	—[c]	—[c]	0.06	0.20	0.05	0.36	0.53	0.17	0.29	0.35
FeO	75.5	51.4	78.2	76.8	25.9	69.9	18.9	72.6	73.9	71.2	76.0	77.7
Sum	95.2	97.3	96.0	95.0	97.2	95.6	101.6	93.1	92.0	98.0	96.6	93.3
					Analyses recalculated on ulvospinel basis							
Fe_2O_3	42.7		44.5	51.5		45.0		38.5	43.6	38.2	37.6	41.8
FeO	37.1		38.2	30.5		29.4		38.0	34.7	36.8	42.2	40.1
Total	99.5		100.5	100.2		100.1		97.0	96.4	101.8	100.4	97.5
Mol% USP	33.4		35.3	24.7		22.9		40.3	35.0	40.2	43.5	37.4
Mol% R_2O_3		23.6										
T°C		1010										
fo_2		$10^{-9.2}$										

[a] Contains 0.12% SiO_2; 0.03% CaO.
[b] Contains 0.04% SiO_2; 0.04% CaO.
[c] Below limit of detection (0.02).
[d] For key to these localities, see Table 1.

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