

COMPOSITION OF PEROVSKITE IN KIMBERLITE

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ABSTRACT

Perovskite in kimberlite occurs as discrete primary crystals in the groundmass and as reaction rims around magnesian ilmenites. The perovskites are of uniform composition consisting essentially of the perovskite component (CaTiO_3). The perovskites contain substantial amounts of niobium (0.59-1.45% Nb_2O_5) and are poor in sodium (0.34-0.88% Na_2O) and iron (1.00-2.05% FeO). Kimberlite perovskite is similar in composition to perovskite in potassic lavas, alkali pyroxenites and etindites but different from that in carbonatites. The low iron content of kimberlite perovskite is discussed with respect to low oxygen fugacities in kimberlite magmas.

PARAGENESIS

Perovskite is one of the characteristic accessory minerals of kimberlite; however, little is known concerning its composition or mode of occurrence. Studies of a number of polished sections of kimberlite from South Africa and North America have shown that perovskite occurs in two parageneses:

1. Discrete crystals in the kimberlite groundmass.
2. Reaction rims about magnesian ilmenites.

The groundmass perovskites occur abundantly as euhedral (cubes) to subhedral single crystals that are unaccompanied by magnesian ilmenite. Although the crystals are in some cases corroded by the groundmass material, they do not show any rounding effects which can be attributed to fluidization. Hence they are considered to have crystallized directly from the kimberlite magma contemporaneously with the groundmass magnetite and second generation olivine but earlier than the carbonate phases. The presence of perovskite in the groundmass as a primary liquidus phase also indicates that a pre-existing titanium bearing phase is not needed as a nucleation point.

Magnesian ilmenites are commonly surrounded by a rim of perovskite of variable thickness. Optical and microprobe studies have shown that this rim is composed of two zones—an outer zone of pure perovskite which exhibits euhedral crystal faces towards the groundmass, and an inner zone composed of a complex intergrowth of perovskite, ilmenite and ferromagnesian silicates (Figs. 1 and 2). This inner zone is shown by microprobe studies to be made up of submicroscopic domains of pure perovskite and ilmenite separated by silicate material

of unknown composition but which is probably serpentine or chlorite.

The textures show that reaction of ilmenite with the kimberlite groundmass fluids does not take place by the simple replacement of cations in the ilmenite structure.

Ilmenite appears to have broken down, releasing magnesium and iron which combine with silica in the groundmass fluids to form ferromagnesian silicate alteration products. Beam-scanning photographs indicate that extensive solid solution between the perovskite and the ilmenite phase does not occur. Once a zone of perovskite-ilmenite domains have formed, further nucleation and growth of perovskite on the rim of the crystal prevents further breakdown of the ilmenite. The reaction can be expressed;



COMPOSITION

Partial analyses of perovskites determined by microprobe are given in Table 1. X-ray emission intensities were corrected for mass absorption, fluorescence, and atomic number by the computer program of Smith and Tomlinson (1970). All the totals given in Table 1 are low, as rare earth elements and strontium were not determined due to lack

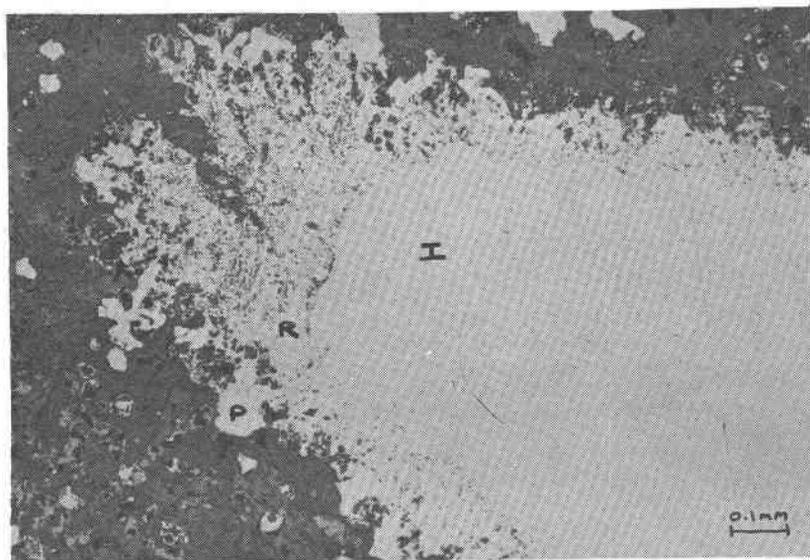


FIG. 1. Broad reaction rim developed about magnesian ilmenite (I), consisting of an outer zone of pure perovskite (P) and an inner zone of perovskite, ilmenite and ferromagnesian silicates (R). Bultfontein pipe, South Africa.

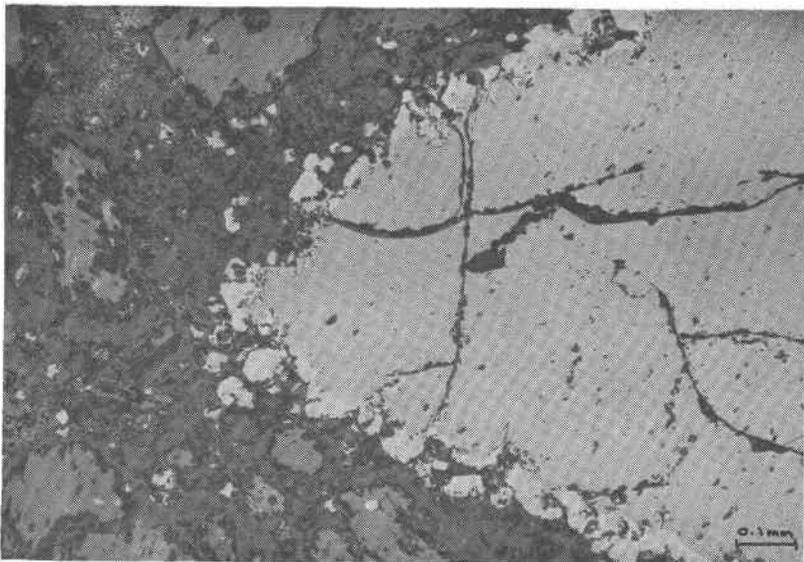


FIG. 2. Reaction rim of perovskite (white) developed about magnesian ilmenite (grey). Inner reaction zone is below limit of resolution. Wesselton pipe, South Africa.

of suitable standards. These elements are the only common elements not determined known to substitute extensively for calcium in perovskite (Nickel and McAdam, 1963; Carmichael, 1967; Smith, 1970). The deviation from 100 percent is considered to be an indication of the amounts of rare earths and strontium present. The conclusions which can be drawn from Table 1 are as follows:

1. Kimberlite perovskites are rich in Ca and Ti and must therefore be composed essentially of the CaTiO_3 component (pure CaTiO_3 ; $\text{CaO} = 41.24\%$, $\text{TiO}_2 = 58.76\%$.)
2. There is no significant difference in composition between ground-mass perovskite and reaction rim perovskite.
3. Perovskites, from different facies of a single kimberlite pipe (Wesselton) do not show a significant difference in composition, nor do perovskites from different pipes.
4. The perovskites contain very little Fe and Mg. This is particularly important with regard to the reaction rim perovskite (see below).
5. As previously noted by Grantham and Allen (1960), kimberlite perovskites can contain a substantial amount of niobium (0.59–1.45% Nb_2O_5). Magnesian ilmenite associated with perovskite rims contains much less niobium (<0.1% Nb_2O_5). No other major

Table 1. Composition of perovskite from kimberlite.

	1	2	3	4	range
CaO	35.95	38.27	38.94	37.01	35.95 - 40.15
Na ₂ O	0.81	0.52	0.63	0.71	0.37 - 0.88
K ₂ O	0.15	0.12	0.11	0.11	0.08 - 0.15
TiO ₂	52.42	55.17	54.26	53.86	52.42 - 55.85
FeO	1.27	1.07	1.21	1.24	1.00 - 2.05
Nb ₂ O ₅	1.11	0.59	1.32	0.76	0.59 - 1.45
Al ₂ O ₃	0.30	0.27	0.31	0.30	0.15 - 0.38
SiO ₂	0.17	0.20	0.19	0.16	0.12 - 0.22
MgO	0.10	0.11	0.13	0.11	0.07 - 0.22
	92.34	96.23	96.81	94.26	

Total iron is expressed as FeO

1. Groundmass perovskite, Wesselton pipe, South Africa.
2. Reaction rim perovskite, Wesselton pipe, South Africa.
3. Groundmass perovskite, aphyric kimberlite dike, Wesselton pipe, 1710' level, South Africa.
4. Groundmass perovskite, Ison Creek pipe, Kentucky, U.S.A.

Range - Compositional range found in 21 samples of groundmass and reaction rim perovskites.

niobium bearing phase was observed during microprobe beam-scanning of sections, and it would appear that perovskite is the principal carrier of niobium in kimberlite.

DISCUSSION

Perovskite occurs as an accessory mineral in a wide variety of undersaturated rock types, including potassic lavas, alkali pyroxenites and etindites. Little is known concerning the composition of perovskites in such rocks but the data of Smith (1970) for alkaline lavas and Frank-Kamenetskii and Vesel'skii (1961) for alkaline pyroxenites indicates that kimberlite perovskites are very similar in composition to perovskites found in such rocks. However, kimberlite perovskites differ markedly in composition from perovskite found in carbonatites (Nickel and McAdam, 1963; Frank-Kamenetskii and

Vesel'skii, 1961) and in leucite madupite lavas (Carmichael, 1967), which are enriched in niobium and rare earth elements.

The low content of Fe in the kimberlite perovskites, even in the reaction rim perovskite where the activity of iron must be locally high, is important. Kimura and Muan (1971a) have studied the system CaO-iron oxide-TiO₂ in air and found that perovskite can contain up to 83 percent iron in substitution for titanium. However, in the same system under a strongly reducing environment (metallic iron-wustite buffer) there is found no appreciable solid solution (Kimura and Muan, 1971b). The lack of iron substitution in kimberlite perovskite might thus be an indication that they formed under reducing conditions. In support of this contention is the fact that the iron content of perovskites formed under conditions of high oxygen fugacity is greater than that observed in kimberlite perovskites, *e.g.*, 4.11 percent Fe₂O₃ in perovskite in an ejected block in an Alban Hills lava (Turi, 1968) and 7.7 percent and 11.4 percent FeO in perovskites associated with strontionobarytes in madupite lavas (Carmichael, 1967). However, contrary evidence is seen in the low iron content of perovskites found in potassic lavas (Smith, 1970) presumed to have formed under high oxygen fugacities ($f_{O_2} = 10^{-11}$ bars; Nicholls *et al.*, 1971). Oxygen fugacity at the time of crystallization of the kimberlite groundmass has been estimated to be on the order of 10^{-20} bars (Mitchell, in press). Further investigations of this problem are desirable.

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