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INSTABILITY OF PEROVSKITE IN A CO_2-RICH ENVIRONMENT: EXAMPLES FROM CARBONATITE AND KIMBERLITE

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ABSTRACT

Intricate multiphase pseudomorphs after perovskite (Nb-, *LREE*-poor) from calcite carbonatite (Sebljavr complex, Kola Peninsula, Russia) and serpentine calcite kimberlite (Iron Mountain, Wyoming) are described. In the kimberlite, the major products of perovskite replacement are (in order of crystallization): kassite, anatase and titanite plus calcite, ilmenite, *LREE*–Ti oxide [? lucasite-(Ce)]. In the carbonatite, perovskite is initially replaced by anatase plus calcite and, subsequently, ilmenite and ancylite-(Ce). In both instances, the development of calcite and Ti-bearing phases after perovskite involved initial progressive leaching of Ca^{2+} from the structure followed by crystallization of ilmenite and *LREE* minerals in the final stages, after the precipitation of groundmass calcite. The formation of kassite and titanite in the pseudomorphs in kimberlite was controlled by a lower Ca leach-rate and higher activity of SiO_2 in this system, compared with the carbonatite. The similarity between the two types of pseudomorphs results from the instability of Nb–*LREE*-poor perovskite in a CO_2-rich fluid at low temperatures. Perovskite is considered an unsuitable host for radioactive ^{90}Sr and *REE* isotopes owing to the low resistance of $CaTiO_3$ to leaching and incompatibility of Sr and the rare earths with the products of perovskite replacement.

Keywords: perovskite, anatase, ilmenite, kassite, ancylite-(Ce), lucasite-(Ce), carbonatite, kimberlite, Sebljavr complex, Kola Peninsula, Russia, Iron Mountain, Wyoming.

SOMMAIRE

La pérovskite à faible teneur en Nb et en terres rares est déstabilisée et transformée en agrégats multiphasés complexes dans la carbonatite à calcite du complexe de Sebljavr, péninsule de Kola, en Russie, et dans la kimberlite à calcite + serpentine de Iron Mountain, Wyoming. Dans la kimberlite, les produits importants du remplacement de la pérovskite sont (dans l'ordre de cristallisation): kassite, anatase et titanite plus calcite, ilménite, oxyde de terres rares légères et Ti [? lucasite-(Ce)]. Dans la carbonatite, la pérovskite est d'abord remplacée par anatase plus calcite, et plus tard, par ilménite et ancylite-(Ce). Dans les deux cas, le développement de la calcite et des phases titanifères aux dépens de la pérovskite implique le lessivage progressif du Ca^{2+} de la structure et de la cristallisation par la suite de l'ilménite et des minéraux de terres rares dans les stades tardifs, après la formation de la calcite de la pâte. La formation de la kassite et de la titanite dans les pseudomorphoses de la kimberlite est régie par un taux inférieur de lessivage du Ca et une activité accrue de SiO_2 dans ce système, comparé au cas de la carbonatite. La ressemblance entre les deux types de pseudomorphoses découle de l'instabilité de la pérovskite à faible teneur en Nb et terres rares légères dans un milieu dont la phase fluide est riche en CO_2 à faible températures. La pérovskite semble être un hôte inapproprié pour l'enfouissement du ^{90}Sr et des isotopes radioactifs des terres rares à cause de la faible résistance de $CaTiO_3$ au lessivage et à l'incompatibilité du Sr et des terres rares par rapport aux produits de remplacement de la pérovskite.

(Traduit par la Rédaction)

Mots-clés: pérovskite, anatase, ilménite, kassite, ancylite-(Ce), lucasite-(Ce), carbonatite, kimberlite, complexe de Sebljavr, péninsule de Kola, Russie, Iron Mountain, Wyoming.

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INTRODUCTION

Perovskite, ideally $CaTiO_3$, is a ubiquitous accessory mineral in SiO_2-undersaturated rocks such as kimberlites, melilitites, foidites, olivinites, clinopyroxenites, and carbonatites. In many magmatic assemblages, perovskite is a stable phase on the liquidus, but it is replaced by other Ti-bearing minerals during subsolidus re-equilibration, metasomatic and secondary alteration. The most common product of alteration is titanite. A reaction rim and pseudomorph of titanite after perovskite occur in a broad variety of silicate rocks including foidites, foidolites and ultramafic plutonic rocks (Chakhmouradian & Mitchell 1997, 1998). In Ca-enriched assemblages such as melilitic rocks, perovskite is typically replaced by Mg- and Al-poor, Ti-rich garnet of schorlomitic or melanitic composition, commonly accompanied by titanite (Chakhmouradian & Mitchell 1997). The development of titanite and titaniferous garnet after perovskite indicates geochemical evolution toward SiO_2-enriched compositions:

$$\underset{\text{perovskite}}{CaTiO_3} + (SiO_2)_{aq} \rightarrow \underset{\text{titanite}}{CaTiSiO_5}$$

$$\underset{\text{perovskite}}{CaTiO_3} + (SiO_2)_{aq} + Ca^{2+} + Fe^{3+} \rightarrow \underset{\text{schorlomite}}{Ca_3Ti_2SiFe_2O_{12}}.$$

The formation of silicate minerals after perovskite is rarely observed in rocks of carbonatitic affinity, and occurs primarily in silica-rich parageneses, *e.g.*, phoscorites. In carbonatites *sensu stricto*, perovskite and related phases (latrappite and lueshite) are typically replaced by oxide minerals, most commonly by Nb-dominant pyrochlore-group phases (Bagdasarov *et al.* 1962, Chakhmouradian 1996, Williams & Kogarko 1996). Experimental data (Jago & Gittins 1993) and mineralogical observations suggest that the formation of pyrochlore-type phases after perovskite results from the increasing activity of volatile components during the latest stages of carbonatite evolution:

$$\underset{\text{perovskite}}{(Ca, Na)(Ti,Nb)O_3} + F^{1-} + OH^{1-} \rightarrow \underset{\text{pyrochlore}}{(Ca,Na)(Nb,Ti)_2O_6(OH,F)}.$$

Other less common products of perovskite replacement in carbonatites include the polymorphs of TiO_2, ilmenite and $(Nb,Ti,Fe,Ta)_2O_5$ (Lebedev & Rimskaya-Korsakova 1949, Kapustin 1964, Mitchell *et al.* 1998). A few examples of perovskite instability in kimberlites have been described (Boctor & Meyer 1979, Mitchell & Clarke 1976). In kimberlites, a thin reaction-induced mantle of TiO_2 is attributed to the interaction of perovskite with a late-stage fluid precipitating calcite and serpentine (Mitchell 1986).

The relationships between perovskite and its replacement products are not well characterized in the mineralogical literature. Only a few recent studies provide compositional data, as well as X-ray diffraction, optical and other relevant information on both perovskite and secondary phases. These studies are of direct relevance to the possible application of perovskite as a long-term repository for high-level radioactive waste (Ringwood *et al.* 1979, 1981, Nesbitt *et al.* 1981, Myhra *et al.* 1984, Lumpkin *et al.* 1997). In the present work, we describe two types of complex pseudomorphs after perovskite in carbonatite from the Sebljavr complex, Kola Peninsula, and calcite – serpentine kimberlite from the Iron Mountain field, Wyoming.

ANALYTICAL METHODS

All mineral compositions were determined by X-ray energy-dispersion spectrometry (EDS) using a Hitachi 570 scanning electron microscope equipped with a LINK ISIS analytical system incorporating a Super ATW Light Element Detector (133 eV FwHm Mn*K*) at Lakehead University, Ontario. EDS spectra of perovskite, anatase, kassite and ilmenite were acquired for 130 seconds, those of ancylite-(Ce) and lucasite-(Ce) for 200 seconds (live time) with an accelerating voltage of 20 kV and beam current of 0.86–0.87 nA. X-ray spectra were collected and processed with the LINK ISIS–SEMQUANT software package. Full ZAF corrections were applied to the raw X-ray data. The following standards were employed for the determination of mineral compositions: loparite (Na, La, Ce, Pr, Nd, Nb), perovskite (Ca, Ti), ilmenite (Fe), periclase (Mg), Mn-bearing olivine (Mn), corundum (Al), wollastonite (Si), synthetic $SrTiO_3$ (Sr), metallic Th and Ta. The accuracy of the method was cross-checked by wavelength-dispersion electron-microprobe analysis of some samples using an automated CAMECA SX–50 microprobe located at the University of Manitoba, using methods described by Mitchell & Vladykin (1993). The compositions of perovskite obtained can be characterized in terms of four major end-members: $CaTiO_3$ (perovskite), $Na_{0.5}\mathit{LREE}_{0.5}TiO_3$ (loparite), $NaNbO_3$ (lueshite) and $CaFe_{0.5}Nb_{0.5}O_3$ (latrappite). Correspondingly, the perovskite compositions were recalculated into these end-members using an APL program for PC following methods suggested by Mitchell (1996). Ilmenite compositions were recalculated into $FeTiO_3$ (ilmenite), $MnTiO_3$ (pyrophanite) and $MgTiO_3$ (geikielite), as calculation of the structural formulae of ilmenite showed no or negligible Fe_2O_3 content in all compositions.

The back-scattered electron (BSE) images were aquired with the LINK ISIS–AUTOBEAM using a Hitachi 570 scanning electron microscope. The images were given false colors using the LINK ISIS–SPEEDMAP software package and stored as "pcx" files. Although false, the colors are defined by relative contrast and brightness on the BSE images, and therefore do reflect the average atomic number of individual phases.

OCCURRENCE AND MINERALOGY

The Sebljavr complex

Sample SB–17/18 originates from the Sebljavr complex of the Kola Peninsula, Russia. The geology of the

Sebljavr intrusion has been decribed in detail elsewhere (Bulakh & Abakumova 1960, Kukharenko *et al.* 1965, Lapin 1979, Subbotin & Mikhaelis 1986). The intrusion is very poorly exposed; most of the data on the structure and petrography of the complex have been obtained from drill core. The intrusion consists mainly of clinopyroxenite, and less common olivinite and olivine – clinopyroxene rocks (Bulakh & Abakumova 1960, Kukharenko *et al.* 1965). [The term "olivinite" is used instead of "dunite" to emphasize that titaniferous magnetite and perovskite, not chromite, are major opaque phases in this rock.] Metasomatic assemblages enriched in amphibole and phlogopite typically occur at the contact between the ultramafic rocks and younger alkaline and carbonatitic rocks. Alkaline rocks are represented predominantly by ijolite, which intrudes the olivinite and clinopyroxenite. Various types of carbonatites, including calcite, calcite – dolomite and ankerite facies, are relatively common at Sebljavr (Bulakh 1961, Kukharenko *et al.* 1965, Subbotin & Mikhaelis 1986). The carbonatites, found as dikes and veins emplaced into the ultramafic suite, contain a number of rare accessory minerals such as calzirtite [$CaZr_3TiO_9$], lueshite [$NaNbO_3$], vigezzite [$CaNb_2O_6$] and ancylite-(Ce) [$CeSr(CO_3)_2(OH)\bullet H_2O$] (Bulakh 1961, Subbotin & Men'shikov 1987). The formation of the carbonatites at Sebljavr involved gravitational and kinetic differentiation of a parental melt, as well as metasomatic interaction between the wall rocks (predominantly ultramafic) and carbothermal fluids (Bulakh 1961, Lapin 1979, Subbotin & Mikhaelis 1986).

Sample SB–17/18 was extracted from a thin vein of carbonatite emplaced in perovskite-rich clinopyroxenite. The carbonatite consists of medium-grained calcite with very low Mg, Mn, Fe and Sr contents (all <0.2 wt.% of the relevant oxides) and coarse-grained ferruginous phlogopite (3.6–3.9 wt.% FeO). The phlogopite crystals are confined to the selvages of the vein. Strontianite, monazite-(Ce), barite and chalcopyrite are present in accessory amounts. These occur as minute euhedral or subhedral crystals set in the calcite groundmass. The examined carbonatite also hosts black ovoid segregations ranging from 1 to 2.5 cm in diameter. These consist predominantly of perovskite at the core, and a multiphase mineral assemblage at the rim (Fig. 1).

The perovskite is brown in color, and exhibits polysynthetic lamellar twinning. Compositionally, it is

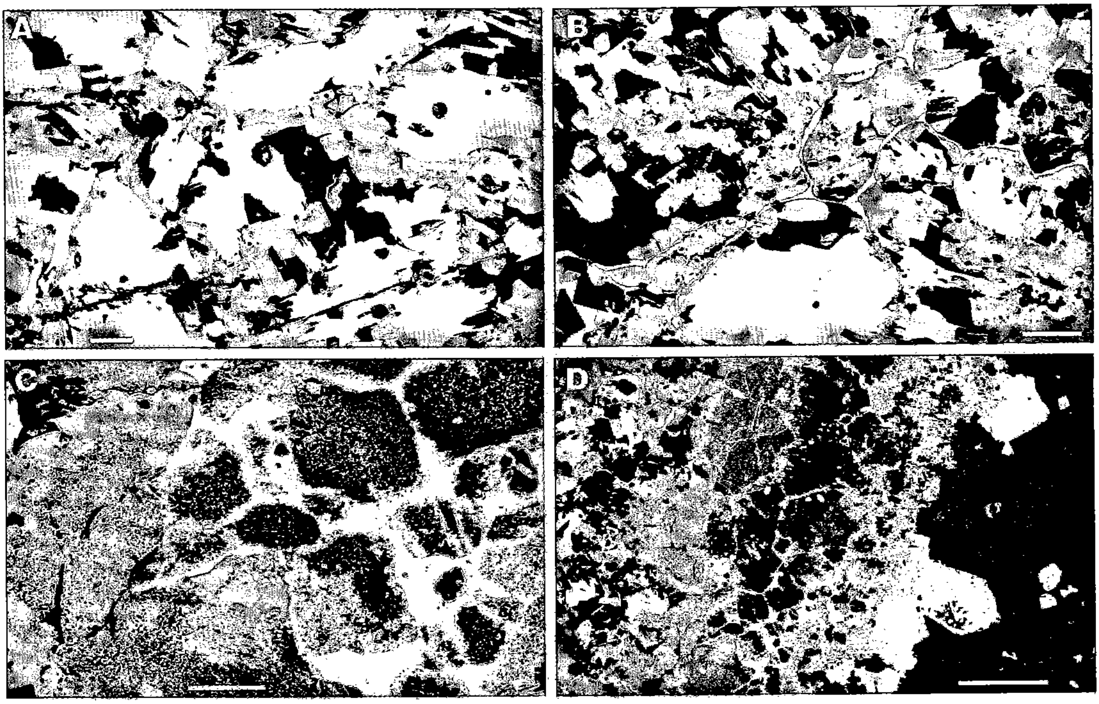

FIG. 1. BSE images of a pseudomorph after perovskite in calcite carbonatite, Sebljavr complex. Green and bluish green: perovskite, blue: anatase, yellow: ilmenite, purple and red: ancylite-(Ce), black: calcite. A. Core of the pseudomorph. Replacement of perovskite by anatase and calcite. B. Development of ilmenite in the perovskite – anatase aggregate. C. Rim of the pseudomorph. Ilmenite network in a fine-grained anatase – calcite aggregate. D. Rim of the pseudomorph. Ancylite-(Ce) decorating the ilmenite "crust". Scale bars are 50 μm (A–C) and 200 μm (D). Note that the black areas are not opaque minerals, but rather low-atomic-number phases, mostly calcite.

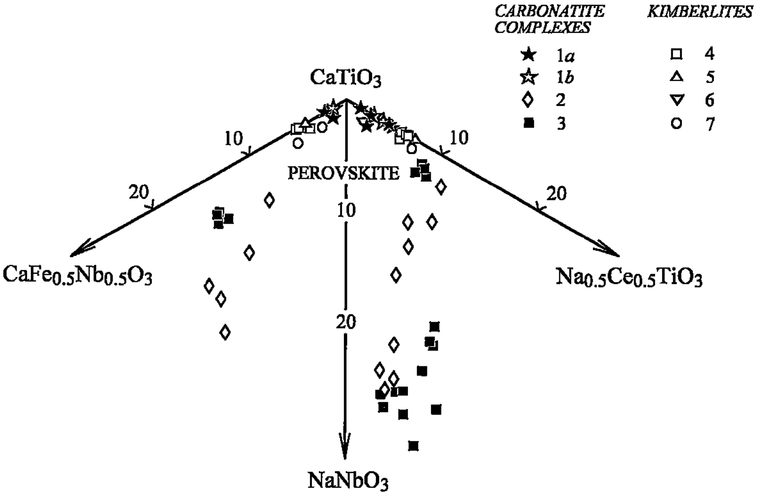

FIG. 2. Composition (mol.%) of perovskite from carbonatites and kimberlites: 1 Sebljavr, Kola (this work): a carbonatite, b clinopyroxenite, 2 Kaiserstuhl, Germany (Mitchell *et al.* 1998), 3 Oka, Quebec (Boctor & Yoder 1980, Treiman & Essene 1985, Mitchell *et al.* 1998), 4 Iron Mountain, Wyoming (this work), 5–7 Benfontein, Wesselton and Premier, respectively, South Africa (Jones & Wyllie 1984). Note clustering of the perovskite compositions from Sebljavr and Iron Mountain around $CaTiO_3$.

almost pure $CaTiO_3$, with low contents of Na, Nb and the light rare-earth elements (*LREE*) (Table 1, anal. 1, 2). This perovskite is compositionally identical to that from the wallrock clinopyroxenite, but markedly different from cumulus perovskite occurring in calcite carbonatites in the Kola and other alkaline provinces (Chakhmouradian & Mitchell 1997, Fig. 2). Typically, the cumulus perovskite from carbonatites is enriched in Na, Nb and Fe^{3+} compared to perovskite from the cognate silicate rocks (ultramafic, melilitic and foidolitic). In terms of end-member compositions, the cumulus perovskite from carbonatites shows enrichment in lueshite ($NaNbO_3$) and latrappite (Ca_2FeNbO_6) (Fig. 2). Therefore, we contend that the perovskite core of the ovoids represents xenocrystic material assimilated from the wallrock.

Toward the rim of the ovoids, the perovskite was successively replaced initially by anatase plus calcite, and then by ilmenite. Anatase fills fractures in perovskite, and forms skeletal and euhedral crystals associated with calcite (Fig. 1A). The crystals have a rectangular outline, distinct blue color, and are uniaxial negative, indicating that this mineral is anatase, rather than rutile or brookite. Compositionally, it is nearly pure TiO_2, with relatively low Fe and Nb contents (Table 1, anal. 3, 4). The amount of anatase and calcite significantly increases at the margin of the perovskite core (Fig. 1B). Here, perovskite, anatase and calcite are cross-cut by thin (3–10 μm) veinlets of ilmenite arranged in a network pattern (Figs. 1B, C). At the rim of the ovoids, perovskite is present only as relict fragments up to 50 μm in size, set in a matrix of cryptocrys-

TABLE 1. PSEUDOMORPHS AFTER PEROVSKITE IN CARBONATITE: MINERAL CHEMISTRY

Wt.%	1	2	3	4	5*	6*	7	8
CaO	40.76	40.51	n.d	n.d	n.d	n.d	1.11	2.06
SrO	0.09	0.29	n.d	n.d	n.d	n.d	14.20	16.48
Na_2O	0.09	0.13	n.d	n.d	n.d	n.d	n.d	n.d
La_2O_3	0.12	0.53	n.d	n.d	n.d	n.d	9.91	10.54
Ce_2O_3	0.80	1.55	n.d	n.d	n.d	n.d	27.20	25.25
Pr_2O_3	n.d	n.d	n.d	n.d	n.d	n.d	4.96	4.05
Nd_2O_3	0.64	n.d	n.d	n.d	n.d	n.d	12.44	11.65
ThO_2	0.15	n.d	n.d	n.d	n.d	n.d	0.09	n.d
MgO	n.d	n.d	n.d	n.d	4.66	4.29	n.d	n.d
MnO	n.d	n.d	n.d	n.d	2.08	2.32	n.d	n.d
FeO	n.a	n.a	n.a	n.a	38.65	38.76	n.d	n.d
Fe_2O_3	0.94	0.98	0.37	0.90	0.12	n.d	n.d	n.d
TiO_2	56.20	55.40	98.83	97.81	54.52	54.38	n.d	n.d
Nb_2O_5	0.85	0.52	1.05	1.37	n.d	n.d	n.d	n.d
Ta_2O_5	0.08	0.18	0.10	0.19	0.07	0.34	n.d	n.d
Total	100.72	100.09	100.35	100.27	100.10	100.09	69.91	70.03
	Structural formulae calculated on the basis of:							
	$\Sigma O = 3$		$\Sigma O = 2$		$\Sigma O = 3$		$\Sigma cat. = 1$	
Ca	0.998	1.002	-	-	-	-	0.040	0.072
Sr	0.001	0.004	-	-	-	-	0.281	0.313
Na	0.004	0.006	-	-	-	-	-	-
La	0.001	0.004	-	-	-	-	0.125	0.127
Ce	0.007	0.013	-	-	-	-	0.340	0.303
Pr	-	-	-	-	-	-	0.062	0.049
Nd	0.005	-	-	-	-	-	0.152	0.136
Th	0.001	-	-	-	-	-	-	-
Mg	-	-	-	-	0.169	0.156	-	-
Mn	-	-	-	-	0.043	0.048	-	-
Fe^{2+}	-	-	-	-	0.787	0.792	-	-
Fe^{3+}	0.016	0.017	0.004	0.009	0.002	-	-	-
Ti	0.965	0.961	0.989	0.982	0.998	0.999	-	-
Nb	0.009	0.005	0.006	0.008	-	-	-	-
Ta	-	0.001	-	0.001	-	0.002	-	-

Compositions: 1 & 2 perovskite, 3 & 4 anatase, 5 & 6 ilmenite, 7 & 8 ancylite-(Ce). n.d = not detected, n.a = not analyzed. Total Fe is given as Fe_2O_3. * The ratio FeO/Fe_2O_3 is calculated from stoichiometry.

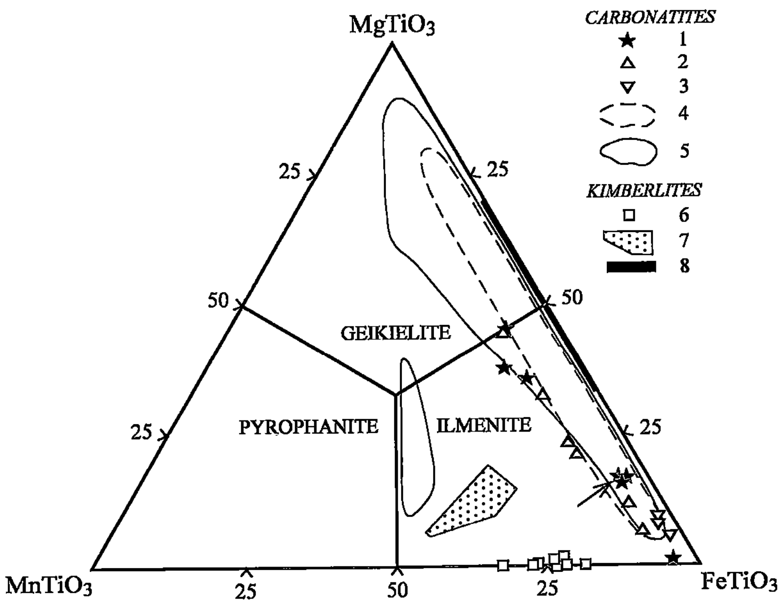

FIG. 3. Composition (mol.%) of ilmenite from carbonatites and kimberlites: 1 Sebljavr, Kola (data from this work indicated by an arrow, other data from Garanin *et al.* 1980), 2 Vuorijarvi, Kola (Garanin *et al.* 1980, Chakhmouradian & Zaitsev, unpubl. data), 3 Turiy Mys, Kola (Garanin *et al.* 1980), 4 Kovdor, Kola (Kopylova *et al.* 1985, Krasnova & Balmasov 1987, Krasnova *et al.* 1991), 5 Jacupiranga, Brazil (Mitchell 1978, Gaspar & Wyllie 1983), 6 Iron Mountain, Wyoming (this work), 7 Premier, South Africa (Gaspar & Wyllie 1984), 8 "kimberlite field" (after Mitchell 1986). Note that the ilmenite compositions at Sebljavr plot along the ilmenite – geikielite join, in the field of typical ilmenite from carbonatites; the ilmenite compositions from Iron Mountain are significantly enriched in pyrophanite.

talline anatase and calcite. The outermost zone of the pseudomorphs consists essentially of ilmenite (Fig. 1D), which is enriched in Mg and, to a lesser extent, Mn (Table 1, anal. 5, 6). Recalculation of the ilmenite compositions shows that it is free of appreciable Fe^{3+}. In the ternary system $FeTiO_3 - MgTiO_3 - MnTiO_3$, most compositions plot near the $FeTiO_3$ – $MgTiO_3$ boundary, in common with ilmenite from other occurrences of carbonatite (Fig. 3). As with other examples of ilmenite from carbonatite, the significant $MnTiO_3$ content distinguishes ilmenite at Sebljavr from that in a typical kimberlite.

From the anatase-rich zone, anhedral grains of ancylite-(Ce) are common in the pseudomorphs. At the rim, ancylite-(Ce) forms large (120–170 μm) euhedral crystals decorating the ilmenite "crust" (Fig. 1D). This ancylite is relatively low in Ca and shows little variation in Sr and *LREE* (Table 1, anal. 7, 8). Note that the pattern of relative enrichment among the *LREE* in ancylite-(Ce) is similar to that in perovskite: Ce > La ≈ Nd > Pr.

Conditions of formation. The replacement textures are observed not only in the carbonatite vein, but also in the wallrock clinopyroxenite. Along the contact, perovskite-rich areas of the wallrock are encrusted with anatase – calcite – ilmenite intergrowths. The same assemblage occurs locally within the wallrock, primarily along fractures. In addition, the clinopyroxenite is enriched in phlogopite and calcite near the contact. As suggested by Kukharenko *et al.* (1965), the replacement of primary diopside in the clinopyroxenite by phlogopite presumably resulted from interaction of the wallrock with a late carbothermal fluid relatively enriched in Al. Ca released from diopside during this interaction presumably precipitated in the form of calcite. This process, commonly referred to as "phlogopitization", is a typical feature of carbonatites associated with alkaline ultramafic rocks (Kukharenko *et al.* 1965, p.721–725). The conversion of diopside to phlogopite plus calcite has been thermodynamically evaluated by Bulakh & Iskoz-Dolinina (1978). These authors have shown that the field of stability of diopside shrinks with increasing $P(CO_2)$ and decreasing activity of silica in the system. In a reasonable range of $P(CO_2)$, the conversion occurs at weakly acid conditions (Bulakh & Iskoz-Dolinina 1978). The crystallization temperature of the calcite

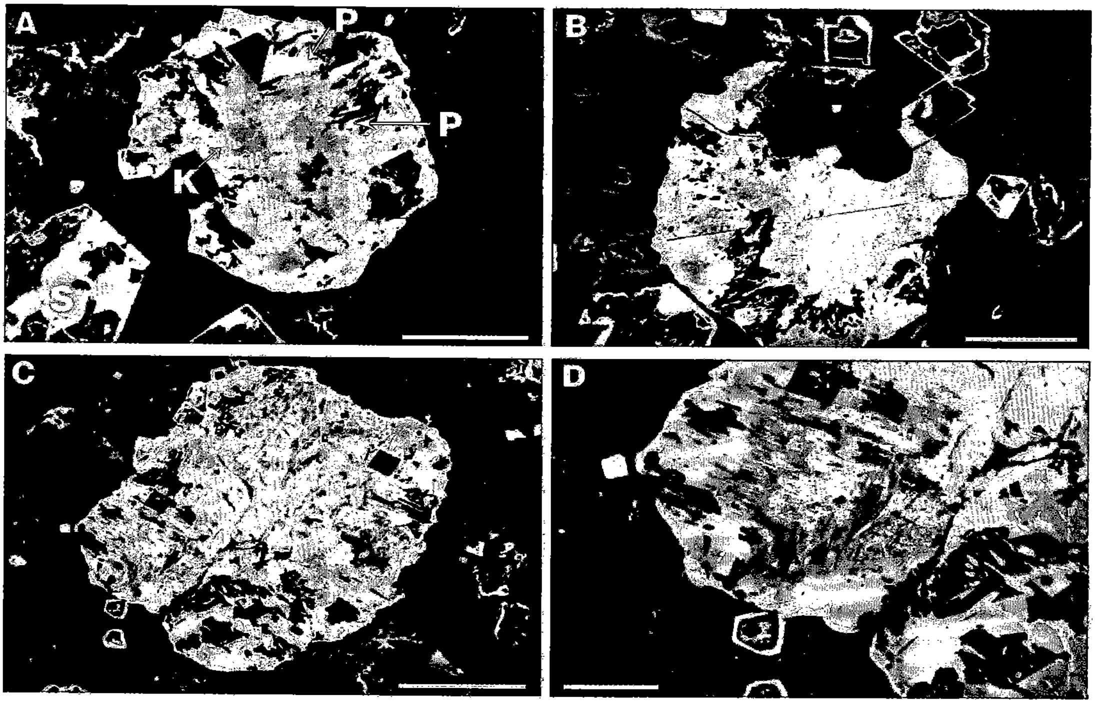

FIG. 4. BSE images of a pseudomorph after perovskite in serpentine calcite kimberlite, Iron Mountain. Bluish green: kassite, blue: anatase and titanite, yellowish green and green: ilmenite, red: lucasite-(Ce), black: calcite (inside the pseudomorphs) and the groundmass minerals (calcite, serpentine, phlogopite, apatite) outside, purple (C): barite. A. Perovskite relics (P) in an essentially anatase – ilmenite pseudomorph. Note that perovskite (P), kassite (K) and chromitic cores of grains of atoll spinel (S) show similar contrast and brightness. B. Regularly zoned pseudomorph with the kassite core, anatase rim and ilmenite developed along the boundary between these two minerals. C. "Patchy" zoned pseudomorph. D. Detail of (C). Note "lamellar" intergrowths of titanite (dark blue) and anatase (light blue). Scale bars are 50 μm (A–C) and 20 μm (D). Note that the black areas are not opaque minerals, but rather low-atomic-number phases, mostly calcite and serpentine.

carbonatite from Sebljavr can be estimated at 250–300°C, based on the data available for other carbonatite complexes of the Kola Peninsula (Bulakh & Iskoz-Dolinina 1978).

The Iron Mountain kimberlite field

The Iron Mountain kimberlite field is situated in southeastern Wyoming, and is a part of the Colorado – Wyoming kimberlite province. The Iron Mountain field is situated on the eastern flank of the Laramie Range and comprises deeply eroded bodies of kimberlite of variable thickness. Most of these are northwest- and northeast-trending dikes (Smith *et al.* 1979).

Sample IM–24a is an aphanitic kimberlite consisting of rounded microphenocrysts of serpentinized olivine set in a uniform groundmass of poikilitic phlogopite – kinoshitalite, fluorapatite and oxide minerals immersed in a serpentine – calcite mesostasis. Phlogopite and apatite occur as elongate crystals and sheaf-like aggregates that poikilitically enclose opaque phases. The oxides comprise nearly 20 vol.% of the rock, and are represented predominantly by spinel-group phases. Two types are distinguishable in the sample: (a) atoll spinel (*sensu* Mitchell & Clarke 1976) ranging from 15 to 75 μm across, and (b) uniform grains ranging from 3 to 20 μm in size. The former are euhedral crystals that have a core of titaniferous magnesian aluminian chromite and a rim composed of Cr-depleted titaniferous magnesian magnetite. The core is separated from the rim by a calcite – serpentine intergrowth. The smaller grains are compositionally similar to the rim of the atoll spinel.

The oxides include complex pseudomorphs after perovskite, which occur as roundish grains ranging from a few tens of μm to 170 μm in diameter. These range from completely opaque to translucent depending on the proportion of their component phases. The primary phase, perovskite, is rarely found in the pseudomorphs. Where present, it occurs as small (usually less than 50 μm) fragments enclosed in the later-crystallizing minerals (Fig. 4A). Compositionally, this perovskite is poor in Na, Nb and *LREE* (Table 2, anal. 1, 2) and approaches ideal $CaTiO_3$ (Fig. 2). Perovskite of similar

TABLE 2. PSEUDOMORPHS AFTER PEROVSKITE IN KIMBERLITE: MINERAL CHEMISTRY

Wt.%	1	2	3	4	5	6	7	8	9*	10*	11
CaO	37.17	36.43	20.96	19.46	1.90	0.68	39.15	34.28	1.06	0.42	5.79
SrO	0.33	0.38	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Na_2O	0.36	0.39	n.d	n.d	n.d	n.d	0.12	0.39	n.d	n.d	n.d
La_2O_3	0.89	1.02	n.d	1.49	n.d	n.d	n.d	0.21	n.d	n.d	12.66
Ce_2O_3	2.09	2.40	2.46	3.48	n.d	n.d	0.07	1.09	n.d	n.d	16.53
Pr_2O_3	0.70	0.68	n.d	n.d	n.d	n.d	n.d	1.60	n.d	n.d	1.60
Nd_2O_3	0.83	0.68	1.23	1.43	n.d	n.d	n.d	n.d	n.d	n.d	4.71
ThO_2	0.35	0.52	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0.78
MgO	n.d	n.d	0.15	n.d	n.d	n.d	n.d	0.31	n.d	n.d	n.d
MnO	n.d	n.d	n.d	0.52	n.d	n.d	n.d	n.d	9.04	14.19	n.d
FeO	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	35.48	30.69	n.d
Fe_2O_3	1.99	1.98	0.99	1.93	0.24	0.27	2.42	5.72	n.d	n.d	0.59
Al_2O_3	n.d	n.d	0.35	n.d	n.d	n.d	n.d	0.03	n.d	n.d	n.d
SiO_2	n.d	n.d	n.d	n.d	n.d	n.d	28.19	27.9	n.d	n.d	0.86
TiO_2	54.62	53.90	62.72	60.31	96.80	96.56	39.15	34.28	52.23	51.87	53.04
Nb_2O_5	1.02	0.63	1.02	1.15	1.13	1.56	0.26	0.37	0.97	0.96	1.95
Ta_2O_5	0.26	0.52	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Total	100.61	99.53	89.88	89.77	100.07	99.07	97.75	96.77	98.78	98.13	98.51
	Structural formulae calculated on the basis of:										
	$\Sigma O = 3$		$\Sigma cat. = 3$		$\Sigma O = 2$		$\Sigma O = 5$		$\Sigma O = 3$		$\Sigma cat. = 3$
Ca	0.928	0.923	1.851	1.763	0.027	0.010	0.991	0.965	-	-	0.303
Sr	0.004	0.005	-	-	-	-	-	-	-	-	-
Na	0.016	0.018	-	-	-	-	0.008	0.026	-	-	-
La	0.008	0.009	-	0.046	-	-	-	0.003	-	-	0.228
Ce	0.018	0.021	0.074	0.108	-	-	0.001	0.014	-	-	0.295
Pr	0.006	0.006	-	-	-	-	-	-	-	-	0.028
Nd	0.007	0.006	0.036	0.043	-	-	-	-	-	-	0.082
Th	0.002	0.003	-	-	-	-	-	-	-	-	0.009
Mg	-	-	0.018	-	-	-	-	0.016	-	-	-
Mn	-	-	-	0.037	-	-	-	-	0.204	0.314	-
Fe^{2+}	-	-	-	-	-	-	-	-	0.792	0.670	-
Fe^{3+}	0.035	0.035	0.061	0.123	0.002	0.003	0.061	0.146	-	-	0.022
Al	-	-	0.034	-	-	-	-	0.001	-	-	-
Si	-	-	-	-	-	-	0.947	0.948	-	-	0.042
Ti	0.957	0.959	3.887	3.835	0.976	0.981	0.989	0.976	0.987	0.994	1.948
Nb	0.011	0.007	0.038	0.044	0.007	0.010	0.004	0.006	0.012	0.011	0.043
Ta	0.002	0.003	-	-	-	-	-	-	-	-	-

Compositions: 1 & 2 perovskite, 3 & 4 kassite, 5 & 6 anatase, 7 & 8 titanite (low-AZ and high-AZ, respectively), 9 & 10 ilmenite, 11 *LREE*-Ti oxide. n.d = not detected. Total Fe is given as Fe_2O_3, in ilmenite as FeO. * Ca and proportional amount of Ti are extracted from structural formula as kassite.

composition is typical of kimberlites, melilitites, nephelinites and ultramafic plutonic rocks associated with carbonatite magmatism (Mitchell 1986, Chakhmouradian & Mitchell 1997).

Most of the pseudomorphs display either regular or complex "patchy" zonation (Figs. 4A–C). The earliest phase to replace perovskite is kassite, essentially $CaTi_2O_4(OH)_2$. This rare mineral was first described from an alkaline pegmatite at the Afrikanda complex on the Kola Peninsula, Russia (Kukharenko *et al.* 1965). At Afrikanda, kassite is a late hydrothermal mineral developed after perovskite and titaniferous magnetite. Other known localities include Magnet Cove, Arkansas (miaroles in nepheline syenite: Evans *et al.* 1986), and Josephine Creek, Oregon (rutile – ilmenite – perovskite – titanite assemblage: Self & Buseck 1991). Dawson & Smith (1977) have described "an unknown Ca-titanate" in a mica – amphibole xenolith of the MARID suite from the Wesselton kimberlite, South Africa. The formula of this mineral calculated from the microprobe data given by Dawson & Smith (1977), is $Ca_{1.01}(Ti_{1.92}Mg_{0.04}Fe_{0.02}Si_{0.01})_{\Sigma 1.99}O_{3.86}(OH)_{2.14}$, thus closely approaching that of kassite.

In the Iron Mountain kimberlite, kassite is translucent with a sand-yellow or brownish color. Optical characteristics of this mineral could not be determined because the grains seem to consist of multiple, possibly twinned individual crystals. Kukharenko *et al.* (1965)

did report the occurrence of polysynthetic twinning in kassite from Afrikanda. The composition of the Iron Mountain kassite deviates only slightly from the ideal formula (Table 2, anal. 2, 3). Most grains show some substitution of Ca by *LREE*, and Ti by Fe and Nb. The presence of *LREE* in the composition indicates a solid solution toward lucasite-(Ce) [$CeTi_2O_5(OH)$], which is isostructural with kassite (Nickel *et al.* 1987, Self & Buseck 1991). The Mg, Mn and Al contents in the Iron Mountain kassite vary from grain to grain, and normally do not exceed 0.4 wt.% oxides.

Further toward the rim of the pseudomorph, kassite is replaced by anatase (Figs. 4B, C). A pale bluish color in thin section, uniaxiality and negative optic sign confirm the identification of this mineral. The mineral contains significant Nb, Ca and minor Fe (Table 2, anal. 5, 6). In common with the Sebljavr pseudomorphs, anatase in the Iron Mountain kimberlite occurs in intimate association with calcite. The latter is found as euhedral to subhedral grains (up to 20 μm) enclosed in anatase. Note that the kassite cores of the pseudomorphs are devoid of calcite (Figs. 4B, C). In some grains, anatase encloses lamellar intergrowths of titanite (Fig. 4D). Back-scattered electron imagery shows that the titanite "lamellae" consist of multiple subparallel zones with slightly differing atomic number (AZ). The individual zones are approximately 4–5 μm in width. The low-AZ zones are depleted in Fe and *LREE* relative to the high-AZ zones (Table 2, anal. 7, 8, respectively). Both types of titanite show some cation deficiency at the tetrahedral site, suggesting that Si^{4+} is partly replaced by Fe^{3+} or Ti^{4+}:

$$Si^{4+} + O^{2-} \rightarrow Fe^{3+} + (OH)^{1-} \qquad (1)$$

$$Si^{4+} \rightarrow Ti^{4+} \qquad (2)$$

Previously obtained spectroscopic, compositional and structural data indicate that Fe^{3+} is a far more common substitute for Si^{4+} in the structure of silicates than Ti^{4+} (*e.g.*, see discussions of site preference in Fe–Ti-bearing garnets, clinopyroxenes and micas in Wu & Mu 1986, Rossman 1982, Mitchell & Bergman 1991, respectively). Hence, it is expected that in the absence of sufficient Al to compensate for the Si deficiency, substitution scheme (1) would preferentially occur in titanite. The accompanying substitution of O^{2-} by $(OH)^{1-}$ explains the low analytical totals characteristic of the Iron Mountain titanite. The amount of Fe^{3+} at the tetrahedral site in our samples does not exceed 5% of the total occupancy (Table 2). Unfortunately, the small size of of the titanite crystals precludes their examination by spectroscopic methods.

In most pseudomorphs, the outermost zone is a thin (less than 8 μm) discontinuous rim of ilmenite (Fig. 4A). In some grains, ilmenite also occurs along the boundary between kassite and anatase and along fractures (Figs. 4B, C). Both types of ilmenite are compositionally identical, thus suggesting that they have crystallized as one generation and developed simultaneously along the rim of the pseudomorphs and zones of weakness within them. Ilmenite is characterized by very low Mg (<0.3 wt.% MgO), high Mn, significant Nb (up to 1.1 wt.% Nb_2O_5) and no appreciable Fe^{3+} (Table 2, anal. 9, 10). These compositional features are commonly observed in ilmenite from carbonatites, but are atypical of Mg-rich ilmenite from kimberlites (Mitchell 1978, 1986, Garanin *et al.* 1980, Fig. 3). However, manganoan ilmenite with up to 17.5 wt.% MnO has been previously described from calcite-rich kimberlites, where this mineral most commonly occurs as "oxy-exsolution" lamellae in spinel or reaction rims on early ilmenite (Agee *et al.* 1982, Gaspar & Wyllie 1984). Interestingly, the EDS spectra invariably show the presence of Ca in the Iron Mountain ilmenite. As demonstrated by experimental studies of Kimura & Muan (1971), there is no solid solution between $FeTiO_3$ and $CaTiO_3$ at low pressures. Therefore, we attribute all Ca in the composition to micro-inclusions of other phases, possibly kassite.

In the Iron Mountain pseudomorphs, the last phase to crystallize, and the major host of the *LREE*, is an unidentified *LREE*–Ti oxide that occurs as minute prismatic crystals measuring up to 10 μm in length and 4 μm in width. This mineral is associated with ilmenite, and developed predominantly along the fractures (Figs. 4B–D). In this oxide, *LREE* (Ce > La > Nd > Pr) and Ti are major elements, and Ca and Nb occur in significant amounts (Table 2, anal. 11). The generalized structural formula of this mineral may be given as $(LREE,Ca)(Ti,Nb)_2(O,OH)_6$ (F was not detected in the EDS spectra). Similar structural formulae are characteristic of a number of minerals, including members of the aeschynite group, *A*- and *Y*-site-deficient pyrochlore-type phases, lucasite-(Ce), and the inadequately characterized mineral "metaloparite" (Fig. 5 and references therein). In terms of the diagram $LREE_2O_3 - TiO_2 - (Nb_2O_5+Ta_2O_5)$, the compositions of the Iron Mountain *LREE*–Ti oxide show the closest correspondence with those of lucasite-(Ce) and "metaloparite". The weight percentages of major components rather than atomic percentages are used in this diagram, because in most early studies, no distinction was made between the individual rare-earth elements (*REE*). Lucasite-(Ce), isostructural with kassite, has been previously found in a heavy-mineral concentrate from olivine lamproite at Argyle, Australia (Nickel *et al.* 1987). "Metaloparite" is a common product of deuteric alteration of loparite-(Ce) from nepheline syenites, foidolites and aegirine – albite rocks. "Metaloparite" has been described from several alkaline complexes in the Kola Peninsula and Siberia (Gerasimovskii 1941, Samoilova 1968, Portnov *et al.* 1983). This mineral is metamict, and differs compositionally from loparite in containing significant H_2O and negligible Na (Gerasimovskii 1941). The compositions of the *LREE*–Ti oxide deviate only slightly from those of lucasite-(Ce) and "metaloparite" on plots of $LREE_2O_3 - TiO_2 - Nb_2O_5+Ta_2O_5$ (Fig. 5). This deviation results from the higher Ca content of the Iron Mountain oxide (5.8–6.0 wt.% CaO), compared to the other

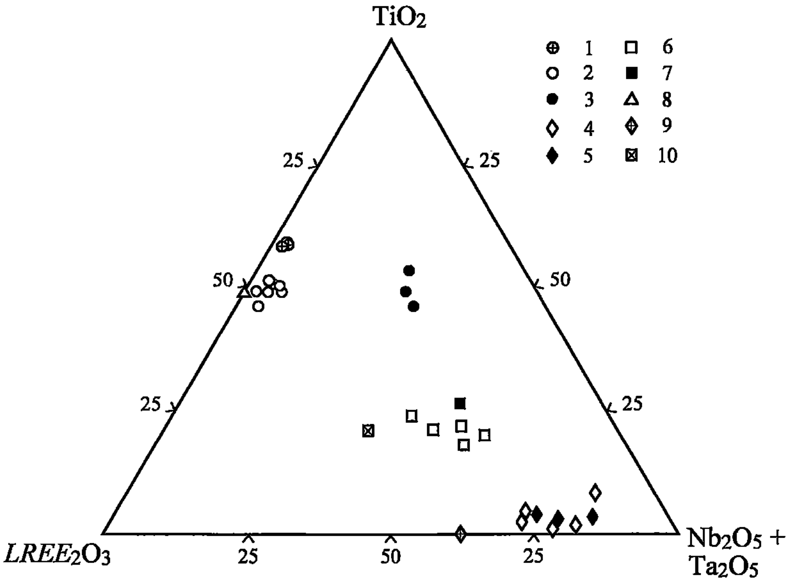

FIG. 5. Composition of various *LREE*–Ti oxides on the triangular diagram $LREE_2O_3 - TiO_2 - Nb_2O_5 + Ta_2O_5$. 1 *LREE*–Ti oxide [? lucasite-(Ce)] from Iron Mountain kimberlite, 2 "metaloparite", Burpala, Siberia (Chakhmouradian & Mitchell, unpubl. data), 3 "ceriobetafite" (Mitchell & Chakhmouradian 1998), 4 ceriopyrochlore, Siberia (Lapin & Kulikova 1989), 5 ceriopyrochlore, Lueshe, Democratic Republic of Congo (Wall *et al.* 1996), 6 niobo-aeschynite-(Ce), Vishnevye Gory, Urals (Lebedeva & Nedosekova 1993), 7 niobo-aeschynite-(Ce), Alaska (Rosenblum & Mosier 1975), 8 lucasite-(Ce), Argyle, Australia (Nickel *et al.* 1987), 9 ideal ceriopyrochlore $CeNb_2O_6(OH)$, 10 ideal aeschynite-(Ce) $CeTiNbO_6$.

two minerals (0.6 wt.% in lucasite-(Ce) and 0.1–2.1 wt.% CaO in "metaloparite"). The accommodation of Ca in the structure of *LREE*–Ti oxide apparently involves the substitution of O^{2-} by $(OH)^{1-}$ in the anionic part:

$$LREE^{3+} + O^{2-} \rightarrow Ca^{2+} + (OH)^{1-} \qquad (3)$$

Note that the scheme (3) essentially describes the solid-solution series between lucasite-(Ce) $LREETi_2O_5(OH)$ and kassite $CaTi_2O_4(OH)_2$. Given that the two minerals are isostructural (Self & Buseck 1991), we suggest that the *LREE*–Ti oxide described here is Ca-bearing lucasite-(Ce).

Conditions of formation. The morphological features and evolutionary trend exhibited by the spinel-group phases in the Iron Mountain kimberlite (Trend 1: Mitchell 1986) suggest interaction between the spinels and a CO_2-rich fluid that precipitated the serpentine – calcite groundmass. The compositional evolution of spinels reflects a rapid fall in $f(O_2)$ due to decrease in temperature during the late stages of groundmass formation (Mitchell & Clarke 1976). The range of temperatures at which this occurred can be estimated as 500–600°C. The replacement of perovskite undoubtedly represents the same event in the crystallization history of the kimberlite, and the very low Fe^{3+} content of the late-stage ilmenite is generally consistent with the decreasing $f(O_2)$ in the system. The complete replacement of microphenocrystal olivine by serpentine, the nearly complete replacement of perovskite, and the abundance of the atoll spinel suggest that $P(CO_2)$ and $P(H_2O)$ remained relatively high, and that the kimberlite evolved essentially as a closed system.

DISCUSSION

Genesis of the pseudomorphs

The pseudomorphs described in the previous section are very similar with respect to their modal composition and mineralogy. In both types of pseudomorphs, perovskite as a primary phase underwent deuteric alteration, which gave rise to a zoned aggregate of calcite and Ti-bearing phases. In both types, Fe–Nb-bearing anatase, calcite and Mn-bearing ilmenite are among the major products of alteration. The pseudomorphs from both occurrences document progressive loss of Ca from perovskite during the initial stages, and increase in Fe^{2+} and Mn^{2+} activities at the late stages of the alteration process. Finally, in both cases, *LREE* minerals are the latest phases to crystallize. The pseudomorphs from the Iron Mountain kimberlite show a more complex assemblage of replacement minerals than those from the Sebljavr carbonatite. Kassite and titanite are important constituents of the pseudomorphs from Iron Mountain, but are not observed in the samples from Sebljavr (Figs. 1, 4). Compared to the Sebljavr carbonatite, anatase and ilmenite from the Iron Mountain kimberlite typically contain variable amounts of Ca (compare Tables 1, 2). The *LREE* released from the early perovskite were accumulated in ancylite-(Ce) in the carbonatite, and in lucasite-(Ce) in the kimberlite.

In the Sebljavr carbonatite and Iron Mountain kimberlite, the pseudomorphs after perovskite occur in a carbonate-rich paragenesis, in which calcite is associated with hydrous minerals (phlogopite and serpentine). Note that in both rocks, perovskite belongs to an earlier assemblage. In the carbonatite, perovskite is a xenocrystic phase assimilated from the wallrock clinopyroxenite; in the kimberlite, it represents the early-forming groundmass mineral. Therefore, the deuteric alteration of perovskite reflects the instability of this mineral in a CO_2-rich fluid. Interaction with the fluid involved progressive leaching of Ca from perovskite, and its successive replacement by kassite or anatase (or both):

$$\mathrm{2CaTiO_3 + CO_2 + H_2O \rightarrow CaTi_2O_4(OH)_2 + CaCO_3} \qquad (a)$$

perovskite kassite calcite

$$\mathrm{CaTiO_3 + CO_2 \rightarrow TiO_2 + CaCO_3} \qquad (b)$$

perovskite anatase calcite

$$\mathrm{CaTi_2O_4(OH)_2 + CO_2 \rightarrow 2TiO_2 + CaCO_3 + H_2O} \qquad (c)$$

kassite anatase calcite

Reaction (b) has been thermodynamically evaluated by Nesbitt *et al.* (1981). These authors have shown that in a variety of groundwater and hydrothermal systems, $P(CO_2)$ is sufficient to shift the equilibrium toward the assemblage TiO_2 plus calcite. The behavior of perovskite and its $BaTiO_3$ analogue in a CO_2-bearing medium has been experimentally studied by Myhra *et al.* (1984). In these experiments, leaching of alkaline-earth elements from perovskite created depletion in Ca coupled with enrichment in Ti and alkaline-earth carbonates in a surface layer. Unfortunately, Myhra *et al.* (1984) did not attempt to identify the structural state of this layer. Hence, it is not clear whether the leaching products in these experiments were represented by TiO_2 or some Ca-deficient Ti-oxide, *e.g.*, kassite or $Ca_2Ti_5O_{12}$.

The occurrence of anatase as a stable TiO_2 polymorph in both kimberlite and carbonatite cannot be explained with certainty. At ambient temperatures, rutile is more stable than anatase or brookite (*e.g.*, Post & Burnham 1986). Correspondingly, in most cases, the secondary TiO_2 polymorph developed after perovskite is labeled as rutile. As established experimentally, minor substitutions of Ti by other cations greatly affect the field of stability of anatase and brookite (Grunin *et al.* 1983). On the basis of mineralogical data for the Kola carbonatite complexes, Kukharenko *et al.* (1965) proposed that anatase is the most stable polymorph in alkaline rocks and associated carbonatites.

Kassite, an intermediate product of conversion of perovskite to anatase [reaction schemes (a) and (c)], is common in the Iron Mountain pseudomorphs, but does not occur at Sebljavr. The simplest explanation may involve different rates of leaching of Ca^{2+} during the initial stages of the alteration process. The work by Nesbitt *et al.* (1981) has shown that there is no simple correlation between the rate of leaching and temperature. Their experiments demonstrate that small crystals of nearly pure perovskite from Wolgidee Hills (Australia) exhibit a lower rate of leaching over a range of temperatures than the large crystal of Nb- and Fe-enriched perovskite from Magnet Cove (Arkansas) (Nesbitt *et al.* 1981). Another controlling factor is $P(CO_2)$ in the fluid. The higher rate of leaching is thus expected in carbonatites, which is supported by our mineralogical observations. Note that the initial difference in composition of perovskite from kimberlitic and carbonatitic source-rocks is very small (Fig. 2), and is unlikely to have any effect on the rate of leaching of Ca^{2+} and pattern of alteration.

In the Iron Mountain samples, anatase and calcite are closely associated with titanite (Fig. 4D). The simultaneous crystallization of anatase with titanite suggests some increase in SiO_2 activity at this stage of the process.

$$\mathrm{CaTi_2O_4(OH)_2 + (SiO_2)_{aq} \rightarrow 2TiO_2 + CaTiSiO_5 + H_2O} \qquad (d)$$

kassite anatase titanite

The absence of titanite in the Sebljavr pseudomorphs reflects the overall low activity of silica in the carbonatite system. The Sebljavr carbonatite is poor in silicate minerals, and the occurrence of phlogopite in the vein is confined to its contacts with the country-rock clinopyroxenite.

The development of an ilmenite rim in both types of pseudomorphs indicates an increase in $a(Fe^{2+})$ and $a(Mn^{2+})$ at the final stages of perovskite alteration. The increase in Fe^{2+} and Mn^{2+} activities most probably resulted from rapid precipitation of the groundmass calcite and corresponding decrease in $a(Ca^{2+})$. Note that in the kimberlite, the groundmass calcite was accompanied by serpentine, whose crystallization consumed most of the Mg present in the system. This explains why the Iron Mountain ilmenite is depleted in Mg, compared to the typical ilmenite from kimberlitic rocks (Fig. 3). The crystallization of ilmenite after anatase can be described by the following reaction scheme:

$$\mathrm{2TiO_2 + 2Fe^{2+} + 2H_2O \rightarrow 2FeTiO_3 + 4H^{1+}} \qquad (e)$$

anatase ilmenite

Perovskite is a principal host for *LREE* in undersaturated ultramafic and alkaline rocks (Kukharenko *et al.* 1965, Mitchell 1986, 1996). Unlike apatite, titanite and other potential carriers of the *LREE* in these rocks, perovskite shows a complete solid-solution series with the *LREE*-dominant counterpart, loparite-(Ce) (Chakhmouradian & Mitchell 1997, 1998). During the replacement of primary perovskite, the *LREE* are released into the fluid and form carbonate complexes stable in neutral and alkaline conditions (Kosterin 1959, Brookins 1989). The precipitation of calcite (see above) and replacement of anatase by ilmenite [scheme (e)] would decrease the stability of these carbonate complexes, and initiate crystallization of the *LREE* minerals ancylite-(Ce) and lucasite-(Ce). As noted above, these minerals are generally confined to the ilmenite-rich zone of the pseudomorphs (Figs. 1D, 4B–D). The occurrence of lucasite-(Ce), not carbonate minerals, as a major host for *LREE* in the Iron Mountain kimberlite presumably indicates the coexistence of *LREE*-carbonate and Ti-bearing complexes in the late portions of the fluid.

Implications for the radioactive waste management

The suitability of perovskite as one of the major components in SYNROC ceramics proposed for long-term conservation of high-level radioactive wastes has been extensively discussed in the literature (Ringwood *et al.* 1979, Nesbitt *et al.* 1981, Myhra *et al.* 1984, Lumpkin *et al.* 1997). Perovskite has been proposed as a principal component of the ceramic waste-forms SYNROC A, B and C, given the high isomorphic capacity of $CaTiO_3$ for Sr and *REE* (Ringwood *et al.* 1979, 1981). Most typical components of the SYNROC perovskite, including Zr, *REE* and actinide elements, may also be incorporated in zirconolite, whereas ^{90}Sr, one of the most hazardous fission products, does not enter the structure of zirconolite in sufficient amounts. Therefore, it is crucial to ensure stability of the perovskite component in the ceramic waste-forms.

The experimental studies on the behavior of perovskite and $BaTiO_3$ in a CO_2-bearing hydrothermal system (Myhra *et al.* 1984) demonstrate that the leaching of Ca^{2+} and Ba^{2+} from the perovskite structure and their subsequent precipitation in carbonates effectively buffers $P(CO_2)$, *pH* and the activity of alkaline-earth cations in the fluid phase. In these experiments, the initially high rate of leaching of the cations is followed by a progressive decrease in leach rate, and the alteration of perovskite is restricted to a very thin surface-layer. However, as shown in the present study, equilibrium with the fluid is rarely achieved in the geological environment. As illustrated in Figures 4B and 4C, the interaction of perovskite with the fluid may result in complete replacement. The conditions at which the replacement occurred are comparable to those experienced by high-level radioactive waste shortly after disposal (McCarthy *et al.* 1979, Come 1986). Importantly, anatase and ilmenite, the major products of replacement of naturally occurring perovskite, are not capable of accommodating Sr and the *REE* leached from the perovskite matrix, owing to their limited structural flexibility. Therefore it is expected that ^{90}Sr, ^{144}Ce and other *REE* isotopes are retained in the leachant fluid (solution) and can migrate from the site of disposal. On this basis, it is recommended here that other potential hosts for *REE* and especially ^{90}Sr be sought, which can provide a more leach-resistant environment for these fission products.

CONCLUSIONS

The results of the present study indicate that perovskite is unstable in a CO_2-rich fluid environment characteristic of some carbonatites and kimberlites. The interaction between the fluid and perovskite involves leaching of Ca^{2+} cations from the perovskite structure and replacement of this mineral by anatase, calcite and ilmenite. The occurrence of kassite and titanite in pseudomorphs is controlled by local factors such as leach rate of Ca^{2+} and activity of silica in the system. The *LREE* released from primary perovskite are deposited at the final stage of the replacement process as carbonates or Ti-bearing oxides. In contrast with the experimental results, our data demonstrate that perovskite alteration in natural environments is not confined to a thin subsurface layer. The alteration process is continuously stimulated by fracturing of perovskite and removal of the buffering carbonate layer, and may proceed to completion.

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