

Perovskite, loparite and Ba-Fe hollandite from the Schryburt Lake carbonatite complex, northwestern Ontario, Canada

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Abstract

Within a suite of felsic-free, mica-rich alkaline ultramafic rocks of the Schryburt Lake carbonatite complex of northwestern Ontario, loparite and Ba-Fe hollandite occur in intimate association with perovskite. The host rocks have variable modal proportions of Mg-olivine, phlogopite, magnetite, ilmenite, apatite and carbonate (generally calcite) with minor Mg-salite. Thus, they correspond to ultramafic lamprophyres (i.e. aillikites), in the sense of Rock (1990) or the lamprophyric facies of the melilitite clan, in the sense of Mitchell (1993).

Perovskite is the principal titanate phase, forming both euhedral and anhedral grains, the latter showing evidence of marginal resorption. It exhibits complex zonal patterns due principally to variations in the light rare earth elements, Na and Nb. In the nomenclature suggested, they may be termed perovskite and cerian perovskite. Loparite forms as small euhedral overgrowths on corroded perovskite cores. Chemically they are essentially solid solutions of loparite, lueshite and perovskite. Consequently, they may be termed calcian-loparite, calcian niobian loparite, niobian calcian loparite, loparite and niobian loparite. Titanates of the hollandite group are rare accessory minerals whose composition closely approach that of the septatitanate $\text{BaFe}^{2+}\text{Ti}_7\text{O}_{16}$.

The complex zoning of the perovskite grains has been attributed to the periodic introduction of carbonatite-derived fluids enriched in REE, Na and Nb into the silicate system during perovskite crystallization. Subsequent reaction of the early perovskite with F-bearing fluids leads to a localized environment enriched in Ti, Na, Nb and REE derived from both the fluid phase and the unstable perovskite. Loparite subsequently crystallizes from these micro-chemical environments.

KEYWORDS: Canada, Ba-Fe hollandite, loparite, perovskite.

Introduction

THE Proterozoic Schryburt Lake carbonatite complex (1145 ± 74 Ma (K-Ar) — Bell and Watkinson as quoted by Sage, 1988) is located at $52^{\circ}37'N$; $89^{\circ}39'W$. This is approximately 128 km northeast of the northwestern Ontario community of Pickle Lake. The complex is essentially unexposed and remains unmapped although it appears to have intruded and, in part, fenitized and Archaean granite gneisses of the Gods Lake Subprovince of the Superior Province. It is marked, however, by a prominent circular positive aeromagnetic anomaly with a surface area of ca. 4.5 km^2 (Sage, 1988).

What little is known of the petrology comes principally from the survey of Sage (1988) and the

associated unpublished study of Higgins (1977). These provide general information on the petrography and geochemistry of samples collected from the regolith, exploration pits and trenches although no claim is made that this suite is necessarily representative of the complex as a whole. However, at the present level of erosion, Sage considers the Schryburt Lake complex to be composed essentially of sövite (calcite carbonatite: Woolley and Kempe, 1989) and silicocarbonatite with minor beforosite and rauhaugite (dolomite carbonatite: Woolley and Kempe, 1989).

A forthcoming manuscript by the author will examine the mineralogy and petrology of the complex in more detail. Particularly evident is the need to re-examine the general field term —

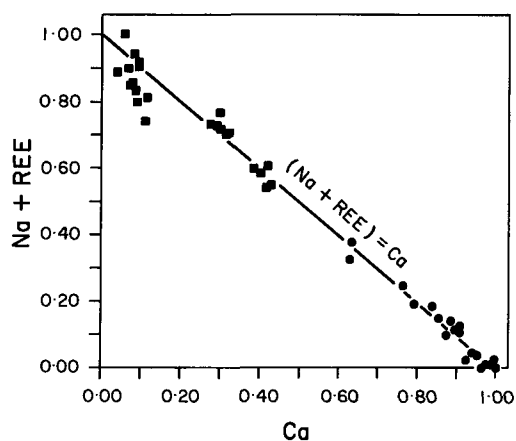


FIG. 1. Plot of (Na + REE) against Ca (atoms) for perovskite (solid circles) and loparite (solid squares). Close proximity of analyses to the line representing a 1:1 replacement of Ca by (Na + REE) indicates essential solid solution between perovskite and loparite.

silicocarbonatite. This appears unfounded for many Schryburt Lake samples and indeed, within this loosely defined group, a discrete suite of felsic-free, mica-rich alkaline ultramafic rocks, which show considerable variation in the development of carbonate, can be recognized. It is within this suite that loparite (Na-REE titanate) and Ba-Fe hollandite are found in intimate association with perovskite.

Host rocks

Mineralogically, the alkaline ultramafic host rocks, which contain perovskite, loparite and Ba-Fe hollandite, are composed principally of Mg-olivine, phlogopite, spinel, ilmenite, apatite and carbonate (generally calcite). Clinopyroxene (Mg-salite) is relatively uncommon and richteritic amphibole is of late metasomatic origin. Zirconolite and sulphides (chalcopyrite, sphalerite, pyrrhotite, pentlandite, millerite) occur in minor amounts and djerfisherite, forming as a metasomatic replacement of pentlandite, is sometimes observed. Modally, this suite of rocks would be classified either as ultramafic lamprophyres (i.e. aillikites) in the sense of Rock (1990) or as members of the lamprophyric facies of the melilitite clan (i.e. olivine phlogopite calcite melnoites) in the sense of Mitchell (1993).

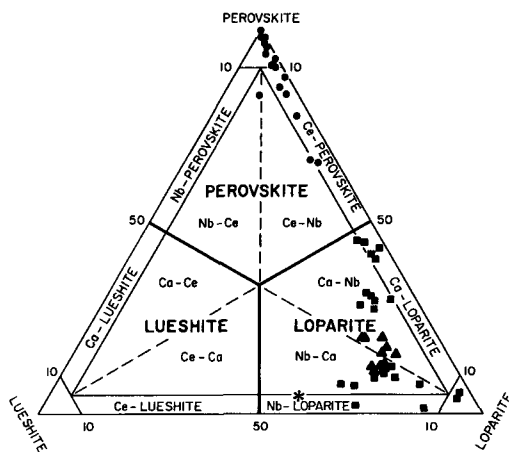


FIG. 2. Perovskite (solid circles) and loparite (solid squares) solid solution compositions, with suggested nomenclature, in terms of mol. percentages of the end-member molecules CaTiO_3 (perovskite), $\text{Na}_{0.5}\text{REE}_{0.5}\text{TiO}_3$ (loparite) and NaNbO_3 (lueshite). Solid triangles represent comparative loparite analyses from the Lovozero complex, Russia (Vlasov *et al.*, 1966). Asterisk represents the composition of nioboloparite (Vlasov, 1966).

Analytical methods

All phases were analysed by standard energy dispersive methods using a Hitachi 570 SEM and a Tracor Northern TN5500 analytical system. Spectra were obtained with an accelerating voltage of 20 kV at a working distance of 28 mm. Multiple least-squares fitting of the sample spectra to reference spectra (McMillan *et al.*, 1985) is used by the Tracor Northern 'standardless' SQ software to obtain quantitative mineral compositions. All such analyses are automatically standardized to 100%. For perovskite and loparite analyses, live-time counting was set at 300 seconds to improve counting statistics for the light elements and in particular for Na. Comparative wavelength dispersive analyses using a Cameca SX-50 microprobe at the University of Manitoba, utilizing synthetic and mineral standards (Mitchell and Vladykin, 1993), gave reasonable agreement with the SQ analyses of perovskite and loparite. Hollandites were analysed by the energy dispersive method, the results of which, as shown by Mitchell and Meyer (1989), are entirely satisfactory.

TABLE 1: Selected perovskite and loparite analyses

Sample	27761	27781	27737	27761	27781	27781	27761	27739	27739
Analysis	1	2	3*	4	5	6	7	8*	9*
TiO ₂	57.65	54.53	53.29	48.11	42.69	41.98	40.55	37.61	32.44
Nb ₂ O ₅	0.72	2.06	2.49	3.43	7.49	8.29	10.50	14.77	20.98
FeO	0.30	0.35	0.80	0.86	0.88	1.54	0.87	0.28	0.71
CaO	38.17	35.87	29.46	14.87	10.59	9.24	10.90	3.08	2.70
SrO	0.00	0.00	0.00	0.32	0.24	0.32	0.00	0.00	0.00
Na ₂ O	0.73	1.98	3.27	7.17	7.62	7.98	7.87	9.95	10.74
La ₂ O ₃	0.74	0.87	2.86	5.51	5.20	5.42	7.61	8.18	9.94
Ce ₂ O ₃	0.46	2.19	5.48	13.39	15.45	15.25	15.35	19.44	18.06
Pr ₂ O ₃	0.00	0.00	0.00	0.93	1.61	1.64	1.28	2.32	1.67
Nd ₂ O ₃	0.29	0.85	2.35	4.88	6.81	7.68	4.09	4.37	2.76
Total	99.06	98.70	100	99.47	98.58	99.34	99.02	100	100
Structural Formulae based on 3 Oxygens									
Ti	0.999	0.968	0.968	0.956	0.891	0.877	0.844	0.806	0.702
Nb	0.008	0.022	0.027	0.041	0.094	0.104	0.132	0.191	0.273
Fe	0.006	0.007	0.016	0.019	0.020	0.036	0.020	0.006	0.017
Ca	0.943	0.907	0.763	0.421	0.315	0.275	0.323	0.094	0.084
Sr	0.000	0.000	0.000	0.005	0.004	0.005	0.000	0.000	0.000
Na	0.032	0.091	0.153	0.368	0.410	0.430	0.422	0.550	0.600
La	0.006	0.007	0.025	0.053	0.053	0.055	0.077	0.086	0.105
Ce	0.004	0.019	0.048	0.130	0.157	0.155	0.155	0.203	0.190
Pr	0.000	0.000	0.000	0.009	0.016	0.016	0.013	0.024	0.017
Nd	0.002	0.007	0.020	0.046	0.067	0.076	0.040	0.045	0.029
Total	2.000	2.028	2.020	2.048	2.027	2.029	2.026	2.005	2.017
Molecular % End-Member Molecules (calculated in the order shown).									
Loparite	3.1	7.1	19.5	51.1	59.9	62.2	58.5	71.4	70.8
Lueshite	1.0	2.0	2.6	4.2	9.6	10.7	13.3	19.1	27.1
Perovskite	95.9	90.9	77.9	44.7	30.5	27.1	28.2	9.5	2.1

* Analysis by Tracor-Northern 'standardless' quantitative analysis package — SQ

Analysis: 1 and 2 — perovskite
 3 — cerian-perovskite
 4 — calcian loparite
 5, 6 and 7 — calcian niobian loparite
 8 — niobian calcian loparite
 9 — niobian-loparite.

Perovskite

Perovskite is the principal titanate phase and becomes modally significant (> 10 vol.%) in perovskite/spinel cumulates with high contents of TiO₂ (27.80 wt.%) and FeO + Fe₂O₃ (22.9 wt.%) (Sage, 1988: Table A-2). Texturally, together with Mg-olivine and spinel, it appears to crystallize as an early phase of the host magma. Morphologically, it forms both euhedral and anhedral grains, with the latter showing evidence of marginal resorption (Fig. 3).

Irrespective of its external form, internally the perovskite exhibits complex zonal patterns which

are often cross-cutting and which often exhibit resorption phenomena (Figs. 3, 4). Compositional variations result from differing concentrations of light REE, Na and Nb (Table 1, Figs. 1, 2) and this is particularly well shown by variations in the average atomic number observed with back-scattered electrons (Figs. 3, 4). No predictable chemical changes from core-to-rim can be established although the complexity of the intergrowths would suggest significant chemical fluctuations in the magma during crystal growth. The cores of the zoned perovskite grains occasionally consist of corroded remnants of essentially pure CaTiO₃ (Fig. 4) which appear to

have acted as seeds for subsequent growth. The origin of these is somewhat circumspect, for at this time, it is not possible to know if they are xenocrysts or early phenocrysts of the host magma. It is quite apparent, however, that they have undergone reaction before the subsequent development of the complex overgrowths. Whether or not this reaction has or has not occurred with the host magma is difficult to assess.

Although no predictable core-to-rim variations are observed, the overall compositional changes essentially involve fluctuations of light *REE* and Na with, to a lesser extent, Nb. The *A*-site substitution: $\text{Na}_{0.5} + \text{REE}_{0.5} \rightleftharpoons \text{Ca}$ (Table 1, Fig 1), also expressed as CaTiO_3 (perovskite) – $\text{Na}_{0.5}\text{REE}_{0.5}\text{TiO}_3$ (loparite) solid solution (Fig. 2), accounts for much of the observed compositional variations. Minor *B*-site replacement of Ti by Nb, representing subordinate NaNbO_3 (lueshite) solid solution, is also consistently observed (Table 1 and Fig. 2). In the nomenclature suggested for the perovskite-loparite-lueshite system (Fig. 2), the majority of the zoned perovskites are termed perovskite and cerian perovskite.

Loparite

Fleischer and Mandarino (1991) express the chemical formula of loparite as $(\text{Ce,Sr,Na,Ca})_2(\text{Ti,Nb})_2\text{O}_6$. However, in this paper, the compositions of the Schryburt Lake loparites are more generally discussed as solid solutions of the end-member molecules CaTiO_3 – $(\text{Na}_{0.5}\text{REE}_{0.5})\text{TiO}_3$ – NaNbO_3 which, hereafter, are referred to as perovskite, loparite and lueshite respectively. In this context, *REE* represents the content of light rare earth elements, principally La and Ce. Tausonite (SrTiO_3) is an insignificant end-member component of the Schryburt Lake loparites (Table 1) and is subsequently ignored. Loparite from Schryburt Lake forms in intimate association with perovskite. Almost without exception it forms as small and distinct euhedral overgrowths on corroded perovskite substrates (Fig. 3). In a strict mineralogical sense, the loparites from Schryburt Lake (Table 1) would be termed loparite-(Ce) (Bayliss and Levinson, 1988). However, as the observed loparites are principally complex solid solutions of the three end-member components mentioned above, in

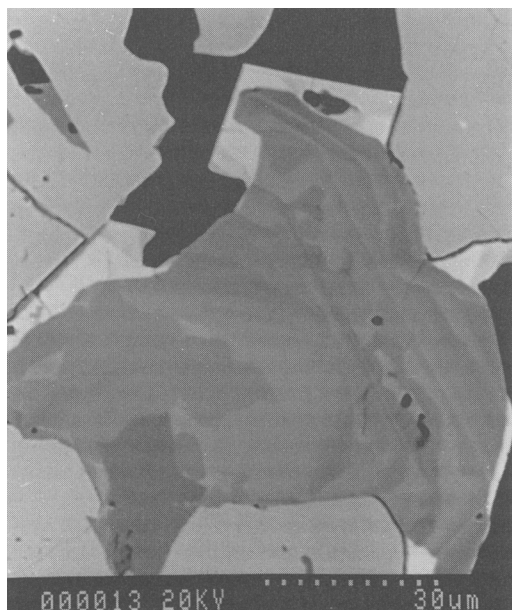


Fig. 3. Back-scattered electron image of a complexly zoned perovskite with embayed margins and a euhedral loparite overgrowth. Variations in grey scale reflect variations in average atomic number of the matrix, lighter shades having higher values. General variation caused by fluctuations in light *REE* and Nb.

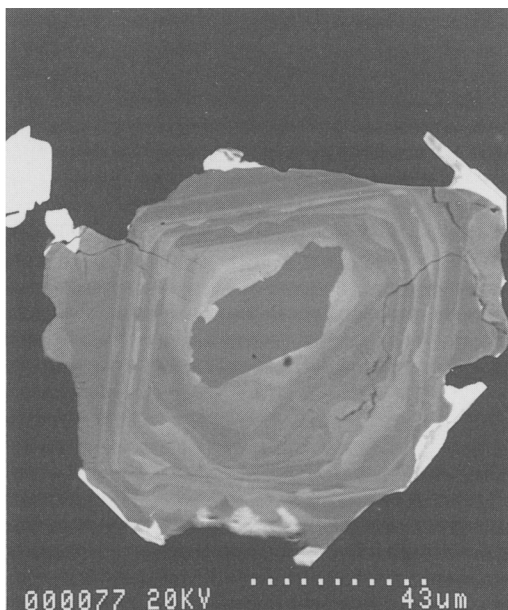


Fig. 4. Back-scattered electron image of complex but generally euhedral perovskite zoning. Dark embayed nucleus is pure CaTiO_3 . Light marginal overgrowths are loparite.

terms of the solid solution nomenclature recommended in Fig. 2, they are here referred to as calcian loparite, calcian niobian loparite, niobian calcian loparite, loparite and niobian-loparite.

Principal *A*-site substitutions in the calcian loparites, calcian niobian loparites and loparites are represented by $\text{Na}_{0.5} + \text{REE}_{0.5} \rightleftharpoons \text{Ca}$ (Fig. 1). In this respect, they are similar to the zoned perovskites and simply represent more loparite-rich members of the perovskite-loparite solid solution. In response to increasing Nb substitution for Ti in the *B*-site cations, and a corresponding substitution of Na for *REE* in the *A*-site cations, compositions of niobian calcian loparites and niobian-loparites become increasingly rich in the lueshite molecule (Fig. 2). Compositions approach that of Nioboloparite (Vlasov, 1966) (Fig. 2) but there seems little justification in treating this as a separate mineral species. Nioboloparite is considered here as niobian loparite with significant lueshite solid solution.

Although a significant range of loparite compositions is observed, compositional variations within individual rocks are much more restricted. Observable groupings of loparite compositions in Fig. 2 reflect this phenomenon. This suggests that localized chemical/physical conditions may play a potentially important role in the formation of loparite.

Loparite has been observed primarily in nepheline syenites, urtites, juvites and alkali pegmatites of alkaline/peralkaline massifs of the Kola Peninsula (Vlasov *et al.*, 1966) and of Siberia (Kravchenko and Vlasova, 1959). Comparative loparite compositions from the Lovozero complex, Russia (Vlasov *et al.*, 1966) are plotted in Fig. 2 on the basis of which they are termed calcian niobian loparite and niobian calcian loparite.

Unusual occurrences of loparite have also been reported by Haggerty and Mariano (1983) from rheomorphic fenites associated with carbonatites in Paraguay (Sarambi and Chiriguelo) and Brazil (Salitre-1). These loparites contain significant Sr when compared to those of Russia and Schryburt Lake and in a recent study by Mitchell and Vladykin (1993), they have been classified as strontian calcian loparite and niobian strontian loparite. In this paragenesis, loparite is again found, as in the Russian examples, with felsic and alkali-rich minerals (sanidine, nepheline and aegirine).

The Schryburt Lake loparite occurrence is therefore highly unusual in a number of ways: it occurs in an environment free of feldspathoids and feldspar and it is found intimately associated with perovskite in a low SiO_2 -activity environment.

Moreover, the host rocks are mafic and potassic in character and in this respect, they differ substantially from the sodic/persodic felsic host rocks of previously described occurrences.

Loparite, which prior to these observations, with the possible exception of the Khibina complex, Russia, in which the carbonatites are not well known, has not been recognized in igneous rocks integral to a carbonatite complex, has subsequently been observed by the author in the Big Beaver House and Prairie Lake carbonatite complexes of northwestern Ontario. These occurrences have not yet been studied in detail. In addition, R.H. Mitchell (pers. comm.) has now observed loparite in the Afrikanda carbonatite complex of Russia.

Ba-Fe Hollandite

Titanates of the hollandite group are rare accessory minerals in the Schryburt Lake complex and to-date, they have only been observed in a single specimen of a perovskite-spinel cumulate. Here, they are found as inclusions in perovskite but never as later marginal overgrowths, as is the case for loparite. Selected and comparative analyses of these phases are given in Table 2.

Hollandites have the general formula $A_xB_yC_{8-z}O_{16}$ with *x*, *y*, and *z* ideally approaching unity. Large *A*-site cations (e.g. Ba, Sr, Ca, K, Cs, Th) occupy tunnel sites formed by corner-sharing of columns of edge-sharing MO_6 octahedra. Smaller *B*-site cations (e.g. Fe^{2+} , Fe^{3+} , Ce, V, Cr, Mg) and *C*-site cations (e.g. Ti, Nb) occupy octahedral framework sites. Structural formulae calculations of hollandite are complicated by common non-stoichiometry and elements existing in more than one valency state (e.g. Fe, Ti). More detailed accounts of hollandite-group mineralogy may be found in Mitchell and Meyer (1989), Mitchell and Bergman (1991) and Mitchell and Vladykin (1993).

Chemically, the *A*-site cations of the Schryburt Lake hollandites are dominated by Ba with minor Ca, Sr and Th (Table 2). Potassium is entirely lacking. *B*-site cations are predominantly Fe with minor Ce, V, Mn and Mg, and the *C*-site cations are essentially Ti with minor Nb (Table 2). Compositionally, these hollandites closely conform to members of the $\text{BaFe}_2^+\text{Ti}_6\text{O}_{16}$ – $\text{BaFe}^{2+}\text{Ti}_7\text{O}_{16}$ solid solution. Although the non-stoichiometric nature of hollandites (Mitchell and Meyer, 1989) makes the estimate of the relative contents of Fe^{3+} and Fe^{2+} in the *B*-sites difficult, the low total Fe-content (i.e. 7.65–9.65 wt.% when

TABLE 2: Selected and comparative Ba-Fe hollandite analyses

Analysis	1	2	3	4	5	6	7	8
TiO ₂	69.02	71.34	69.52	70.59	72.00	67.2	68.7	70.13
Nb ₂ O ₅	0.71	0.47	0.66	0.70	n.a	0.0	0.6	0.18
V ₂ O ₃	0.52	0.59	0.18	0.44	n.a	0.0	1.3	0.28
Fe ₂ O ₃ *	8.87	7.90	9.19	7.79	11.39	14.4	12.0	8.01
Ce ₂ O ₃	1.38	1.16	1.36	1.73	n.a	n.a	n.a	0.0
MnO	0.21	0.09	0.23	0.18	n.a	0.5	0.0	n.a
MgO	0.26	0.46	0.45	0.35	0.0	0.0	0.0	0.0
CaO	0.74	1.12	0.61	0.80	n.a	n.a	n.a	n.a
SrO	0.24	0.00	0.17	0.14	n.a	n.a	n.a	n.a
BaO	17.79	16.87	17.36	17.08	15.00	16.7	17.1	20.45
ThO ₂	0.26	0.00	0.27	0.20	n.a	n.a	n.a	n.a.
K ₂ O	0.00	0.00	0.00	0.00	0.40	0.3	0.4	0.0
Total	100.00	100.00	100.00	100.00	98.79	99.1	99.5	99.05

*Total Fe reported as Fe₂O₃ for comparative purposes.

n.a - not available

Structural Formulae of Schryburt Lake Hollandites based on 16 Oxygens with total Fe as FeO

Analysis 1: (Ba_{0.92}Ca_{0.10}Sr_{0.02}Th_{0.01})Σ1.05(Fe_{0.88}Mn_{0.02}Mg_{0.05}Ce_{0.07}V_{0.06})Σ1.08(Ti_{16.85}Nb_{0.04})Σ6.89O₁₆

Analysis 2: (Ba_{0.86}Ca_{0.16})Σ1.02(Fe_{0.77}Mn_{0.01}Mg_{0.09}Ce_{0.05}V_{0.06})Σ0.98(Ti_{16.94}Nb_{0.03})Σ6.97O₁₆

Analysis 3: (Ba_{0.89}Ca_{0.09}Sr_{0.01}Th_{0.01})Σ1.00(Fe_{0.91}Mn_{0.03}Mg_{0.09}Ce_{0.07}V_{0.02})Σ1.12(Ti_{16.87}Nb_{0.04})Σ6.91O₁₆

Analysis 4: (Ba_{0.87}Ca_{0.11}Sr_{0.01}Th_{0.01})Σ1.00(Fe_{0.76}Mn_{0.02}Mg_{0.07}Ce_{0.08}V_{0.05})Σ.08(Ti_{16.85}Nb_{0.04})Σ6.96O₁₆

Analyses: (1–4) Schryburt Lake; (5) Kovdor (Zhuraleva *et al.*, 1978); Murun complex (Mitchell and Vladykin, 1993); (7) Sover North kimberlite (Mitchell and Vladykin, 1993); (8) Prairie Creek lamproite (Mitchell and Bergman, 1991).

calculated as Fe₂O₃, Table 2), and close to ideal values in the formulae calculated with total Fe as FeO (Table 2), suggest a preponderance of the septatitanate molecule (cf. Mitchell and Vladykin, 1993).

Similar Ba–Fe hollandites have been recorded in the Kovdor carbonatite complex of Russia (Mitchell and Vladykin, 1993), the Prairie Creek lamproite of Arkansas (Mitchell and Bergman, 1991), the Wesseltin and Benfontein kimberlite sills of South Africa (Mitchell, 1992), and the Sover North kimberlite of South Africa (Mitchell and Vladykin, 1993). Minor compositional differences of Ba–Fe hollandites from these locations occur principally within the B-site cations, particularly with respect to V, Ce and Mg (Table 2 and original references). Variations in A-site K and C-site Nb are also observed. The Schryburt Lake hollandites also fall into this general scenario, being, for example, the first recorded with significant Ca, albeit minor, in the A-site.

In the only other previously recorded occurrence of such hollandites from carbonatite complexes at Kovdor, the hollandites appear to replace earlier Ti-rich minerals (Zhuraleva *et al.*, 1978). At Schryburt Lake, the relationship of

perovskite and hollandite is difficult to assess, although occurring as it does within perovskite grains (Fig. 5), as opposed to a marginal overgrowth, the hollandite appears to be an early phase of the magma. In this respect, it conforms to the formation of similar hollandites in lamproites and kimberlites (Mitchell and Vladykin, 1993).

Discussion

The association of loparite with complexly zoned and often corroded perovskites may well be fortuitous although a more intimate association seems probable. Major questions about perovskite concern the origin of its complex and irregular zoning and the formation of the external reaction surfaces adjacent to loparite. Discussion of the paragenesis of the loparite itself must address the role of both magmatic and metasomatic processes.

The complex, intricate and unpredictable zonal variations of Na, light REE and Nb in perovskite are not easily explained by simple closed-system differentiation. Perovskites zoned with respect to Na, REE and Nb may form by the effective fractionation of early Mg-olivine and spinel from a low SiO₂ activity alkali magma. In and of itself,

however, this would not explain the random complexities of the zonal patterns.

If, however, the magmatic system were open to periodic influxes of fluids with elevated but variable concentrations of the required elements, the random effects on perovskite compositions could explain the complex zoning. At Schryburt Lake, the source of such fluids is difficult to assess due in part to an incomplete knowledge of the complex. Potential fluid sources could originate from (1) (agpaitic) nepheline syenite; (2) ijolite/urtite; and/or (3) carbonatite magmas. No evidence exists at Schryburt Lake for either of the first two magma types but neither can be totally discounted.

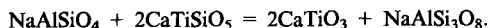
Agpaitic nepheline syenites, for example, are the principal host of major loparite occurrences in Russia (Vlasov *et al.*, 1966) although such magmas are rarely found associated with carbonatite complexes. However, ijolites/urtites are often associated with such complexes (le Bas, 1977), and although not observed directly at Schryburt

Lake, the associated positive gravity anomaly may support their presence at depth. Interestingly, they are known to occur as an integral part of the closely associated (geographically and temporally) Big Beaver House carbonatite complex (Sage, 1987) in which the author has identified similar perovskites and loparites.

Carbonatite magmatic systems are an alternative attractive source of fluids enriched in Na, light REE and Nb. Sodium-metasomatism associated with carbonatite occurrences has been well documented and at Schryburt Lake, it manifests itself by the development of metasomatic richteritic amphibole. Residual carbonates rich in Na and/or light REE (i.e. ancylite, burbankite, huanghoite) are also observed. There seems little doubt that fluids enriched in Na and light REE exist as part of the Schryburt Lake carbonatite systems. Such fluids may also be capable of scavenging Nb.

To be effective, these fluids must be periodically introduced into the silicate magma during perovskite crystallization. This requires that both the carbonatite and silicate parts of the magmatic system coexist in close spatial and temporal proximity. Evidence for this comes from certain streaky-textured rocks in which MnO-rich, Ni-poor Mg-olivines coexist side by side with MnO-poor, Ni-rich Mg-olivines of similar Mg number. The former olivines are indicative of the carbonatites, the latter of the alkali ultramafic silicate rocks (manuscript in prep.).

Whatever the legitimate origin of the zoning, perovskite becomes locally corroded prior to the formation of the euhedral loparite overgrowths (Figs. 1, 2). Given the low SiO₂-activity alkali character of the host magma and the early crystallization phases of Mg-olivine and spinel, ascribing this instability to simple fractionation with a concomitant late-stage increase in SiO₂-activity seems unlikely. If anything, a late-stage increase in alkali-activity would be expected on fractionation. However, Veksler and Teptev (1990) have shown that perovskite stability is, in fact, enhanced in the silica-undersaturated part of the system SiO₂-TiO₂-Al₂O₃-CaO-MgO-Na₂O by an increase in the Na/Al ratio due to the reaction:



Unfortunately, the absence of feldspathoids and feldspars in the perovskite-host rocks makes the role of the Na/Al ratio on the ultimate stability of perovskite difficult to assess.

The composition of the invading fluid phase may provide the key to perovskite stability and, in this respect, the role of fluorine presents

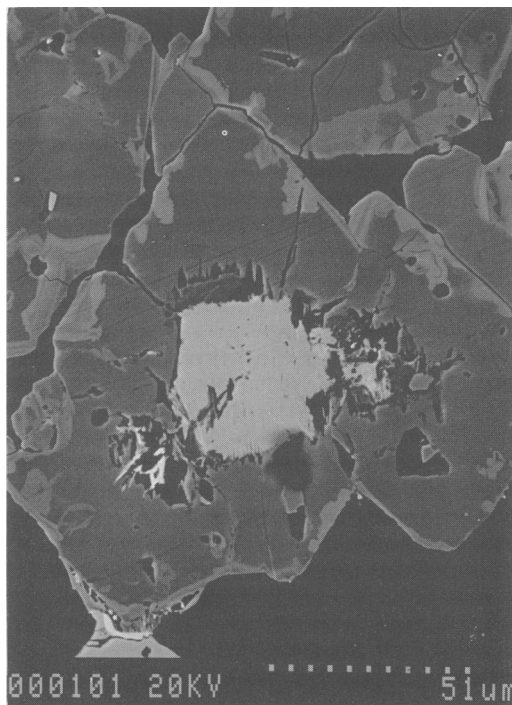


FIG. 5. Back-scattered electron image and Ba-Fe hollandite (light grey) associated with euhedral perovskite (dark grey) showing marginal development REE and Nb enriched perovskite (medium grey).

interesting possibilities. In the simplified carbonate system $\text{CaCO}_3\text{-Na}_2\text{CO}_3\text{-F-Pyrochlore}$, perovskite becomes unstable at F contents >1 wt.% at temperatures $>930^\circ\text{C}$ (Jago *et al.*, 1993). Although not completely analogous to the Schryburt Lake environment, the possibility of late F-rich fluids emanating from the carbonatites and subsequently reacting locally with perovskite must be seriously considered.

The local chemical environment created by a fluid-perovskite reaction would be enriched in TiO_2 as well as those other elements scavenged from the perovskite (i.e. Nb, light REE and Na). Concentrations of these latter elements may also be enhanced from the pervading carbonatite fluid phase. The local environment may thus become conducive for the precipitation of loparite on the corroded perovskite surfaces. This particular hypothesis infers that loparite would tolerate a more F-rich environment than perovskite. No specific information is available on this tolerance but considering the pinnacle of loparite formation is in the apgaitic nepheline syenites of the Kola Peninsula, this may not be an unreasonable assertion.

Composition fluctuations of the invading fluids, and the localized chemical environments of loparite formation, may also explain the variations of Ca, Na, Nb and light REE in loparite compositions observed between the various alkaline ultramafic host rocks.

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