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LOVERINGITE AND BADDELEYITE IN LAYERS OF CHROMIAN SPINEL FROM THE BRACCO OPHIOLITIC UNIT, NORTHERN APENNINES, ITALY

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ABSTRACT

Loveringite and baddeleyite are found within layers of chromian spinel in gabbroic cumulates from the ophiolitic Bracco Unit, Liguria, northern Apennines, Italy. Altered plagioclase or olivine represent the major phases interstitial to the chromian spinel; loveringite and baddeleyite, together with magnesian or manganoan ilmenite, sodium phlogopite, Ti-rich pargasite, rutile, Zr-rich titanite, apatite, Cu and Ni sulfides, are accessory phases. Electron-microprobe analyses indicate low *REE* contents in loveringite, and relatively high Cr and Mg contents in both loveringite and baddeleyite. An origin involving an interstitial liquid enriched in incompatible elements introduced by metasomatic infiltration during fractionation of chromian spinel seems likely. The presence of such minerals provides important evidence that it is possible to crystallize rare incompatible-element-rich oxides in a pile of cumulates in a tholeiitic ophiolite.

Keywords: baddeleyite, loveringite, oxides, mineral chemistry, ophiolite, Apennines, Liguria, Italy.

SOMMAIRE

Nous documentons la présence de loveringite et de baddeleyite dans des niveaux de spinelle chromifère dans des cumulats gabbroïques de l'unité de Bracco, de nature ophiolitique, en Ligure, dans le secteur nord des Apennins, en Italie. Le plagioclase et l'olivine altérés constituent les phases interstitielles au spinelle chromifère. La loveringite et la baddeleyite, avec ilménite magnésienne ou manganifère, sodium phlogopite, pargasite titanifère, rutile, titanite zirconifère, apatite, et sulfures de Cu et de Ni sont les minéraux accessoires. Les analyses à la microsonde électronique démontrent de faibles teneurs des terres rares dans la loveringite, et des teneurs élevées en Cr et en Mg dans la loveringite et la baddeleyite. Une origine à partir d'un liquide interstitiel enrichi en éléments incompatibles introduit par infiltration métasomatique au cours du fractionnement du spinelle chromifère semble probable. La présence de tels minéraux démontre qu'il est possible de cristalliser des oxydes enrichis en éléments incompatibles dans un amas de cumulats dans un massif ophiolitique à tendance tholéiitique.

(Traduit par la Rédaction)

Mots-clés: baddeleyite, loveringite, oxydes, composition des minéraux, ophiolite, Apennins, Ligure, Italie.

INTRODUCTION

Loveringite is a relatively uncommon mineral generally occurring in ultramafic–mafic layered intrusions (Gatehouse *et al.* 1978, Campbell & Kelly 1978, Kelly *et al.* 1979, Alapieti 1982, Alapieti & Lahtinen 1986, Tarkian & Mutanen 1987, Lorand *et al.* 1987, Merkle 1992, Barkov *et al.* 1994). It represents the Ca end-member of the crichtonite group of minerals (general formula: $AM_{21}O_{38}$). The other isostructural members, subdivided according to the dominant cation occupying the large *A* site, are landauite (Na), davidite (*REE* + U), crichtonite (Sr), lindsleyite (Ba), mathiasite (K) and senaite (Pb). The *M* position is mostly occupied by Ti and, in minor amounts, by other small cations such as Fe, Cr, Zr, Nb, Mn, Zn, and V (Haggerty 1991, and references therein). Loveringite normally exhibits a variable amount of solid solution with davidite. In their investigation of the high-pressure synthetic members of the loveringite–davidite solid-solution series, Green & Pearson (1987), partitioned the light rare-earth elements (*LREE*) on the *A* site and the heavy rare-earth elements (*HREE*) on the *M* site.

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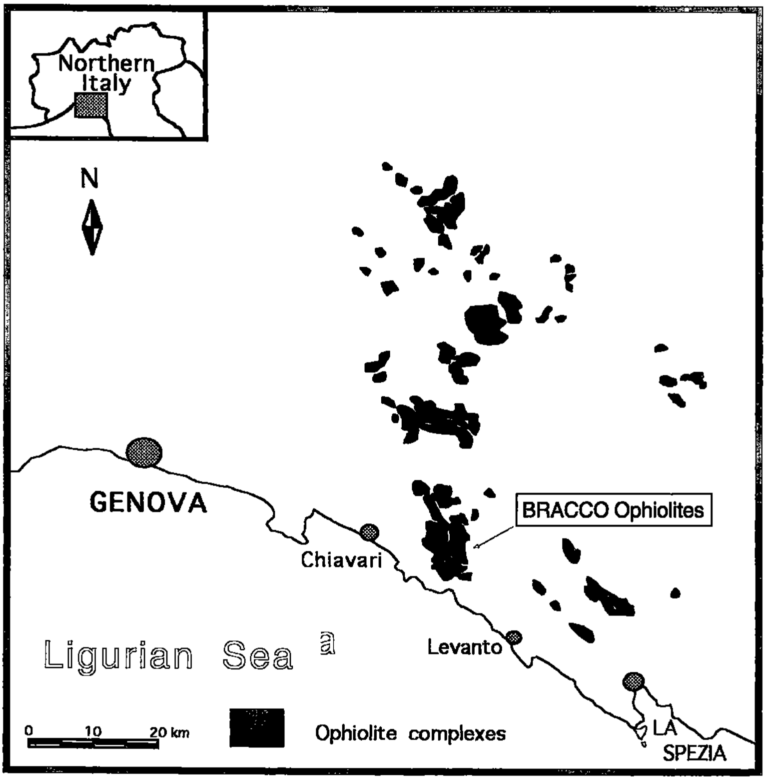

FIG. 1. Ophiolite complexes of the northern Apennine belt, Italy.

Baddeleyite (ZrO_2) is one of the more important mineral carriers of Zr and Hf in magmatic rocks; Ti, Fe and U commonly are present as minor elements. In the past, it was considered as a uniquely lunar and meteoritic mineral, but it has recently been found in a large variety of terrestrial rocks. A comprehensive review of baddeleyite occurrences, their petrology and geochemistry has been published by Heaman & LeCheminant (1993), who grouped the occurrences in terms of mafic and ultramafic rocks, alkaline rocks, "mantle" baddeleyite and metacarbonates.

Many authors, such as Lorand *et al.* (1987) and Heaman & LeCheminant (1993), have pointed out that the relative paucity of data about these minerals is mostly due to oversight during routine microscope analysis. However, the presence of loveringite and baddeleyite has important petrological and geochemical implications as evidence of local enrichment of some incompatible elements in a basic-ultrabasic magmatic intrusive system.

Loveringite and baddeleyite have been identified by reflected-light microscopy and by electron-microprobe investigation in pods of chromian spinel in melatroctolites of the sequence of gabbroic cumulates from the ophiolitic Bracco unit, Val di Vara Supergroup, Liguria, northern Apennines, Italy (Cortesogno *et al.* 1987). This is the first Italian occurrence of loveringite and, according to the review of Talkington *et al.* (1984), the first discovery of loveringite and baddeleyite included in chromite from an ophiolitic complex.

GEOLOGICAL FRAMEWORK

The Bracco Unit (BU) represents one of the larger outcrops of Jurassic ophiolites of the northern Apennines (Fig. 1). The gabbro massif occurs as a body 500 m in thickness and several kilometers in width, intruding upper mantle lherzolites. It is represented by a pile of troctolitic and clinopyroxene gabbro cumulates, with minor melatroctolite, plagioclasite, and dunite (Bezzi & Piccardo 1971, Cortesogno *et al.* 1987). A volcano-sedimentary sequence, consisting of ophiolitic breccias, basalts and cherts capped by calcareous shales, directly overlies the ultramafic and gabbroic rocks.

The mafic and ultramafic rocks record a sequence of ocean-floor metamorphic events, which partially affected the breccias and basalts also. In the basement to the ophiolitic sequence, metamorphism evolved from a high-T amphibolite facies to low-T hydrothermal conditions (Cortesogno & Lucchetti 1982, 1984). The

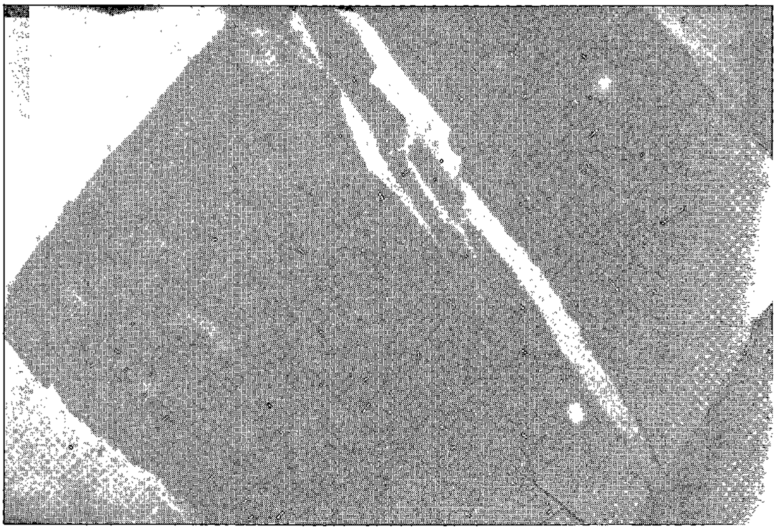

FIG. 2. Reflected-light micrograph of exsolution-induced rods of rutile in chromian spinel; the field of view is *ca.* 1 mm in maximum dimension.

whole ophiolitic sequence was affected during the Alpine orogeny by a tectono-metamorphic overprint under conditions of the prehnite-pumpellyite facies (Cortesogno *et al.* 1987).

PETROGRAPHIC FEATURES OF THE CHROMIAN SPINEL LAYERS

Chromian spinel is a common constituent of dunites and melatroctolites. The small disseminated grains (0.1–3 mm) show a euhedral to subhedral habit. Locally, the chromian spinel occurs as chromitite bands 0.1 to 10 cm thick, showing cumulus textures. Plagioclase and olivine were the main interstitial minerals, and have been replaced by metamorphic phases. Grains of chromian spinel are most commonly concentrated in irregularly shaped pockets up to 15 cm thick, in a plagioclase matrix. Exceptionally, layers of chromian spinel 1–7 cm thick occur rhythmically interbedded between melatroctolite and leucotroctolite, which grade to anorthosite layers. In some cases, the chromian spinel grains have undergone partial to complete replacement by ferrian chromite ("ferritchromit") or magnetite, during metamorphism and alteration.

Grains of chromian spinel commonly contain solid inclusions having polygonal (negative crystal) to subrounded shapes. The inclusions rarely exceed 1 mm across, most being less than 100 μm. They contain silicates, sulfides and oxides, in decreasing order of abundance. These minerals, where unaltered, exhibit anomalous abundances of incompatible elements. The silicates are mainly phlogopite and sodium phlogopite, Ti-rich pargasite and subordinate clino- and orthopyroxenes. Both micas and amphiboles commonly exhibit lamellae of Ti-rich oxides. Chalcopyrite, pentlandite and pyrrhotite are dominant among primary sulfides, with bornite and pyrite definitely subordinate. The oxide minerals in the inclusions are well represented by rutile (Fig. 2) and magnesian or manganoan ilmenite, and minor loveringite and baddeleyite; apatite and Zr-rich titanite are rarely found. The inclusions are characterized by minerals enriched in incompatible elements (Ti, Zr, Na, Cu, Mn). This may indicate that spinel crystallization possibly has been affected by interaction with the intercumulus liquid (Lorand & Cottin 1987a).

TEXTURES SHOWN BY LOVERINGITE AND BADDELEYITE

Loveringite occurs in one of four different textural sites: a) as a member of unaltered silicate- or sulfide-rich inclusions (Figs. 3, 4 and 5), b) as monomineralic inclusions, c) as small grains on the surface of chromian spinel (Fig. 6), and d) as interstitial grains. Loveringite crystals of type a and b are subhedral to euhedral or, rarely, form elongate rods. The dimensions of the grains vary from 2 × 2 μm to approximately 10 × 10 μm. Type-a crystals commonly are located along the walls of the inclusion, with the major axis parallel or subparallel to the cleavage of the enclosing silicate.

In many cases, loveringite is hosted within Ti-rich sodium phlogopite associated with rutile or sulfides such as chalcopyrite or pentlandite (Fig. 3). In a few cases (types b and c), crystals occur within grains of chromian spinel or as micrometric crystals located at grain boundaries (Fig. 6). A very few crystals (type d), up to 50 × 30 μm, were found as lobate grains interstitial to olivine in the groundmass.

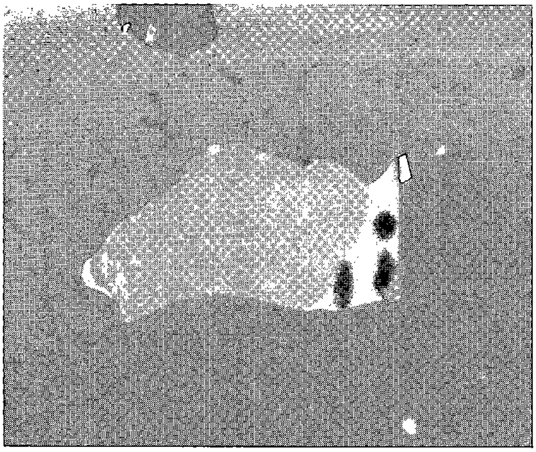

FIG. 3. Reflected-light micrograph of loveringite (light gray), pentlandite (white), and silicate (phlogopite and pargasite, dark gray) in chromian spinel. Maximum dimension of loveringite grain is *ca.* 35 μm.

Baddeleyite is rarer than loveringite, the proportions being roughly 1:5; no grains of baddeleyite were found outside grains of chromian spinel. It occurs solely in silicate inclusions, either alone or with rutile (Fig. 7). Where present in an unaltered inclusion, baddeleyite is subhedral to euhedral, whereas in altered inclusions, it has irregular boundaries. Generally, the dimensions vary from <2 μm to 4 × 5 μm.

IDENTIFICATION AND ANALYTICAL METHODS

In reflected light, loveringite is opaque, with a grey tone and a pinkish hue similar to ilmenite, from which it is distinguished quite easily by its isotropism (Tarkian & Mutanen 1987). It can be confused with Cr–Zr-bearing armalcolite, having a very similar chemical composition (Contini *et al.* 1993). However, Cr–Zr-bearing armalcolite appears to be anisotropic and to have a more bluish hue (Anderson *et al.* 1970, Williams & Taylor 1974). Unfortunately, the very small dimensions of the loveringite grains prevented discrimination between loveringite and armalcolite by single-crystal diffractometry. The identification of baddeleyite in reflected-light microscopy is not simple because of its similarity to rutile. However, where the two coexist, baddeleyite shows higher reflectance and deeper yellow internal reflections.

Qualitative chemical analyses were carried out in the energy-dispersion mode on an electron microscope (Philips SEM 515) equipped with an X-ray analyzer (EDAX PV9100), using an accelerating voltage of 15 kV and a beam current of about 2 nA. Quantitative chemical analyses were performed with an ARL–SEMQ microprobe in wavelength-dispersion mode, using an accelerating voltage of 20 kV, a sample current of 20 nA, a peak counting time of 20 seconds, an off-peak counting time of 5 seconds, and a minimum beam-spot size of about 4 μm. The following standards were used: diopside for Ca, Mg and Si, chromite for Cr, Fe and Al, monazite for

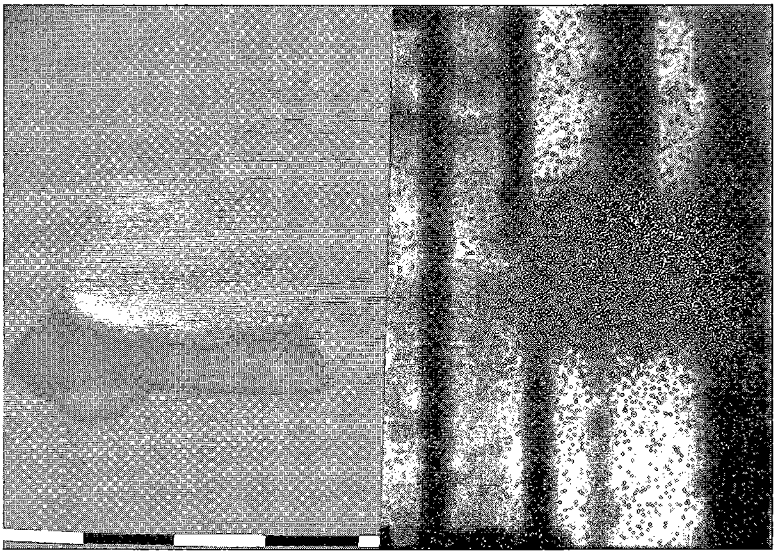

FIG. 4. Loveringite included in chromian spinel; on left: back-scattered electron (BSE) image; on right: X-ray distribution image for Ti. Divisions on scale bar: 5 μm.

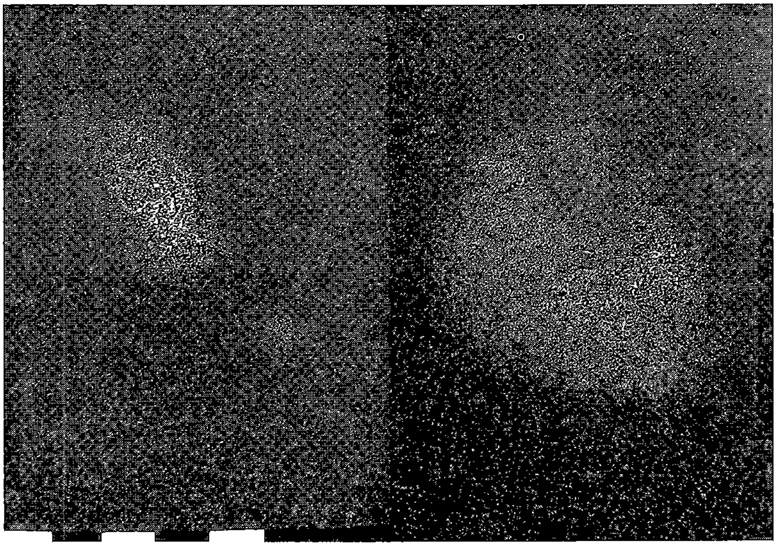

FIG. 5. Loveringite and pentlandite included in chromian spinel; on left: X-ray distribution image for Ti; on right: X-ray distribution image for Ni + S. Divisions on scale bar: 5 µm.

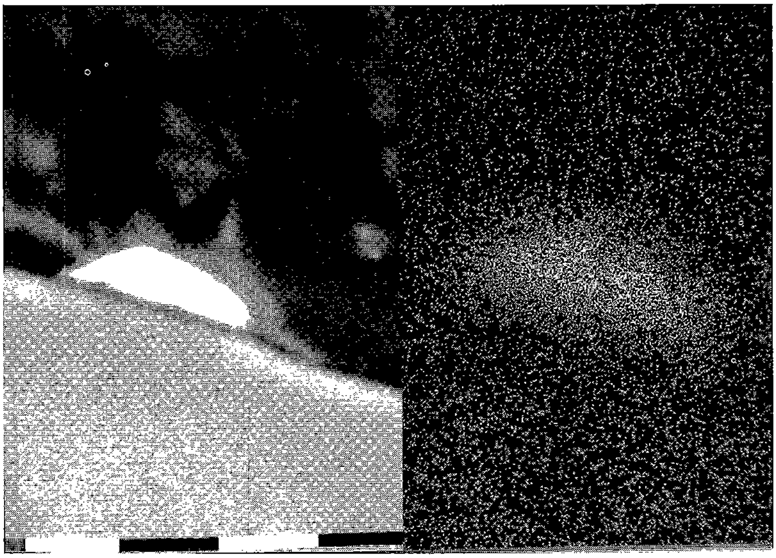

FIG. 6. Micrometric crystal of loveringite located at the rim of a grain of chromian spinel. Divisions on scale bar: 5 µm. On left: BSE image; on right: X-ray distribution image for Ti.

Ce, La, Nd and Pr, rhodonite for Mn, rutile for Ti, zirconia for Zr, metals for V, Ni, Hf and Nb, ThO_2 glass for Th, and Y_2O_3 glass for Y; the synthetic glasses *REE*1, *REE*2, *REE*3, *REE*4 (Drake & Weill 1972) were used to verify and eliminate interferences due to peak overlap (Roeder 1985). The *REE* content of loveringite and baddeleyite is near the detection limits; hence, some very low reported values may have no quantitative meaning.

MINERAL CHEMISTRY

Table 1 lists representative mineral compositions. The *chromian spinel* shows a high TiO_2 content (> 0.3 wt%), correlating with the observation of rutile or ilmenite inclusions formed as exsolution lamellae. This high TiO_2 value is not characteristic of podiform (ophiolitic) chromite, but is similar to that for stratiform

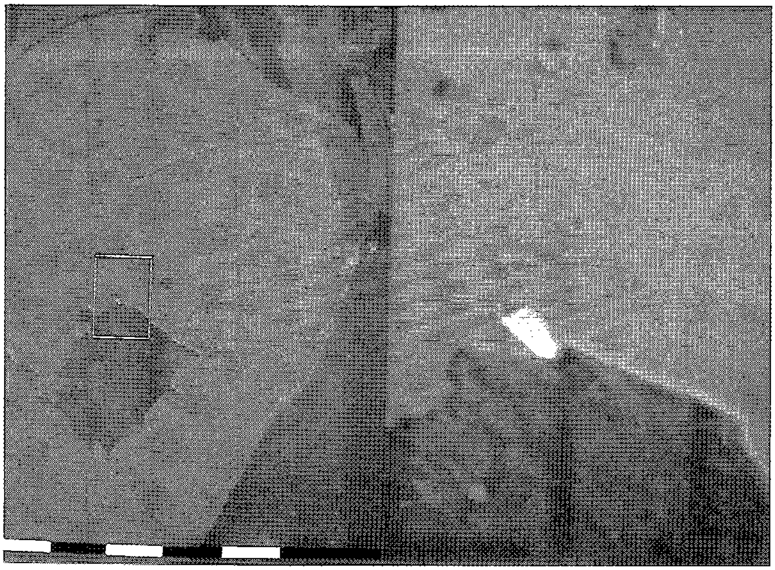

FIG. 7. BSE image of baddeleyite (light gray) in silicate inclusion in chromite. Divisions on scale bar: 50 μm.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF OXIDE MINERALS FROM LAYERS OF CHROMIAN SPINEL, BRACCO UNIT

	ILMENITE			SPINEL			RUTILE	
SiO_2 wt%	0.00	0.02	0.00	0.00	0.00	0.00	0.16	0.06
TiO_2	52.30	52.91	56.91	1.44	0.37	0.91	96.32	97.13
ZrO_2	0.28	0.00	0.00	n.d.	n.d.	n.d.	0.58	0.83
Nb_2O_5	0.00	0.00	0.00	n.d.	n.d.	n.d.	0.01	0.00
Al_2O_3	0.00	0.07	0.05	24.65	35.22	8.98	0.18	0.08
Cr_2O_3	0.91	0.86	0.92	35.83	33.73	49.27	0.51	0.67
FeO total	14.95	35.36	29.52	26.70	14.24	33.03	0.40	0.30
MgO	0.13	1.70	11.30	11.93	16.47	6.56	0.16	0.07
MnO	31.28	9.01	1.19	0.00	0.00	0.65	0.02	0.01
NiO	0.00	0.00	0.00	n.d.	n.d.	n.d.	0.02	n.d.
CaO	0.12	0.09	0.06	n.d.	n.d.	n.d.	0.02	0.33
V_2O_3	0.00	0.00	0.00	n.d.	n.d.	n.d.	1.08	n.d.
Y_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	0.00
La_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
Ce_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
Pr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
Nd_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
HfO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	0.00
ThO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	0.00
Total	99.97	100.02	99.95	100.55	100.03	99.40	99.69	99.48
Al	0.000	0.002	0.001	7.073	9.496	2.881		
Ti	0.989	0.990	0.993	0.264	0.064	0.186		
Zr	0.003	0.000	0.000	n.d.	n.d.	n.d.		
Cr	0.018	0.017	0.017	6.897	6.101	10.603		
Fe^{3+}	0.000	0.000	0.000	1.502	0.276	2.144		
Mg	0.005	0.064	0.391	4.329	5.616	2.661		
Fe^{2+}	0.317	0.737	0.575	3.934	2.448	5.375		
Mn	0.667	0.189	0.023	0.000	0.000	0.150		
Ni	0.000	0.000	0.000					
Ca	0.003	0.003	0.001					
Nb	0.000	0.000	0.000					
V^{3+}	0.000	0.000	0.000					
% $FeTiO_3$	31.60	73.60	57.80					
% $MgTiO_3$	0.50	6.30	39.30					
% $MnTiO_3$	67.00	19.00	2.40					
$Mg/(Mg + Fe^{2+})$				0.52	0.70	0.33		
$Cr/(Cr + Al)$				0.49	0.39	0.79		

The empirical formulae were calculated according to the general formulae ABO_2 (ilmenite) and $A_8B_{16}O_{24}$ (spinel).

TABLE 2. REPRESENTATIVE COMPOSITIONS OF LOVERINGITE FROM LAYERS OF CHROMIAN SPINEL, BRACCO UNIT

	1	2	3	4	5	6	7	8	9
SiO_2 wt.%	0.14	0.16	0.13	0.10	0.09	0.12	0.10	0.05	0.03
TiO_2	64.51	64.73	65.38	65.08	65.46	67.34	66.00	65.91	65.62
ZrO_2	3.76	3.71	3.75	3.67	3.63	3.42	3.68	3.56	3.61
Nb_2O_5	0.00	0.04	0.00	0.05	0.00	0.00	0.00	0.07	0.02
Al_2O_3	1.59	1.51	1.58	1.55	1.53	1.37	1.60	1.53	1.60
Cr_2O_3	7.80	7.94	8.27	8.01	8.09	7.48	7.95	7.95	8.06
FeO total	13.63	13.99	13.35	12.94	12.89	12.25	12.78	12.63	12.72
MgO	2.40	2.36	2.37	2.41	2.33	2.03	2.24	2.28	2.39
MnO	0.28	0.30	0.29	0.26	0.20	0.23	0.25	0.23	0.23
NiO	0.06	0.03	0.04	0.03	0.03	0.06	0.06	0.03	0.04
CaO	3.72	3.72	3.62	3.55	3.68	3.28	3.34	3.39	3.39
V_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y_2O_3	0.18	0.08	0.11	0.14	0.15	0.18	0.15	0.16	0.15
La_2O_3	0.00	0.00	0.01	0.02	0.00	0.02	0.00	0.01	0.05
Ce_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pr_2O_3	0.00	0.00	0.01	0.00	0.01	0.03	0.00	0.01	0.00
Nd_2O_3	0.02	0.03	0.01	0.05	0.00	0.04	0.03	0.05	0.04
HfO_2	0.07	0.00	0.06	0.09	0.04	0.10	0.00	0.09	0.07
ThO_2	0.00	0.00	0.02	0.00	0.00	0.03	0.03	0.00	0.02
Total	98.15	98.59	98.99	97.95	98.11	97.99	98.20	97.94	98.01
Si	0.039	0.045	0.036	0.027	0.027	0.033	0.027	0.015	0.008
Al	0.538	0.508	0.529	0.524	0.513	0.461	0.536	0.515	0.537
Ti	13.904	13.905	13.952	14.014	14.055	14.409	14.138	14.156	14.096
Zr	0.525	0.517	0.519	0.513	0.505	0.474	0.511	0.496	0.503
Cr	1.767	1.793	1.855	1.813	1.825	1.682	1.790	1.795	1.819
Fe^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	1.024	1.003	1.001	1.029	0.991	0.862	0.952	0.970	1.015
Fe^{2+}	3.268	3.341	3.167	3.098	3.078	2.915	3.045	3.016	3.039
Mn	0.068	0.072	0.071	0.063	0.048	0.055	0.061	0.057	0.055
Ni	0.015	0.007	0.009	0.008	0.008	0.013	0.013	0.006	0.009
Ca	1.143	1.140	1.099	1.088	1.125	0.999	1.018	1.036	1.037
Y	0.027	0.013	0.017	0.021	0.022	0.027	0.023	0.025	0.022
La	0.000	0.000	0.001	0.002	0.000	0.002	0.000	0.001	0.005
Ce	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pr	0.000	0.000	0.001	0.000	0.001	0.004	0.000	0.001	0.000
Nd	0.002	0.003	0.001	0.005	0.000	0.004	0.003	0.005	0.004
Hf	0.005	0.000	0.005	0.007	0.003	0.008	0.000	0.007	0.005
Th	0.000	0.000	0.001	0.000	0.000	0.002	0.002	0.000	0.001
Nb	0.000	0.005	0.000	0.006	0.000	0.000	0.000	0.009	0.003
V^{3+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
A	1.187	1.163	1.129	1.124	1.156	1.051	1.059	1.074	1.078
M	21.138	21.189	21.135	21.094	21.045	20.899	21.060	21.036	21.080
Ti/Zr	26.48	26.90	26.88	27.32	27.83	30.40	27.67	28.54	28.02

Empirical formulae were calculated according to the general formula $AM_{21}O_{38}$.

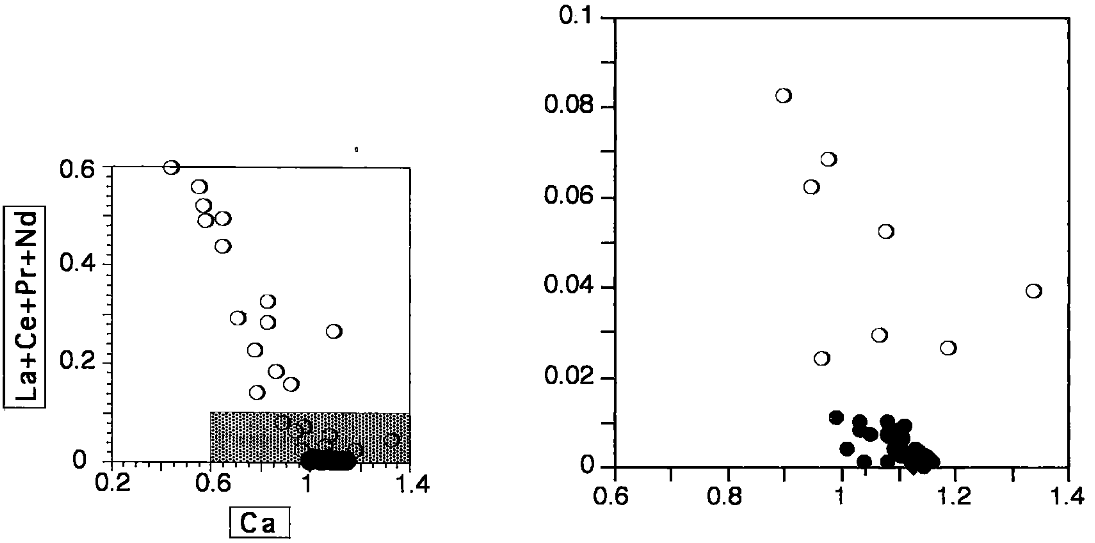

FIG. 8. Ca *versus* La + Ce + Pr + Nd in atoms per formula unit (*apfu*). Loveringite from Bracco (filled circles), loveringite in layered intrusions (open circles: Barkov *et al.* 1994, Gatehouse *et al.* 1978, Lorand *et al.* 1987, Tarkian & Mutanen 1987).

chromite (Duke 1983). *Ilmenite* has a wide compositional field, ranging from Mg-rich (MgO up to 12 wt%), to Mn-rich (MnO up to 35 wt%). Textures suggest that manganoan ilmenite crystallized as a residual phase, after magnesian ilmenite. *Rutile* has an anomalously high Cr content; some grains also contain up to 1 wt% ZrO_2.

Loveringite compositions and empirical formulae, calculated on the basis of 38 oxygen ions, according to the general formula of the crichtonite-group minerals, $AM_{21}O_{38}$, are listed in Table 2. Commonly, Ca is the dominant large cation in the *A* site, partially substituted by *REE*, whereas the small *M* cation is mostly Ti, with Fe, Mg, Cr and Zr as minor constituents. Unfortunately, these analyses were taken from interstitial grains (type d) only. Other crystals are too small to be analyzed without serious interference from the host chromite. Nevertheless, some qualitative and semiquantitative analyses exhibit low Zr and very low *REE* contents.

TABLE 3. REPRESENTATIVE COMPOSITIONS OF BADDELEYITE FROM THE BRACCO UNIT

	1	2	3	4
SiO_2 wt%	0.70	0.34	0.43	0.44
TiO_2	0.66	0.64	0.93	0.74
ZrO_2	91.66	95.65	91.74	93.73
Nb_2O_5	0.00	0.00	0.00	0.00
Al_2O_3	1.47	0.07	1.39	0.84
Cr_2O_3	1.30	1.26	1.36	1.31
FeO total	1.01	0.85	1.92	1.22
MgO	1.05	0.40	0.46	0.53
MnO	0.01	0.02	0.06	0.03
NiO	0.04	0.00	0.09	0.05
CaO	0.03	0.00	0.09	0.04
V_2O_3	0.00	0.00	0.00	0.00
Y_2O_3	0.00	0.03	0.00	0.02
La_2O_3	0.00	0.00	0.00	0.00
Ce_2O_3	0.13	0.11	0.00	0.06
Pr_2O_3	0.01	0.00	0.00	0.01
Nd_2O_3	0.02	0.00	0.02	0.01
HfO_2	1.06	0.98	0.79	0.97
ThO_2	0.00	0.06	0.00	0.02
Total	99.14	100.42	99.28	100.02

The loveringite grains from the Bracco Unit have homogeneous compositions, with very low *REE* contents; thus, compared with other occurrences, they have very low proportions of the davidite component (Fig. 8), indicating a strong depletion of *REE* in the interstitial melt. The electron-microprobe data indicate relatively high Cr, and a distinct negative correlation between Ti and Mg + Fe (Fig. 9). The negative correlation between Ti and Zr reported by many authors (Campbell & Kelly 1978, Cameron 1978, Lorand *et al.* 1987) is less evident. Spot analyses performed across the largest grain of loveringite did not reveal any heterogeneity or zonation.

Analytical data for *baddeleyite* are reported in Table 3. They show relatively low Zr, Hf, Ti and Fe contents, and an enrichment in Cr and Mg. The low levels of Hf and Ti are comparable to those for baddeleyite from other gabbroic complexes [Heaman & LeCheminant (1993) and references therein; Fig. 10]. Owing to the very small grain-size, we cannot exclude that the relatively high Cr, Mg, and Al contents could be related to secondary fluorescence effects from the host spinel and silicates. Alternatively, the enrichment of Cr and Mg could be due to crystallization in equilibrium with a primitive melt.

DISCUSSION

Tarkian & Mutanen (1987) and Barkov *et al.* (1994) argued, on the basis of textural and mineralogical evidence, that loveringite could have crystallized after

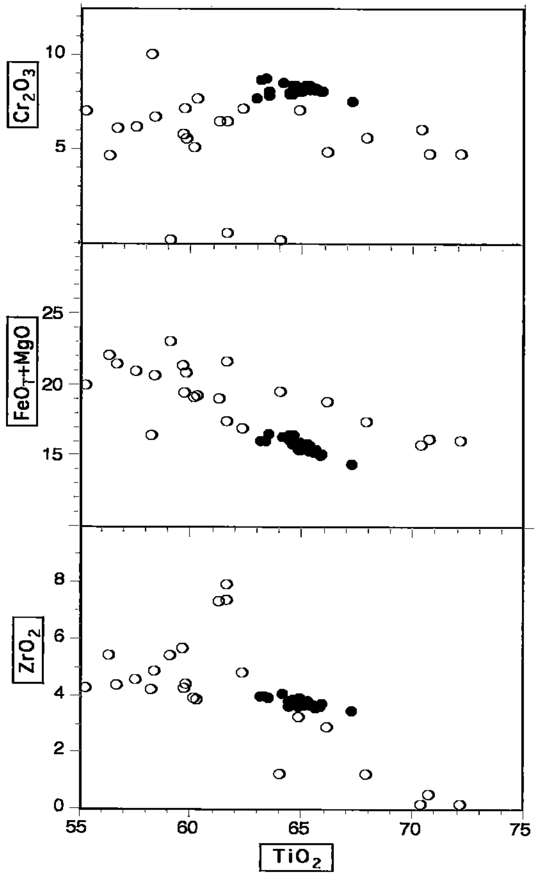

FIG. 9. Cr_2O_3, FeO_t + MgO and ZrO_2 *versus* TiO_2 in loveringite from the Bracco unit and layered intrusions. Symbols and references as in Figure 8.

contamination of magma. They cited the coexistence with Mn-rich ilmenite as the main line of evidence. Alternatively, Williams (1978) and Lorand *et al.* (1987) proposed infiltration metasomatism as the principal mechanism of formation. This may have occurred as enrichment of incompatible elements (such as Zr and Ti) after fractionation of olivine and chromian spinel and subsequent filter pressing of the interstitial liquid through the pile of cumulates (Irvine 1980). This is the genetic mechanism proposed for the occurrence in the Laouni layered intrusion (Lorand & Cottin 1987b, Lorand *et al.* 1987). Merkle (1992) found a similar assemblage in chromitites from the Bushveld complex and argued that chromite inclusions (and loveringite + baddeleyite + srilankite as well) were formed by resorption of chromite crystals during magma mixing. Although he focused his work on PGM formation, the hypothesis is not so different from that of Lorand *et al.* (1987).

Both models were applied to layered mafic-ultramafic complexes where the textural relations of loveringite and baddeleyite appear to be mainly interstitial or included in cumulate phases (Tarkian & Mutanen 1987). In many occurrences, the assemblage of interstitial minerals associated with loveringite is represented by minerals very rich in incompatible elements, such as phlogopite, Ti-rich pargasite, Mn-rich ilmenite, rutile, K-feldspar, zircon, quartz and various Cu- and Ni-rich sulfides. Unfortunately, the primary interstitial assemblage in the chromian spinel layers of the Bracco Unit has been modified by several low-T metamorphic events (Cortesogno *et al.* 1987, Principi *et al.* 1992). However, the unaltered minerals from inclusions in grains of chromian spinel are nearly coincident with the mineral assemblage reported here.

We contend that the crystallization of loveringite and baddeleyite in chromian spinel layers of the ophiolitic Bracco Unit may be due to an enrichment of incompatible elements, such as Ti and Zr, in the crystal mush by a process like infiltration metasomatism, producing Ti-rich spinel and Ti- and Zr-rich oxides. Locally, this process could lead to crystallization of discrete interstitial Ti–Zr phases, such as loveringite. This points to a common genesis for both minerals, probably involving a Zr–Ti-enriched interstitial liquid, sufficiently hot to re-equilibrate the chemical composition and texture of the chromian spinel.

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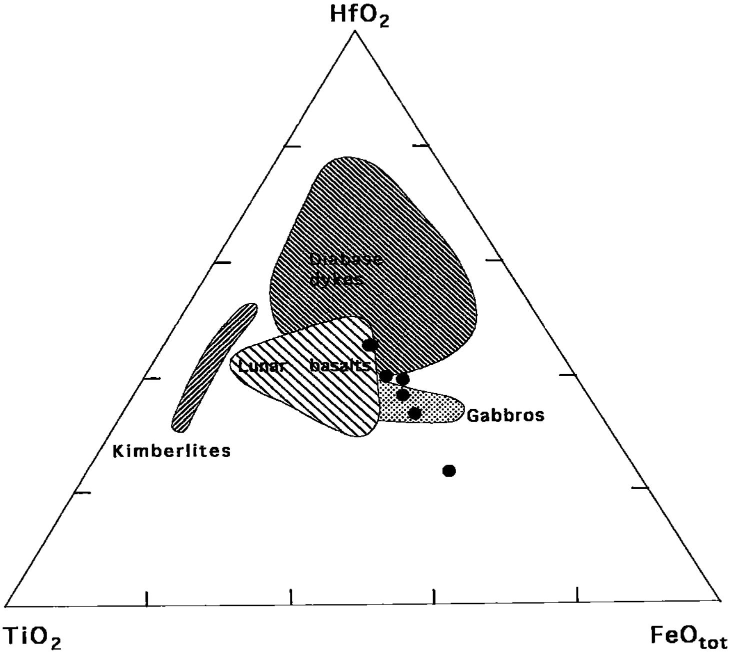

FIG. 10. $TiO_2 - FeO_{tot} - HfO_2$ diagram for baddeleyite from the Bracco unit (filled circles). The fields are those of Heaman & LeCheminant (1993).

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