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Magmatic osumilite in an ultrapotassic dyke, southern Peru: first occurrence

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Abstract : Osumilite-Mg ($0.69 < $ Mg / (Mg + Fe) $ < 0.79$) has been discovered for the first time in an ultrapotassic rock. It occurs both as microlites (with up to 10.73 Si p.f.u.) in the groundmass and as partial melting products of magnesian biotite xenocrysts incorporated from peraluminous granites spatially associated with the ultrapotassic rock. The P-T-fO_2 conditions of osumilite deduced from the coexisting mineral assemblage (< 1-5 kbar, 950°C $< $ T < 1050°C and $fO_2 = $ WM) are in good agreement with the experimentally determined stability of this mineral. It is concluded that osumilite in ultrapotassic rock would be symptomatic of alumina-rich siliceous and magnesian melts.

Key-words : osumilite-Mg, ultrapotassic rocks, magma mixing, Peru.

Introduction

Osumilite is an anhydrous tectosilicate of the milarite group (Olsen & Bunch, 1970; Forbes *et al.*, 1972) of general formula :

$$(C)^{XII} (M)_2^{VI} (T2)_3^{IV} (T1)_{12}^{IV} O_{30}$$
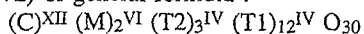
where T1 = (Si, Al); T2 = (Al, Fe, Mg); M = (Mg, Fe, Mn) and C = (K, Na, Ca, Ba). It was first discovered in a rhyodacite from Sakurazima volcano, Japan (Miyashiro, 1956). As yet, osumilite has been reported from about twenty localities in acid volcanic rocks (Schreyer *et al.*, 1983; Parodi *et al.*, 1989), in rocks metamorphosed at high temperature (Chinner & Dixon, 1973), in granulite-facies contact aureoles of anorthositic complexes (Berg & Wheeler, 1976; Arima & Gower, 1991) and in granulite-facies rocks, like in Enderby Land, Antarctica (Ellis *et al.*, 1980; Sheraton *et al.*, 1980; Grew, 1982). In acid volcanic rocks (rhyolite, rhyodacite, *dacite*) osumilite crystallizes essentially in drusy cavities and, more rarely, as euhedral or anhedral crystals in the groundmass (Deer *et al.*, 1976, and references therein). Nevertheless, the origin of the crystals immersed in the groundmass (microlites, phenocrysts or xenocrysts) is still unclear.

The present paper provides evidence that osumilite may crystallize directly from a silicate melt. In addition, we document this mineral for the first time in an ultrapotassic rock. Although other milarite-related minerals such as chayesite (Velde *et al.*, 1989) or roedderite (Wagner & Velde, 1986; Contini *et al.*, 1993) have previously been reported in these rocks, they all differ markedly from osumilite by their Al_2O_3-free composition.

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Table 1. Bulk rock composition of the Chili Palca osumilite-bearing ultrapotassic sample (1) compared to a US felsic minette (2) and a Si-rich Spanish lamproite (3).

wt %	1	2	3
SiO_2	62.45	61.61	61.88
TiO_2	0.77	0.76	1.43
Al_2O_3	13.55	13.89	11.34
FeO	3.37	4.45	4.09
MnO	0.05	0.08	0.05
MgO	4.80	3.69	5.50
CaO	1.92	4.63	3.92
Na_2O	2.38	2.79	1.02
K_2O	5.55	5.49	5.57
P_2O_5	0.76	0.36	0.88
LOI	3.45	1.04	3.74
Total	99.05	98.79	99.42
K_2O / Al_2O_3	0.41	0.40	0.49
K_2O / Na_2O	2.33	3.21	5.46
$Mg / (Mg + Fe)$	0.72	0.65	0.73

The Chili Palca sample has been analysed by ICPAES at the CRPG (Nancy, France). US felsic minette (2) and Si-rich Spanish lamproite (3) analyses from Roden et al. (1979) and Borley (1967), respectively.

Occurrence and nomenclature of the osumilite-bearing ultrapotassic rock

Our sample has been collected 1.5 km NE of the Chili Palca Hacienda (70° 30' 48" W, 14° 17' 43" S), Puno Department, Southern Peru. It comes from one of the numerous metre-thick lamprophyric dykes closely associated with per-aluminous granite stocks intruded in the Eastern Cordillera of southern Peru during the Oligocene (Audebaud & Vatin Pérignon, 1974). Its whole-rock major-element chemistry fulfils all the criteria of Foley et al. (1987) for ultrapotassic rocks (K_2O = 5.5 wt%, MgO = 4.8 wt% and K_2O/Na_2O = 2.33, Table 1). Classifications of ultrapotassic rocks based on mineralogical criteria yielded to a considerable array of rock names (for more detail see Foley et al., 1987) which somewhat obscured genetic links existing between these rocks. Modern attempts based on whole-rock geochemistry (Foley et al., 1987; Foley, 1992; Sheppard & Taylor, 1992) distinguish between a lamproite$_{ss}$ group, characterized by low Al_2O_3 (< 14 wt%), CaO (< 11 wt%), Na_2O (< 2.5 wt%) contents and high K_2O/Al_2O_3 (> 0.7) and K_2O/Na_2O (> 4) ratios, a plagi-oleucitite group which has high Al_2O_3 (> 11 wt%) content and low K_2O/Al_2O_3 (< 0.5), a kama-fugite group with low SiO_2 (< 45 wt%), Al_2O_3 (< 13 wt%), Na_2O (< 2.5 wt%) but high CaO (> 6 wt%) contents and a fourth transitional group having intermediate chemical charac-teristics between the lamproite and plagioleucitite

groups. The fourth group comprises "Spanish lamproites" (e.g. jumillite), kajanite, cocite and US felsic minettes. By its chemical charac-teristics (Al_2O_3 = 13.6 wt%, CaO = 1.9 wt%, Na_2O = 2.4 wt%, K_2O/Al_2O_3 = 0.41, K_2O/Na_2O = 2.33, Table 1), our sample is very similar to both the US felsic minettes (e.g. Roden, 1981) and the SiO_2-rich Spanish lamproites (e.g., Borley, 1967, Table 1). Accordingly, it enters the fourth group of ultrapotassic rocks for which Sheppard & Taylor (1992) proposed the term "transitional lamproite". Like our sample, ultrapotassic rocks from the transitional lam-proite group frequently contain Al-rich augite, Na-rich alkali feldspar or plagioclase that lack from the first lamproite$_{ss}$ group (Sheppard & Taylor, 1992).

Main petrographic features and evolution of the Chili Palca lamproite

Petrography and mineralogy of the Chili Palca transitional lamproite are discussed in detail in a separate paper (Carlier et al., submitted). So only a brief summary of the main petrographic fea-tures is given here. Like the SiO_2-rich Spanish lamproites and US felsic minettes, our sample displays many characters of hybrid rocks. It is composed mainly of a microlitic groundmass (87 vol.%) containing xenocrysts and larger mafic inclusions (13 vol. %). Microlites are by decreas-ing order of abundance, phlogopite (mg = (Mg/(Mg + Fe) = 0.76-0.86, F/(F + OH) = 0.44-0.45), hypersthene (En$_{55-65}$), plagioclase (An$_{35-40}$ Ab$_{54-57}$ Or$_{6-8}$), Fe^{3+}-free ilmenite, osumilite, alkali feldspar (Or$_{71-56}$ Ab$_{27-37}$ An$_{2-7}$), graphite and apatite. All these phases are immersed in a colourless glass. The mafic inclusions (2-5 mm in diameter) present all textural characteristics (ellipsoidal to rounded shapes and contorted mar-gins) of mafic magma blobs chilled into colder more silicic melts (Bacon, 1986 and reference therein). They consist of about 50 % olivine (Fo$_{85-89}$) phenocrysts and highly magnesian phlogopite (mg = 0.88-0.93) phenocrysts with Si + Al < 8 in the tetrahedral site. Both olivine and phlogopite enclose euhedral chromite (Cr/(Cr + Al) = 0.76-0.85, mg = 0.38-0.46). This phenocryst paragenesis dominated by magnesian olivine and phlogopite, its phase compositions and crystallization order (chromite → olivine → olivine + phlogopite), all suggest crystallization from an olivine-lamproite melt (see Foley, 1989).

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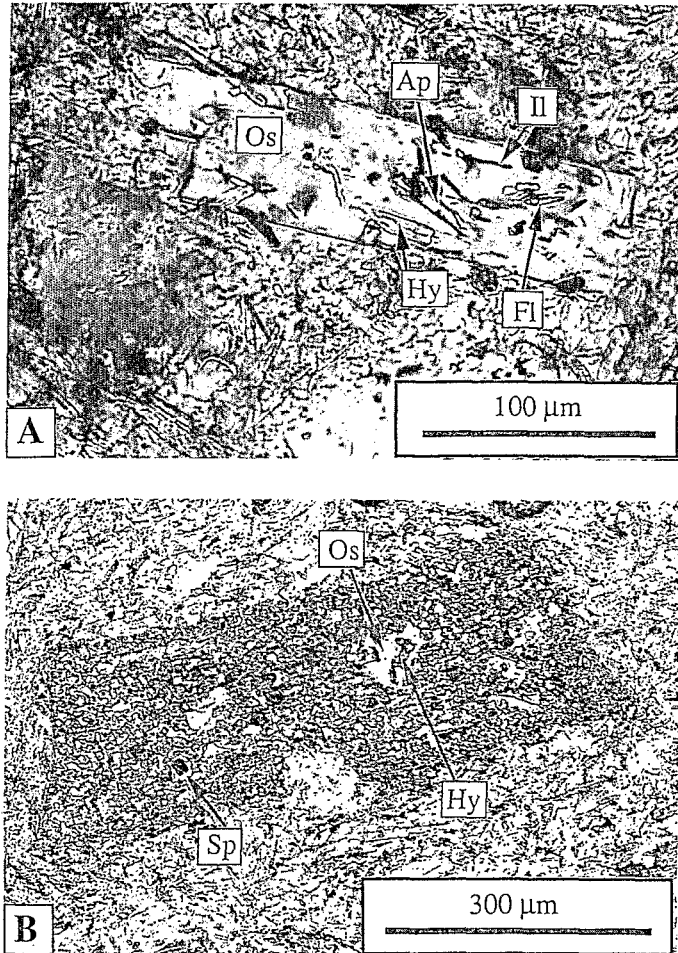to the r
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Fig.1. A : Euhedral osumilite microlite (Os) immersed in the microlitic groundmass. Note the numerous hexagonal flattened ilmenite (Il), acicular orthopyroxene (Hy), apatite (Ap) and fluid inclusions (Fl). B : spongy biotite xenocryst partially replaced by anhedral osumilite (Os), acicular orthopyroxene (Hy) and spinel-hercynite (Sp).

The xenocrysts are olivine and highly magnesian phlogopite which result from disaggregation of the mafic inclusions, as well as Al-rich biotite (mg = 0.58, Al_2O_3 = 18.1 wt%), oligoclase (An_{16-30} Ab_{67-71} Or_{3-13}) and quartz. Al-rich biotite and oligoclase are compositionally similar to the near-liquidus phases of the peraluminous granites coexisting with the ultrapotassic rocks in the field. The coexistence of mafic inclusions showing an early paragenesis of olivine lamproite and of xenocrysts derived from a peraluminous granitic melt has led Carlier et al. (submitted) to interpret the Chili Palca transitional lamproite as a product of mixing between these two different melt compositions. The groundmass would represent the hybrid melt produced by the mixing. All the xenocrysts systematically exhibit evidence of disequilibrium with the groundmass. Olivine is rimmed by orthopyroxene + phlogopite coronas. Highly magnesian phlogopite, oligoclase and quartz are partially resorbed. The biotite preserves its original euhedral shape but shows the typical spongy aspect of biotites having experienced a partial melting at the contact with a hotter magma (see for example, Brearley, 1987). Its mg ratio varies
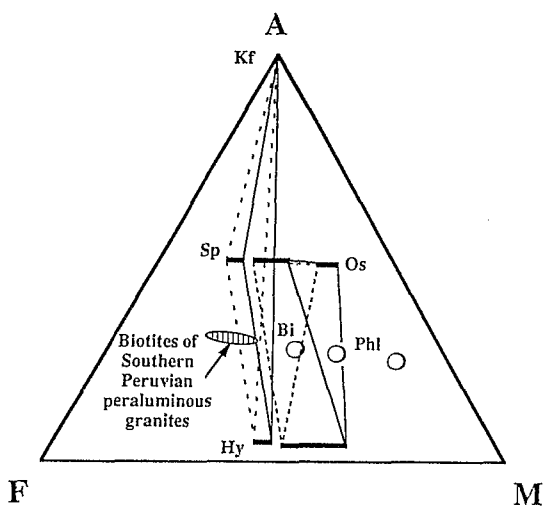
Fig. 2. AFM projection from the K_2O apex showing the change in the biotite breakdown products as a function of mg ratios in the micas. Osumilite only occurs in Mg-rich assemblages resulting from destabilization of phlogopite (mg > 0.6) xenocrysts. Note that the most Mg-rich phlogopite does not react (Carlier et al., submitted). Alkali feldspar (Kf), biotite (Bi), phlogopite (Phl), spinel-hercynite (Sp), orthopyroxene (Hy) and osumilite (Os) projections are based on electron-microprobe analysis. The compositional field of biotites from peraluminous granites in southern Peru is from Carlier (unpublished data).

between 0.58, the ratio of the biotites from the peraluminous granites, to 0.87 close to the phlogopite microlites from the groundmass. Such variations are due to various stages of re-equilibration with the parental liquid of the groundmass. Moreover, the spongy biotite xenocrysts are replaced by fine-grained mineral assemblages comprising alkali feldspar, osumilite, spinel-hercynite, orthopyroxene and Fe^{3+}-free ilmenite.

Textural relationships of osumilite

Osumilite occurs both as microlites in the groundmass and as a replacement product of spongy biotite xenocrysts. It is recognized under the microscope by its colourless to blue-pale dichroism (Deer et al., 1986). The small crystal size and their interpenetration with associated phases ruled out characterization by X-ray diffraction.

The osumilite microlites are euhedral, tabular (100-500 x 20-50 μm), with hexagonal basal sections. They usually contain small ilmenite, apatite and orthopyroxene crystals and numerous fluid inclusions (Fig. 1A).

Osumilite replacing biotite xenocrysts is anhedral and finer-grained (10-20 μm, Fig. 1B). Only biotite with mg ratio > 0.6 is replaced by osumilite, which is associated with spinel-hercynite (Hc_{46-69} Sp_{27-54} Mt_{0-4}) ± orthopyroxene (En_{52-60}) ± ilmenite. Less magnesian biotite xenocrysts (mg ≤ 0.6; Fig. 2) are replaced by a less magnesian K-feldspar-bearing assemblage lacking osumilite : hercynite (Hc_{73-68} Sp_{24-28} Mt_{3-4}), orthopyroxene (En_{46-47}) + ilmenite + (Or_{71-56} Ab_{27-37} An_{2-7}). The phases replacing biotite are so fine-grained and intimately intergrown that textural relationships are difficult to establish.

Chemical composition of osumilite

Quantitative electron-microprobe data have been obtained at the CAMPARIS Microprobe Centre, Pierre and Marie Curie University (Paris, France) with the fully automated CAMEBAX and SX 50 electron microprobes. The analytical conditions were 15 kV acceleration voltage, 30 nA sample current and 10 s counting times for both peak and background. Natural albite, orthoclase, diopside, barite and synthetic Fe_2O_3 and $MnTiO_3$ were used as standards.

The Chili Palca osumilite can be classified as Mg-rich (mg = 0.69-0.79, Table 2) although its composition varies significantly between its two sites of crystallization. The osumilite replacing biotite xenocrysts is compositionally similar to osumilites-Mg reported in volcanic rocks and their crustal pelitic xenoliths (Schreyer et al., 1983; Deer et al., 1986; Parodi et al., 1989). It is distinguished from the microlites by lower SiO_2 (61-62 vs. 62-65 wt%), higher Na_2O (0.7-0.8 vs. 0.5-0.6 wt%) and BaO (0.2-0.5 vs. 0.0-0.2 wt%) contents and lower mg ratio (0.69-0.74 vs. 0.72-0.79). Consequently, the cationic sum in the C (K + Na + Ca + Ba) site is often higher than 1 (1.0-1.2 vs. 0.85-1.00) (Table 2). Osumilite microlites have the highest SiO_2 content so far published for osumilite (Olsen & Bunch, 1970; Berg & Wheeler, 1976, Table 2). The Si/(Si + Al) ratio in the T1 site varies between 0.87 and 0.89.

Si and Mg contents are positively correlated and both decrease when the Al content increases (Fig. 3). These correlations suggest that the

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Table 2. Representative electron microprobe analyses of the Chili Palca osumilite.

weight %	1	2	3	4	5	6
SiO_2	61.38	61.64	61.50	63.09	64.42	64.93
TiO_2	n. d.	n. d.	0.04	0.10	0.09	0.04
Al_2O_3	22.42	22.13	21.91	20.46	19.45	19.15
FeO	5.12	4.57	4.16	4.93	3.82	3.77
MnO	n. d.	n. d.	0.11	0.20	0.10	n. d.
MgO	6.44	6.57	6.75	6.95	7.90	8.00
CaO	0.11	0.69	0.51	0.07	n. d.	n. d.
Na_2O	0.66	0.75	0.82	0.64	0.59	0.51
K_2O	3.44	3.59	3.21	3.45	3.37	3.24
BaO	0.53	0.20	0.42	0.18	n. d.	0.06
Total	100.08	99.52	99.43	100.07	99.75	99.71

Number of cations based on 30 oxygens

Site T1						
Si	10.262	10.321	10.308	10.508	10.669	10.735
Al	1.738	1.679	1.692	1.492	1.331	1.265
Site T2						
Al	2.680	2.687	2.636	2.524	2.465	2.467
Mg	0.320	0.313	0.364	0.476	0.535	0.533
Site M						
Ti	0.000	0.000	0.005	0.013	0.011	0.005
Fe	0.715	0.640	0.583	0.687	0.529	0.521
Mn	0.000	0.000	0.016	0.028	0.014	0.000
Mg	1.286	1.325	1.322	1.250	1.415	1.439
Sum	2.001	1.965	1.926	1.977	1.969	1.965
Site C						
Ca	0.020	0.012	0.092	0.012	0.000	0.000
Na	0.212	0.242	0.266	0.207	0.189	0.163
K	0.734	0.767	0.686	0.733	0.712	0.683
Ba	0.034	0.013	0.027	0.012	0.000	0.004
Sum	1.000	1.034	1.071	0.964	0.903	0.852
Total cations	18.001	17.999	17.997	17.941	17.873	17.817
Mg/(Mg + Fe)	0.69	0.72	0.74	0.72	0.79	0.79
$(Si/(Si + Al))_{T1}$	0.86	0.86	0.86	0.88	0.89	0.89

1-3 : osumilites replacing Al-phlogopite xenocrysts; 4-6 : osumilite microlites.
n. d. : not detected

substitution (M^{2+}) + Si = 2 Al, classically described in osumilite (Berg & Wheeler, 1976; Olesch & Seifert, 1981; Ellis et al., 1980; Grew, 1982; Arima & Gower, 1991), also operates in our sample. In addition to this substitution, the Si content shows a positive correlation with the number of vacancies in the C (K + Na + Ca + Ba) site (Fig. 3). Such a correlation suggests that the entry of Si could also be controlled by the substitution Si + □ = (M^{3+}) + (Na,K) as already proposed by Berg & Wheeler (1976).

Discussion and conclusion

Intensive parameters that governed the crystallization of osumilite in the Chili Palca transitional lamproite can be determined from both the microlite paragenesis of the groundmass and the mineral assemblages replacing the biotite xenocrysts. The liquidus temperature of the groundmass is constrained by the coexistence of phlogopite (0.76 < mg < 0.86) and orthopyroxene (En_{60}) microlites. In F-free hydrous systems, this assemblage reacts with the liquid to form olivine + melt above 930-1050°C for pressures varying between 0.5 and 10 kbar (Fig. 4) (Luth, 1967; Modreski & Boettcher, 1972). Nevertheless, the high F/(F + OH) ratio of the phlogopite microlites suggests that the parental melt of the groundmass contained some fluorine. The effect of fluorine is to shift the reaction curve olivine + melt → phlogopite + enstatite toward higher temperatures. The temperatures deduced from F-free systems are probably underestimated although experimental data so far available do not permit a quantitative assessment of the error generated by disregarding the role of fluorine.
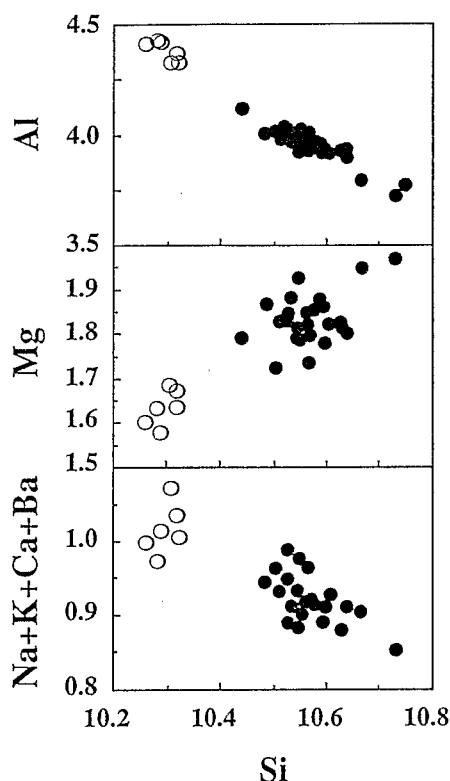
Fig. 3. Compositional variations of the Chili Palca osumilite. Full circle, osumilite microlite; open circle, osumilite replacing biotite xenocrysts. The number of atoms per formula unit is calculated on the basis of 30 oxygens.

Constraints on pressure are provided by the crystallization conditions of the peraluminous granite involved in the mixing with the lamproite melt and by the assemblages resulting from the partial melting of biotite xenocrysts. The peraluminous granitic melts from Southern Peru are considered to have crystallized at about 4-5 kbar and 760-820°C, on the basis of the cordierite-free xenocryst assemblage (quartz + oligoclase + biotite) (Clemens & Wall, 1981; Kontak, 1985). On the other hand, the assemblage spinel-hercynite + melt ± alkali feldspar replacing biotite is not stable below 2.9 kbar (Montel et al., 1986). By analogy with the silica-saturated system, the stability field of hercynite + liquid is bounded at low pressures by cordierite and at high pressures by garnet + sillimanite. The location of both curves bounding this stability field

depends on the SiO_2 activity in the liquid. The fact that orthopyroxene replaces olivine xenocrysts determines a lower limit on SiO_2 activity in the hybrid melt. This activity calculated at 1000°C between 0.5 and 10 kbar using Nicholls et al. (1971) thermodynamic formulation for the reaction olivine (mg = 0.86) → orthopyroxene (mg = 0.86) + liquid, varies between 0.72 and 0.84 (Carlier et al., submitted). Assuming an SiO_2 activity of 0.8, the largest pressure range at which spinel-hercynite can coexist with orthopyroxene and phlogopite at 1000°C is 3 to 6 kbar (Fig. 4), in agreement with the pressure estimated from the neighbouring peraluminous granites. Of course valid for the osumilite intergrown with partial melting products of biotite, the latter pressure range cannot pertain to the osumilite microlites which obviously crystallized at near-surface conditions, when the hybrid melt was quenched to give the groundmass. At this stage, crystallization of orthopyroxene and ilmenite microlites suggests high SiO_2 activity (> 0.84) in the coexisting liquid. This feature is probably due to the progressive dissolution of quartz xenocrysts in the hybrid melt. Therefore, the high silica content of osumilite microlites likely results from the progressive SiO_2 enrichment of the hybrid melt. Both the temperature (> 950°C) and pressure (5 to < 1 kbar) range recorded by the Chili Palca osumilite are consistent with the stability field deduced from both natural occurrences (Berg & Wheeler, 1976; Parodi et al., 1989) and experimental data of Hensen (1977) and Motoyoshi et al. (1993) (Fig. 4). According to Olesch & Seifert (1981) osumilite is not stable for water pressure above 0.8 kbar. Its presence in the Chili Palca sample would therefore be indicative of a very low water pressure (<< total pressure) at the time of the crystallization of the groundmass, a feature also suggested by the high F/(F + OH) ratio (0.44-0.45) in the phlogopite microlites intimately associated with osumilite.

The presence of magmatic graphite microlites fixes the fO_2 near the WM synthetic buffer curve, following Ulmer & Luth (1991) calibration of the C-O-CO_2 buffer at 3 to 6 kbar total lithostatic pressure. This result is in agreement with the absence of Fe^{3+} in ilmenite microlites from the groundmass. Osumilite coexisting with graphite, i.e. formed under reducing conditions, has already been reported by Berg & Wheeler (1976) and Grew (1982). On the other hand, it may be associated with hematite + pseudobrookite

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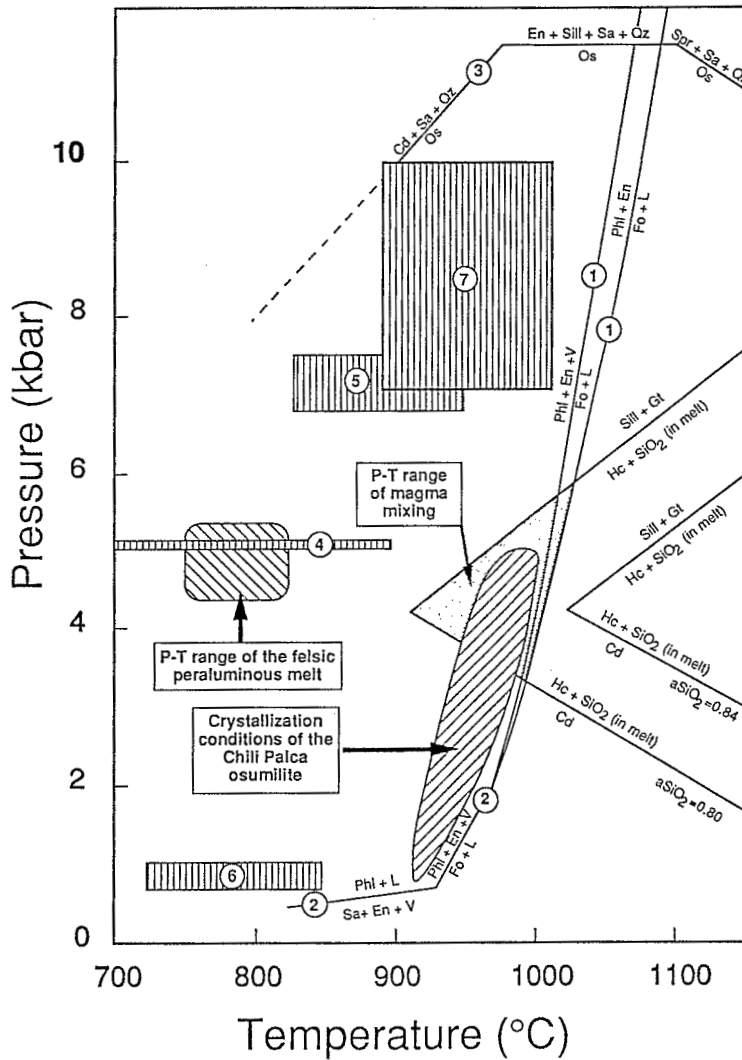En = en;

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Fig. 4. Crystallization conditions of the Chili Palca osumilite. The hatched domain corresponds to the P-T conditions of the peraluminous granitic melt before mixing (after Clemens & Wall, 1981). Curves 1, 2 and 3 are from Modreski & Boettcher (1972), Luth (1967) and Motoyoshi et al. (1993), respectively. See Carlier et al., (submitted) for further discussion of the stability field of hercynite + SiO₂ (in melt). The fields 4, 5 and 6 show the stability field of natural osumilite as estimated by Berg & Wheeler (1976), Arima & Gower (1991) and Parodi et al. (1989), respectively. The P-T range of osumilite in granulite-facies rocks of Enderby Land, Antarctica (7) is deduced from Ellis et al. (1980), Sheraton et al. (1980) and Grew (1982). Os = osumilite, Cd = cordierite, Sa = sanidine, Qz = quartz, Sill = sillimanite, Spr = sapphirine, Phl = phlogopite, Fo = forsterite, Hc = hercynite, Gt = garnet, En = enstatite, L = liquid, V = vapour.

(Schreyer et al., 1983; Parodi et al., 1989) or hematite + magnetite assemblages (Chinner & Dixon, 1973; Arima & Gower, 1991) in strongly oxidized rocks. This is the best proof that osumilite is rather insensitive to redox condi- tions. By contrast, it is highly dependent on the chemical composition of the system. Group-I lamproites that are indisputably Al-deficient (see Mitchell & Bergman, 1991) crystallize only Al-deficient milarite-related minerals such as

chayesite and roedderite (Wagner & Velde, 1986; Velde *et al.*, 1989; Contini *et al.*, 1993). As suggested by our sample, the chemical system has to be not only siliceous and magnesian but also Al-rich for osumilite to precipitate. The coupled effect of Mg and Al + Si is emphasized by the relationships between mg ratio of biotite xenocrysts and the presence of osumilite in their partial melting products. There is no doubt that such an unusual ultrapotassic composition has been reached through the mixing between the olivine lamproite which supplied Fe and Mg and the peraluminous granitic melt which provided Si and Al.

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