American Mineralogist, Volume 70, pages 1143–1150, 1985

The origin of Al-rich spinel inclusions in leucite from the leucite lamproites of Western Australia

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Abstract

Aluminous spinels (pleonaste-hercynite) occur as tiny (mostly $<20\ \mu m$) inclusions in leucite phenocrysts (and pseudomorphs) in leucite lamproites from the West Kimberley region, Western Australia. These spinels differ markedly from the "co-existing" groundmass titaniferous magnesiochromites which, like the other ferromagnesian phases in the rock, are poor in alumina. Similar Al-spinel inclusions in leucites were found in experiments at atmospheric pressure on another lamproite, the Gaussberg olivine leucitite. Based on mineralogical and experimental evidence the formation of the aluminous spinel inclusions in leucite in these peralkaline volcanics is attributed to exsolution under conditions of supersaturation from non-stoichiometric leucites originally incorporating Mg, Al and Fe^{2+} in solid solution.

Introduction

Spinels belonging to the $MgAl_2O_4$–$FeAl_2O_4$ series are uncommon in volcanic rocks; most spinels in basic to intermediate magmas show extensive solid solution towards (Mg, Fe)Cr_2O_4, Fe_3O_4 and, to a lesser extent, Fe_2TiO_4 (e.g., Haggerty, 1976). Aluminous spinels, commonly intergrown with silicates or in some cases other oxides (e.g., titanomagnetite), are well documented in plutonic and metamorphosed igneous rocks where they are inferred to result from sub-solidus reactions and re-equilibration, and/or oxidation. However, a number of occurrences of unusual, essentially Cr-free Al-spinel have been reported from basic to ultrabasic alkalic volcanics. Arculus (1978) described Fe-pleonaste rimmed by chromite enclosed in augite which was in turn enclosed by phenocrystal olivine in a basanitoid from Grenada. Fe-pleonaste has also been reported from ultrapotassic lavas (lamproites) from Leucite Hills (Kuehner et al., 1981) and southeastern Spain (Venturelli et al., 1984). Both Arculus (1978) and Kuehner et al. (1981) suggested that the Fe-pleonaste was of xenocrystal origin derived from disaggregated granulite or ultramafic nodules whereas Venturelli et al. (1984) suggested that the tiny Al-spinel inclusions in biotite phenocrysts (xenocrysts?) resulted in part from the breakdown of the host mica. In addition to these occurrences Mg-rich pleonaste rims on groundmass chromite/titanomagnetite have been described from several kimberlites (Haggerty, 1975; Pasteris, 1983).

This paper describes the occurrence of aluminous spinel inclusions in leucite phenocrysts in lamproites from the West Kimberley region of Western Australia observed in the course of detailed petrologic and geochemical study of the lamproite suite. Although previously unreported, the aluminous spinel inclusions are comparatively widespread, occurring in a wide range of lamproite types within the West Kimberley suite, all of which contain mica, alumina-deficient pyroxene, and amphibole and, commonly, alumina-free alkali-rich accessory phases. A similar occurrence of aluminous spinel inclusions in leucite was found independently by the second author during experimental studies of another lamproitic rock, the olivine leucitite of Gaussberg volcano, Antarctica.

Mineralogical, petrographic and experimental evidence are presented to explain the origin of the aluminous spinels in leucite in these ultrapotassic rocks. It is suggested that under appropriate conditions similar inclusions might occur in strongly leucite-phyric volcanics elsewhere.

Occurrence

Natural rocks

The Miocene leucite lamproites of the Fitzroy area of the West Kimberley region of Western Australia have been described by Wade and Prider (1940), Prider (1960, 1982), Derrick and Gellatly (1972) and, more recently, by Jaques et al. (1984). Petrological and geochemical studies indicate a continuum from the leucite-rich lamproites described by the earlier workers which contain phlogopite, diopside, or titanian potassium richterite as the major mafic phases, through lamproite with abundant olivine and leucite to the newly-discovered olivine lamproites (leucite-poor) some of which contain diamond (Atkinson et al., 1984; Jaques et al., 1984).

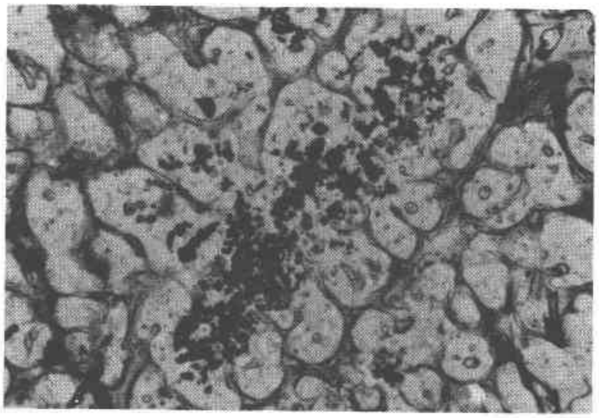

Fig. 1. Photomicrograph of Al-spinel (pleonaste-ferrian pleonaste) inclusions in leucite, glassy leucite lamproite, sample 71160408, Oscar Plug. Note irregular shape of aggregated leucite phenocrysts. Width of field is 0.55 mm.

The aluminous spinels occur exclusively as small—mostly less than 20 μm, rarely more than 40 μm—inclusions in aggregated leucite phenocrysts in fine grained to glassy, strongly leucite-phyric lamproites. The inclusions are more readily recognized in the rare rocks containing fresh leucite but can also be distinguished in lamproites where the leucite is replaced, generally pseudomorphed, by mixtures of K-feldspar, zeolite, chalcedony, opaline silica or clay (Prider and Cole, 1942). Fine grained inclusions of Fe oxide, particularly hematite are also common inclusions in altered leucite.

The leucite phenocrysts are typically euhedral and, where unaltered, weakly birefringent, twinned, and commonly contain inclusions of glass arranged in concentric zones. Many phenocrysts in the more glassy rocks are strongly resorbed and embayed. The leucite phenocrysts containing the aluminous spinel inclusions occur as amoeboid-shaped to strongly rounded, embayed, coalesced aggegates with numerous melt inclusions (Fig. 1). The aggregates range in size up to 5 mm and are irregularly distributed in the rock, apart from being more common in the finer-grained marginal phases of intrusives. No aluminous spinels have been observed in single, discrete leucite phenocrysts nor in any other phase; all are entirely contained in leucite.

Rock types containing the aluminous spinel inclusions include most of the types described by Wade and Prider (1940), and Prider (1960, 1982) except for the coarser grained lamproites of Rice (formerly Moulamen) Hill and Walgidee (formerly Wolgidee) Hills. The majority of the rocks containing aluminous spinel inclusions have phenocrysts of Al-poor diopside, phlogopite and/or olivine in addition to the leucite; potassic richterite is generally restricted to the groundmass. Alumina-free, alkali-rich accessory minerals (typically priderite, less commonly wadeite) are generally present in the groundmass as small prisms, and apatite is also invariably present. Most of the lamproites also contain a chrome-rich spinel which is present as tiny (<10 μm) inclusions in olivine and as small (mostly 50 μm or less) euhedra in the groundmass. The chromian spinels are mostly titaniferous magnesiochromites rich in Cr and Ti (50–65% Cr_2O_3, 3–6% TiO_2) and poor in Al but also include titaniferous chromian magnetites (see below). Ilmenite is comparatively rare occurring in the groundmass of only a few lamproites.

Experimental studies

The olivine leucitites of Gaussberg volcano in Wilhelm II Land, eastern Antarctica (Sheraton and Cundari, 1980), are closely comparable in composition to the mid-range (in terms of silica content) of the West Kimberley lamproites. The composition studied in the experiments is typical of the suite and is a good candidate for being a primary liquid; it is a fresh, glass-rich lava with phenocrysts of olivine, leucite and clinopyroxene, and carries mantle-derived spinel lherzolite xenoliths.

Two series of near-liquidus atmospheric pressure experiments have been conducted on the Gaussberg composition with controlled oxygen fugacities. Experiments were carried out in a one inch diameter vertical furnace using iron-doped Pt capsules included in evacuated silica tubes above a separate Pt capsule containing the oxygen buffer. The buffers used were hematite–magnetite, manganosite–haussmanite, nickel–nickel oxide, and magnetite–wüstite. Details of the composition and experiments are given elsewhere (Foley, 1985). The two series of experiments were conducted under similar conditions but with slightly different starting compositions. The first series involved an average Gaussberg composition, whereas the second series had additional Cr_2O_3 (0.2 wt.% cf. 0.045% in the first series) in order to ensure crystallization of chrome-spinel. The aluminous spinel inclusions in leucites occurred only in the second series runs. Apart from the slight difference in Cr_2O_3 content, the only other difference between the two series was run duration. The first series experiments were run for 2.5 hours, whereas the second were run for 5 hours to allow time for growth of chrome-spinel crystals to a size more easily analyzed. Both series of experiments were run under varying oxygen fugacity ranging between that controlled by magnetite-wüstite (MW) and the hematite–magnetite (HM) buffer reactions.

Aluminous spinel inclusions occurred exclusively in aggregated leucites in the second series runs. Groups of leucites also occurred in the first series runs but did not contain spinels. Although initially difficult to observe owing to their transparency in plane polarized light and isotropy under crossed polarizers, the spinels were identified in all of the second series runs containing leucites. The Al-spinels never occurred in direct contact with the glass.

Analytical method

Electron probe analyses of the spinels in the natural rocks were mostly obtained by wave-length dispersive methods using a Camebax (CAMECA) Microbeam fully automated EPMA employing an accelerating voltage of 15 kV, a beam current of 30 nA, a beam diameter of less than 1 micron, and full ZAF corrections. The majority of the leucite analyses were made by energy-dispersive probe employing an accelerating voltage of 15 kV, a beam current of 3 nA, and a beam diameter of about 1 micron following the method of Reed and Ware (1975) and Ware (1980). Under these conditions leucite suffered little volatilization.

Analyses of experimental products were obtained using a JEOL JXA 50A microprobe fitted with an EDAX energy-dispersive analyzer calibrated on Cu. Owing to the small size of many crystals, compositions were frequently calculated by subtraction of average glass analyses from crystal/glass overlap analyses. Chrome-spinel compositions were obtained by linear regression for each oxide from several area scans of crystal plus glass overlap of varying sizes.

Compositions of the aluminous spinel inclusions

West Kimberley lamproites

The aluminous spinels occur mainly as either irregular clusters of discrete euhedra, mostly of green pleonaste, or elongate trains and clusters or aggregates of green to greenish brown euhedral to subhedral grains of pleonaste-ferrian pleonaste composition some of which are clustered in schlieren-like aggregates of leucite (Fig. 1). In addition one lamproite contained very rare coalesced aggregates of brownish black subhedra of hercynite included within aggregated leucite phenocrysts (Fig. 2).

A crude correlation exists between spinel composition and crystal form and size. The larger discrete green spinels are the most magnesian and are highly aluminous ($X_{Al} > 0.9$ where $X_{Al} = Al/(Al + Cr + Fe^{3+})$ and contain only minor magnetite in solid solution (Table 1; Fig. 3). The greenish brown to brown pleonaste-ferrian pleonaste grains are less magnesian, have higher magnetite contents (Fig. 3), and are commonly richer in TiO_2 than the green pleonaste grains although compositions overlap. The brownish ferrian pleonaste grains have the lowest Mg and highest magnetite contents. There is a correlation between Mg and X_{Al} (Fig. 3) and to a lesser extent between Mg and $X_{Fe^{3+}}$. The brownish black hercynite inclusions of sample 71449A are compositionally distinct from the other inclusions being much richer in Fe (Fig. 3). Like the discrete green pleonastes they have very low magnetite contents ($X_{Fe^{3+}} < 0.1$).

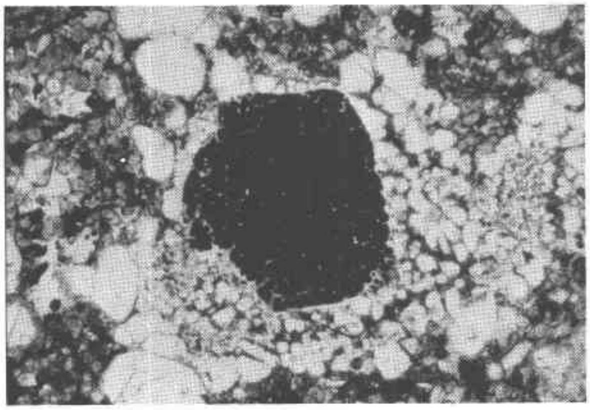

Fig. 2. Photomicrograph of aggregated hercynite inclusions in clustered leucite phenocrysts, olivine–diopside–leucite lamproite, sample 71449A, Ellendale No. 7. Width of field is 1.5 mm.

A feature of the spinel inclusions is their uniformly low Cr contents (<0.2%, commonly <0.1% Cr_2O_3). These contrast sharply with the high Cr contents of the groundmass titanium magnesiochromites (Table 1; Fig. 3). Other differences between the two generations of spinels are the much higher Ti and Mn, much lower Al contents, and generally higher Fe^{3+} and lower $Mg/(Mg + Fe^{2+})$ ratios of the groundmass spinels.

Experimental

The aluminous spinels in the Gaussberg experiments occur as tiny transparent single or, occasionally, grouped crystals. They contain negligible TiO_2 and Cr_2O_3, and have much higher $Mg/(Mg + Fe)$ ratios than those in the West Kimberley rocks. They are also slightly more magnesian than coexisting Cr-rich spinels (Table 2). The Fe oxidation state in the spinels corresponds qualitatively to the oxygen buffer used, but the variable Fe^{3+}/Fe^{2+} indicates that f_{O_2} equilibrium was probably not fully reached for the Al-spinel inclusions.

Compositions of the leucites

Previous studies of leucite have shown that significant substitution of monovalent and trivalent cations into $KAlSi_2O_6$ may occur. End-members of the heavier alkalis (e.g., Rb, Cs) can be synthesized (Henderson and Taylor, 1969), but Na is the only important alkali substitution in natural leucites. Fudali (1963) showed that up to 28 wt.% $NaAlSi_2O_6$ may be incorporated in leucite at 1 kbar P_{H_2O} and 800°C on the join $KAlSi_2O_6$–$NaAlSi_2O_6$, but natural leucites are not known to incorporate more than 10 wt.% $NaAlSi_2O_6$. The Na contents of leucites in lamproitic rocks are very low, in accord with their ultrapotassic chemistry.

Leucites from areas of ultrapotassic volcanism such as the Leucite Hills commonly show an excess of silica and alkalis over alumina and ferric iron (e.g. Carmichael, 1967; Cundari, 1975; Barton, 1979). Experimental studies have shown that leucite may incorporate up to 8 wt.% $KAlSi_3O_8$ at 1 kbar and 800°C (Fudali, 1963) and less than 5 wt.% $NaAlSi_3O_8$ at 1 atmosphere and 800°C (Gupta and Edgar, 1975). Ferric iron forms the dominant substitution on the smaller Al site: Gupta and Yagi (1980, p. 142–146) suggested that solid solution between $KAlSi_2O_6$ and $KFe^{3+}Si_2O_6$ is limited to less than 6 wt.% $KFe^{3+}Si_2O_6$ at atmospheric pressure but increases with $P_{H_2O_2}$ to 7.7 wt.% at 2 kbar $P_{H_2O_2}$.

Incorporation of divalent cations is much rarer, although leucites of CaO contents in excess of 1 wt.% have been reported from potassic volcanics of the East African rift valley (Deer et al., 1963). Schairer (1948) observed the coupled substitution of Mg into leucite by the mechanism MgSi = AlAl, but did not state the extent of this substitution. The large W site favors cations of large ionic radius, and hence the solubility of Mg in leucite can be expected to be small, as is typically observed in natural leucites. How-

Table 1. Representative microprobe analyses of spinels in West Kimberley leucite lamproites

	Al-spinel inclusions					Groundmass		
	1	2	3	4	5	6	7	8
SiO_2	0.12	0.05	0.06	0.06	0.03	0.05	0.05	0.05
TiO_2	0.21	0.24	0.62	0.96	0.38	4.33	4.35	3.95
Al_2O_3	64.87	63.60	59.62	50.91	57.66	2.16	1.51	1.67
Cr_2O_3	0.23	0.16	n.d.	n.d.	0.02	55.20	57.15	58.98
FeO	13.23	21.86	20.74	28.37	34.02	29.68	27.25	24.21
MnO	0.05	0.09	0.12	0.19	0.16	0.93	0.31	0.48
MgO	21.77	14.59	18.88	18.18	7.46	7.15	8.95	10.47
CaO	0.02	0.02	n.d.	n.d.	0.02	n.d.	0.03	n.d.
Total	100.49	100.61	100.04	98.67	99.75	99.50	99.60	99.81
Fe_2O_3	3.72	1.82	8.64	17.07	4.67	5.80	5.57	5.35
FeO	9.88	20.22	12.96	13.01	29.82	24.46	22.24	19.40
Total	100.86	100.79	100.90	100.38	100.22	100.08	100.16	100.35
				O = 4				
Si	0.003	0.001	0.001	0.002	0.001	0.002	0.002	0.002
Ti	0.004	0.005	0.012	0.019	0.008	0.114	0.113	0.101
Al	1.905	1.950	1.812	1.611	1.886	0.089	0.062	0.067
Cr	0.006	0.003	-	-	0.001	1.526	1.563	1.591
Fe^{3+}	0.070	0.036	0.167	0.345	0.097	0.153	0.145	0.137
Fe^{2+}	0.206	0.439	0.279	0.292	0.692	0.716	0.644	0.554
Mn	0.001	0.002	0.003	0.005	0.004	0.027	0.009	0.014
Mg	0.808	0.564	0.725	0.727	0.308	0.373	0.462	0.533
Ca	0.001	0.001	-	-	0.001	-	0.001	-
XAl	0.962	0.981	0.915	0.824	0.950	0.050	0.035	0.037
XFe^{3+}	0.035	0.018	0.085	0.176	0.049	0.087	0.082	0.076
XCr	0.005	0.001	-	-	0.001	0.863	0.883	0.887
Mg#	0.797	0.562	0.722	0.713	0.308	0.343	0.418	0.490

Fe determined as FeO; Fe_2O_3 calculated from AB_2O_4 stoichiometry
n.d. = not detected (detection limit 0.02%)
XAl, etc. = $Al/(Al+Cr+Fe^{3+})$ etc; Mg# = $Mg/(Mg+Fe^{2+})$

1. Pleonaste, 20 μm inclusion in leucite, 81210125.
2. Pleonaste, 20 μm inclusion in leucite, 71160408.
3. Pleonaste, 30 μm inclusion in leucite pseudomorph, 68165028.
4. Pleonaste, 15 μm inclusion in leucite pseudomorph, 68165028.
5. Hercynite, aggregate in leucite, 71449A.
6. Titaniterous magnesiochromite, 10 μm euhedra, 81210125.
7. Titaniferous magnesiochromite, 20 μm euhedra, 71160408.
8. Titaniferous magnesiochromite, 40 μm euhedra, 71449A.

ever, the coupled nature of the substitution leads to relationships more complex than this. For example, Henderson (1965) showed that Sr may be favored over Ba in leucites despite its smaller ionic radius.

West Kimberley lamproites

Analyses obtained for both inclusion-bearing and inclusion-free leucites from the same sample as well as bulk analyses of Al-spinel inclusion plus host leucite from the West Kimberley lamproites are given in Table 3 and projected into the system $KAlSiO_4$–$KFe^{3+}SiO_4$–SiO_2 (Fig. 4) following the method of Carmichael (1967). Both the leucite phenocrysts with Al-spinel inclusions and those without inclusions are of similar near-stoichiometric composition (Fig. 4) as previously found for West Kimberley leucites (Carmichael, 1967; Prider, 1982; Jaques et al., 1984). In general Fe, Ca and Na contents are low. Leucite cores and rims appear to show little difference in composition apart from slightly higher Fe at the rim.

Bulk analyses obtained with a defocussed beam or by scanning with a 40 to 50 μm raster of leucite host plus Al-spinel inclusion show an excess of Al and Fe over Si and alkalies (Table 3). These analyses, which deviate from stoichiometry, also have much higher Fe and Mg contents, and appear to exhibit limited solid solution towards $KFe^{3+}Si_2O_6$ (Fig. 4). Tie lines between the bulk analyses

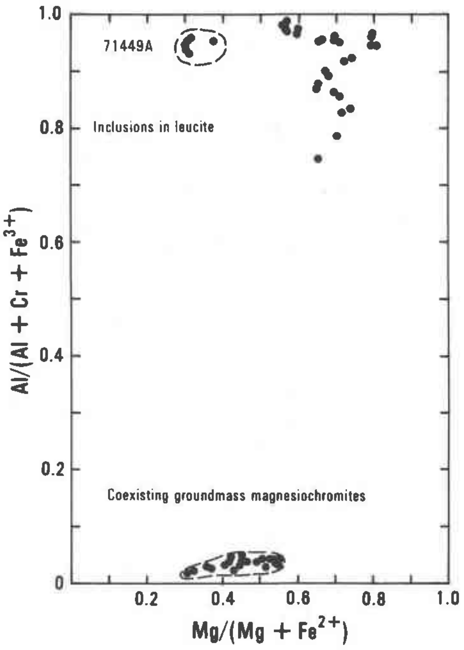

Fig. 3. Compositions of aluminous spinel inclusions in leucite in West Kimberley leucite lamproites contrasted with groundmass titanian magnesiochromites in terms of Al/(Al + Cr + Fe^{3+}) versus Mg/(Mg + Fe^{2+}).

and those of the leucite hosts (excluding spinel) show a trend towards the ideal leucite composition.

Gaussberg experiments

Compositions of leucites from both series of experiments are pertinent here and are listed in Table 4. The second series leucites containing Al-spinel inclusions were so small that clean (spinel-free) leucite analyses could not be obtained; these compositions are thus analogous to the bulk scan analyses in the West Kimberley rocks. The first series analyses listed in Table 4 are from run AT-116 (MnO–Mn_3O_4 buffer) which contains unusually large leucites which permitted direct analysis without the need to subtract included glass. Since the first series leucites contain no inclusions, the Mg and Fe reported in the analyses are considered to be incorporated in solid solution. Foley (1985) has shown that ferric iron contents in leucite increase with increasing oxygen fugacity, in agreement with the conclusions of Gupta and Yagi (1980) that increased $P_{H_2O_2}$ promoted solubility of Fe^{3+} in leucite. The first series experimental leucites have excess Si, indicating that Mg (and possibly some Fe) forms a coupled substitution MgSi–AlAl as originally proposed by Schairer (1948).

The second series leucite plus spinel overlap analyses form a range broadly similar to the West Kimberley leucites but displaced towards SiO_2 (Fig. 4), as a consequence of excess Si in their structural formulae (Table 4). The silica-poor nature of the West Kimberley bulk (spinel plus

Table 2. Compositions of aluminous spinel inclusions in leucite [1–4] and coexisting chromian spinels from experiment AT-126 [5–6]

	1	2	3	4	5	6
Buffer	HM	HM	NNO	NNO	HM	NNO
TiO_2	-	-	-	-	2.27	2.71
Al_2O_3	66.3	68.2	69.6	69.9	4.36	3.78
Cr_2O_3	-	-	-	-	45.6	59.6
FeO*	6.9	4.86	6.10	5.84	26.7	17.2
MgO	28.8	27.0	24.3	24.3	21.1	16.7
			0 = 4			
Ti	-	-	-	-	0.053	0.066
Al	1.918	1.951	1.996	2.001	0.159	0.150
Cr	-	-	-	-	1.120	1.519
Fe	0.142	0.099	0.124	0.119	0.692	0.464
Mg	0.981	0.975	0.880	0.877	0.975	0.801
Total	3.041	3.025	3.000	2.999	2.999	3.000
Mg**	0.874	0.908	0.876	0.881	0.926	0.751

* Fe as FeO
** Mg = Mg/(Mg+Fe)

Table 3. Representative microprobe analyses of leucite, West Kimberley leucite lamproites

	1	2	3	4	5
SiO_2	55.33	55.56	55.90	49.40	55.98**
TiO_2	0.17	0.16	0.11	0.35	0.06
Al_2O_3	21.03	20.85	21.12	25.57	20.86
Cr_2O_3	n.d.	n.d.	n.d.	0.07	n.d.
Fe_2O_3	1.08	1.11	0.56	3.36*	0.96
MnO	n.d.	0.03	n.d.	0.02	0.02
MgO	0.46	0.70	0.26	1.83	0.14
CaO	n.d.	n.d.	n.d.	0.08	0.12
Na_2O	0.09	0.02	0.10	0.09	0.09
K_2O	21.25	21.27	21.34	16.91	21.50
Total	99.41	99.70	99.39	97.66	99.75
		0 = 6			
Si	2.029	2.031	2.045	1.840	2.046
Ti	0.005	0.004	0.003	0.010	0.002
Al	0.909	0.899	0.911	1.122	0.899
Cr	-	-	-	0.002	-
Fe^{3+}	0.030	0.031	0.015	0.105*	0.026
Mn	-	0.001	-	0.001	0.001
Mg	0.025	0.038	0.014	0.102	0.008
Ca	-	-	-	0.003	0.005
Na	0.006	0.001	0.007	0.007	0.006
K	0.995	0.992	0.996	0.803	1.002
Total	3.999	3.997	3.991	3.993	3.994

Fe determined as FeO, recalculated to Fe_2O_3 except for 4;
* = Fe as FeO, ** BaO = 0.04%. n.d. = not detected
(detection limit 0.02%)

1. Leucite host to Al-spinel, 81210125
2. Leucite host to Al-spinel, 71449A
3. Leucite host to Al-spinel, 71160408
4. Bulk analysis of leucite host plus inclusions (60 um scan), 71160408
5. Leucite phenocryst, 71160408

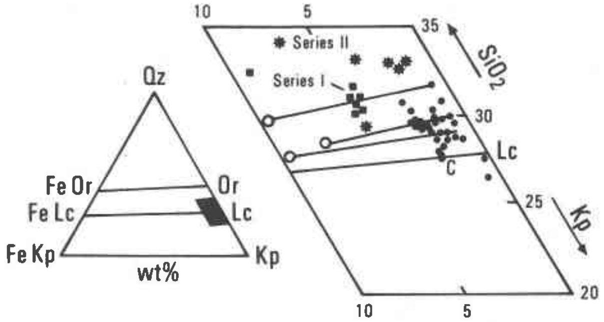

Fig. 4. Compositions of leucites in the West Kimberley lamproites (dots) compared with experimental leucite compositions in the system SiO_2–$KFe^{3+}SiO_4$–$KAlSiO_4$ (after Carmichael, 1967). Squares = first series experiments; crosses = second series experiments; open circles = bulk scans of Al-spinel plus leucite host in West Kimberley lamproites.

leucite host) analyses may be due to the predominance of Fe over Mg which causes a trend toward $KFe^{3+}SiO_4$. Alternatively, it might result from an excessive proportion of spinel in the rastered area of the analysis.

Origin of the Al-spinel inclusions

Several factors both preclude an origin for the Al-spinel inclusions in leucite by direct equilibrium crystallization from the host lamproite melt and strongly indicate an origin related to the crystallization of the leucite. (1) Al-spinel inclusions are restricted to leucite, particularly to poorly crystallized leucite aggregates. (2) Chrome-rich spinel coexists in the groundmass of the lamproite. Crystallization of two coexisting spinels one Al-rich with no Cr and the other Cr-rich, from the lamproite is highly unlikely since there is complete solid solution between $MgAl_2O_4$ and $MgCr_2O_4$ (e.g., Muan et al., 1972). (3) Equilibrium crystallization of Al-rich spinel containing negligible Cr (<0.2 wt.%) from a melt containing more than 250 ppm Cr is most unlikely under any conditions in view of the very high partition coefficient between chromite and liquid (e.g., Irving, 1978; and others).

Table 4. Representative compositions of leucite from first series [1–3] and second series (leucite + spinel overlap) experiments [4–6]

	1	2	3	4	5	6
SiO_2	56.11	56.19	56.34	57.3	57.9	54.7
Al_2O_3	20.76	20.88	21.04	22.0	21.7	22.7
FeO*	1.86	1.98	1.87	0.74	0.85	1.83
MgO	0.81	0.28	0.33	0.58	0.19	0.97
K_2O	20.22	20.43	20.40	19.4	19.4	19.8
Total	99.76	99.76	99.98	100.0	100.0	100.0
		O = 6				
Si	2.044	2.049	2.050	2.053	2.074	1.987
Al	0.891	0.898	0.902	0.931	0.915	0.971
Fe	0.057	0.060	0.057	0.022	0.025	0.056
Mg	0.044	0.015	0.018	0.031	0.010	0.052
K	0.940	0.950	0.946	0.887	0.890	0.920
Total	3.976	3.972	3.973	3.924	3.914	3.986

* Fe as FeO

Two possible explanations for the origin of the Al-spinel inclusions are considered: (1) crystallization during unmixing or "exsolution" of non-stoichiometric leucite, (2) crystallization from melt included within the leucite phenocrysts.

Evidence in favor of the first explanation includes the poorly crystallized, often aggregated, nature of the West Kimberley leucite hosts which suggests very rapid crystallization of the leucite as a consequence of supersaturation of the melt in leucite. Although solid solution between leucite and kaliophilite is apparently very limited under any conditions (Barton, 1979) and solid solution between leucite and $KFe^{3+}Si_2O_6$ is restricted, the substitution MgSi–AlAl is known to occur (Schairer, 1948). Formation of non-stoichiometric leucite would be promoted under conditions of supersaturation where crystallization would be rapid.

It is proposed that during crystallization of the leucite to a more ordered structure, excess Mg, Al and Fe were exsolved and recrystallized as spinel. The incorporation of Mg in leucite is proven by the first series of experiments. Furthermore, an indication of the kinetics of unmixing can be obtained by comparing the first series Mg-bearing leucites with the second series leucites in which unmixing has taken place. The first series near-liquidus experiments were run for 2.5 hours, whereas the second ran for 5 hours. The only other difference between the two series was the Cr_2O_3 content which could not have caused crystallization of Cr-free spinels. The experiments provide further indications of the conditions under which the natural spinels might have formed. The unmixing between 2.5 and 5 hours occurred at all oxygen fugacities studied (equivalent to $\log f_{O_2}$ of -8 to -2), demonstrating that f_{O_2} has minimal effect. In addition, the fact that the experiments were anhydrous shows that elevated P_{H_2O} is not necessary for incorporation of Mg and Fe into leucite.

The very low Fe^{3+} content of Al-spinels in the West Kimberley rocks indicates that much of the iron originally in the non-stoichiometric leucite was present in the divalent state. This view is supported by the Gaussberg experiments (Foley, 1985) which suggest an initially reducing environment for many lamproitic magmas. The Gaussberg olivine leucitites contain poorly-crystallized, inclusion-filled aggregates of leucite similar to the West Kimberley examples but to date no Al-spinels have been found in these. The Gaussberg leucites formed early in the crystallization sequence, are poor in Fe^{3+}, and have low excess Si relative to later phenocrystal leucites.

The second possible explanation for the Al-spinel inclusions, crystallization of the spinel from melt included within leucite, appears to require local super-saturation of the melt in alumina. Experimental support for the operation of this mechanism was serendipitously provided by an initial attempt to run the Gaussberg experiments in alumina sample capsules. This was attempted in order to eliminate the problem of iron loss to noble metal capsules because experiments by Hill and Roeder (1974) showed that alumina contamination of basaltic samples run in alumina capsules was minimal. However, because of the alumina-undersaturated nature of the Gaussberg composition reaction with the capsule was much greater: the melt gained appreciable Al_2O_3, and aluminous spinels together with leucite crystallized near the liquidus. The spinels are remarkably similar to those occurring as inclusions in leucite in second series experiments (Table 5). Alumina addition to this experiment may be analogous to melt inclusions gaining alumina from surrounding leucites or, possibly, by localized incorporation of Al-rich (pelitic) country rock. There is no evidence of widespread assimilation in the West Kimberley lamproites but country rock inclusions are locally evident.

Both of the above mechanisms are suggested as viable mechanisms for the formation of Al-spinel in leucite. The key to operation of the first mechanism, which seems the more likely for the bulk of the spinel inclusions, may be the degree of supersaturation of the melt in leucite. The experimental method of rapidly heating a mixture of oxides to the run conditions means that the melt formed will be strongly supersaturated in all phases initially crystallizing. In natural rocks a high degree of supersaturation may be necessary to initially incorporate appreciable Mg and Fe^{2+} in leucites, which may account for the apparent rarity of these inclusions; supersaturation may have led to the rapid crystallization of leucites with numerous melt inclusions. Some of the spinels might have crystallized in melt inclusions by the second mechanism, or alternatively, the melt inclusions may have acted as nucleation sites for spinels which then grew by exsolution from the non-stoichiometric leucites. The large size of the hercynite inclusions compared to the enclosing leucites in sample 71449A suggests local supersaturation in alumina.

Although solid inclusions are common in leucite (Gupta and Yagi, 1980, p. 19) Al-spinel has not, to the best of our knowledge, been reported as inclusions from leucites in other ultrapotassic suites. The closest analogues appear to be the inclusions of magnetite (and augite) in leucite from Utsuryo Island, Japan (cited by Gupta and Yagi, 1980, p. 19) and the occurrence of Fe-pleonaste inclusions in biotite of presumed xenocrystal origin in the Spanish lamproites. The latter inclusions were attributed by Venturelli et al. (1984) to breakdown of biotite due to a near isothermal decrease in pressure at constant or increasing f_{O_2}. The Fe-pleonastes and associated salitic pyroxenes in some of the Leucite Hills rocks (wyomingites) have been interpreted as xenocrysts. Most of the pleonastes are included within mica although some occur as large, irregular, discrete grains. These probably formed in the upper mantle as a result of local metasomatism or by crystallization of previous unrelated magmas (Barton and van Bergen, 1981; Kuehner et al., 1981).

Table 5. Compositions of Al-spinels produced by addition of alumina to experiment on Gaussberg leucitite

	1	2	3
SiO_2	0.36	0.38	1.45
Al_2O_3	69.80	69.58	69.19
FeO*	9.35	9.36	9.14
MgO	20.27	20.43	19.58
Total	99.78	99.75	99.36
Mg**	0.795	0.795	0.792

* Fe as FeO
** Mg = Mg/(Mg+Fe)

The Mg-pleonaste rims on groundmass chromite and titanomagnetite in the Kao (Haggerty, 1975) and De Beers kimberlite (Pasteris, 1983) pipes differ from the pleonastes reported here in having significantly lower Al and higher Ti, Cr and Fe^{3+} contents. Pasteris (1983) suggested that the Mg–Al spinel rims in the De Beers kimberlite resulted from increased Mg and Al in the magma, probably as a consequence of temporary cessation of phlogopite crystallization by reactions such as:

$$\underset{\text{phlogopite}}{4KMg_3AlSi_3O_{10}(OH)_2} \rightarrow \underset{\text{forsterite}}{5Mg_2SiO_4} + \underset{\text{spinel}}{2MgAl_2O_4} + \underset{\text{melt}}{(2K_2O + 4H_2O + 7SiO_2)}$$

Such a mechanism is unlikely to have resulted in the formation of the Al-spinel inclusions in leucite since: (1) the evolutionary trend of the groundmass spinels is to lower Al compositions (titaniferous magnesian aluminous chromite–titaniferous magnesian chromite–titaniferous chromian magnetite; Jaques et al., 1984); (2) there is no compelling evidence of a cessation or hiatus of phlogopite crystallization in the inclusion-bearing rocks; and (3) the evolutionary trend of the groundmass (commonly glassy) compositions is to higher K_2O and SiO_2 contents which would tend to stabilize phlogopite.

Therefore, with the possible exception of the magnetite inclusions in leucite from Utsuryo Island the mechanism proposed for the origin of the Al-rich spinel in leucite in the West Kimberley lamproites does not appear applicable to these other occurrences of Al-rich spinels. However, we suggest that under appropriate conditions aluminous spinels could form inclusions in leucite in other ultrapotassic suites. In the case of the West Kimberley leucite lamproites, the textural evidence from the leucites and their inclusions indicates rapid, near-surface (sub-volcanic) crystallization from magmas supersaturated in leucite. Low pressure fractionation resulted in silica-saturated residual liquids. Crystallization of olivine + leucite is restricted to less than 1.2 kbar under water-saturated conditions (Luth, 1967) but under water-undersaturated conditions olivine and leucite can coexist up to 4 kbar (Barton and Hamilton, 1982).

Acknowledgments

ALJ acknowledges CRAE Pty Ltd and J. D. Lewis (Geological Survey of Western Australia) for provision of one of the samples used. M. B. Duggan, J. W. Sheraton, and R. Wendlandt are thanked for reviews of the draft manuscript. SFF thanks K. L. Harris for technical assistance with the experiments, and D. J. Ellis, D. H. Green and S. M. Kuehner for helpful discussions and comments. SFF acknowledges a University of Tasmania post-graduate award. ALJ publishes with the permission of the Director, Bureau of Mineral Resources.

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Manuscript received, December 14, 1984;
accepted for publication, June 18, 1985.