NA, K, P AND TI IN MINERALS IN XENOLITHS FROM AFRICAN KIMBERLITES.

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Little is known about the distribution of minor and trace elements in the upper mantle. Xenoliths provide the only direct information, although interpretation can be complicated by possible complex history. We report analyses for Na,K,P and Ti in garnet, pyroxenes and olivine in xenoliths from southern African kimberlites and the Lashaine ankaramite-carbonatite volcano (Tanzania). The xenoliths, mostly granular lherzolites, eclogites and a clinopyroxene megacryst, were chosen because their mineral homogeneity suggests equilibrium. Application of existing geothermometers and geobarometers indicates derivation from a range of depths (Boyd, 1973; Råheim and Green, 1974).

Presence of micron-sized impurities within mineral grains, especially for minerals in xenoliths that may have been subject to host-rock contamination, requires micro-analytical techniques whenever feasible. Ion microprobe techniques are still under development and are not yet fully established. Although electron microprobe analyses typically have a detection level of 0.02 wt.%, analyses conducted under conditions which maximized the sensitivity of the instrument lowered the detection level to 20 ppmw (2σ) for the elements studied. Operating conditions were 3 μA beam current, 15 kV, several minutes counting times, beam size 5 to 10 μm. Four background determinations symmetrically disposed around the peak wavelength were taken for each analysis. For concentrations less than 200 ppmw, the background was profiled at 60 wavelengths for each analysis. Matrix corrections for Na,Ti and K in the silicates were insignificant on the ARL-EMX instrument, but the correction for P averaged 1.27.

Ranges and means of Na,P,K and Ti concentrations in the minerals are summarized in Table 1.

Garnet contains ~0.01-0.1 wt.% Na_2O and P_2O_5 and 0.02-0.8% TiO_2. There is enough P + Ti in every analysis to account for all Na in components such as $Na_3Al_2P_3O_{12}$ and $(Na_2Mg)Ti_2Si_3O_{12}$; thus, there is no need to invoke octahedrally-coordinated Si, as proposed by Sobolev and Lavrentyev (1971). Although the atomic radii of Na+P sum to less than for Ca + Si, the P content of garnet does not correlate with the pressure estimated from the Al_2O_3 content of coexisting orthopyroxene. Our results corroborate Erlank's (1973) conclusion that K_2O in garnet does not exceed 20 ppmw.

Olivine Concentrations of Na,P and Ti in upper mantle olivines are low, but are important because of the high modal abundance of olivine in peridotites. The electron microprobe spectrum was carefully checked for possible higher-order interferences with the Na peak, and P140 olivine from an alpine peridotite (Balsam Gap, NC) was found to be Na-free. Upper mantle olivines were found to have a mean concentration of 90 ppmw. K_2O concentrations are below the limit of detection.

Orthopyroxene contains <100 ppmw K and P, although containing significant Na. Orthopyroxenes from granular peridotites have a moderate 1:1 correlation between Na and Cr. Sodium is >>Cr in opx megacrysts and grains from kimberlite concentrates, while Cr<Na in orthopyroxene from spinel peridotite xenoliths.

Clinopyroxene contains the highest amounts of K and Na. In fact, clinopyroxene is the only significant host for K_2O in all of the mica-free xenoliths. All diffractions in a long-exposure precession photograph of an optically-homogeneous omphacite with 1600 ppmw K_2O can be indexed on the pyroxene cell, thereby precluding the presence of intergrown potassic richterite, which was previously suggested as the host for K.

Mica. Detailed analyses of micas are reviewed in another Extended Abstract. Three analyses showed up to 0.4 P_2O_5. Thus, mica must be considered as a potentially important host for P at depths in which it is stable.

Distribution Coefficients. In general, a distribution coefficient for an element between two phases may vary with the composition of the phases as well as pressure, temperature and oxidation state. Since our xenoliths came from different depths within the earth, even for xenoliths from the same kimberlite, a simple correlation of the concentrations of an element between two minerals cannot be expected. For example, the ratio of P_2O_5 in garnet to cpx varies widely from 0.7 to 4.6 for xenoliths from the same kimberlite pipe. This indicates that caution should be exercised when using one distribution coefficient for models of the entire upper mantle.

$K_D(Fe/Mg)$ [= $(FeO/MgO)^{gt}/(FeO/MgO)^{cpx}$] was found experimentally to be relatively insensitive to bulk composition, while increasing with decreasing temperature and increasing pressure (Råheim and Green, 1974). We found that $K_D(Na) = (Na_2O)^{gt}/(Na_2O)^{cpx}$ correlates with $K_D(Fe/Mg)$ (Fig. 1) suggesting that it may also depend on P and T, and hence be a possible depth indicator. Fig. 2 shows the positive correlation between $K_D(Na)$ and both the Wood-Banno (1973) estimate of temperature and the MacGregor (1974) estimate of pressure. Until detailed syntheses under controlled conditions have been made, these correlations are only indicative, but the steepening of the trend in Fig. 1 for high $K_D(Na)$ suggests that it may prove more useful than $K_D(Fe/Mg)$ at pressures over 40kb. Note that values of $K_D(Na)$ for deformed peridotites are mostly higher than those for granular peridotites. Data for garnet and pyroxene inclusions in diamond are widely scattered, and the reason is unknown.

Trace Elements in the Mantle. Recognizing that problems arise because the upper mantle is inhomogeneous and peridotite xenoliths may be unrepresentative, we tentatively propose the following ideas as a guide to experimentation on trace element distribution and to speculation on the origin of the Earth.

Mean analyses for Na,P,K and Ti in the Table taken together with the estimated mode of the upper mantle (Harris *et al*., 1967) give the following bulk values: Na_2O 2510 P_2O_5 180 K_2O 22 TiO_2 470 ppmw. K_2O would be greatly increased by addition of phlogopite. The P_2O_5 content is much lower than in bulk chemical analyses of Lashaine garnet peridotites, and even lower than estimates by Ringwood (1966). Apatite has recently been found in Lashaine peridotite, and may account for most P in upper-mantle peridotites. Since P is strongly partitioned into basaltic melt during partial melting (Anderson and Greenland, 1969; Thompson, 1975), residual peridotite could be strongly depleted.

In matching a cosmochemical model for the bulk chemistry of the Earth with mineralogical-geophysical data, Smith (1977) suggested that K_2O is confined to the crust and upper mantle, and that Na_2O is present to considerably greater depth in order that it be not depleted more than K. Perhaps Na is replacing Ca with a coupled substitution to give valence balance, e.g. as $NaPO_3$ in perovskite structure, or perhaps (Liu, 1977) in calcium ferrite structure ($NaAlSiO_4$).

References. Anderson & Greenland (1969), GCA 33, 493. Boyd (1973), GCA 37. 2533. Erlank (1973), Int. Conf. Kimberlites, Ext. Abstr., 103. Harris, Reay & White (1967), JGR 72, 6359. Liu (1977), EOS 58, no. 7, 613. MacGregor (1974), AM 59, 110. Råheim & Green (1974), CMP 48, 179. Smith (1977), Proc. 8th Lunar Sci. Conf. Rhodes & Dawson (1975), Phys. Chem. Earth 9, 545. Ringwood (1966), Adv. in Earth Sci., Hurley, ed., MIT Press, 287. Sobolev & Lavrentyev (1971), CMP 31, 1. Thompson (1975), EPSL 26, 417. Wood & Banno (1973), CMP 42. 109.

Table Range and mean of some oxides.

	Na_2O	P_2O_5	K_2O	TiO_2
	lherzolite and ultramafic rocks			
garnet	150-790(340)	200-1040(460)	<20	160-5190(1470)
olivine	40-130(90)	50-200(130)	<20	0-390(130)
orthopyroxene	530-1900(1070)	0-90(50)	10-110(30)	10-1650(480)
clinopyroxene	1.12-3.43(2.08)	90-630(350)	20-370(170)	100-4400(1630)
	eclogites and cpx megacryst			
garnet	100-1420(610)	160-940(530)	<20	210-7800(2000)
clinopyroxene	1.9-9.1(4.3)	110-520(300)	50-1620(370)	330-3800(2000)

ppmw except for Na_2O in clinopyroxene given as wt.%.

NSF EAR 76-0304 and Materials Research Laboratory.

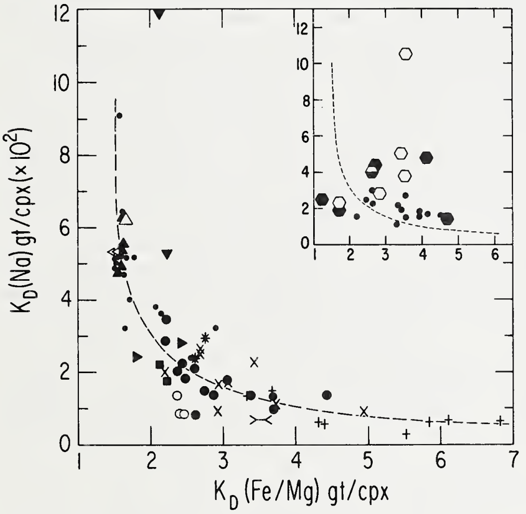

Fig. 1. Main diagram: eclogites, horizontal cross, Bobbejaan, inclined cross, Roberts Victor, star, Newlands, bridge, Vissuri; peridotites; large dot, S. Africa, circle, Lashaine; cpx megacryst, open triangle, Monastery; sheared lherzolite, small dot; enstatite megacryst, downward triangle; other symbols, see paper submitted to Lithos. Inset diagram: inclusions in diamond, hexagons; diamondiferous eclogites, dots.

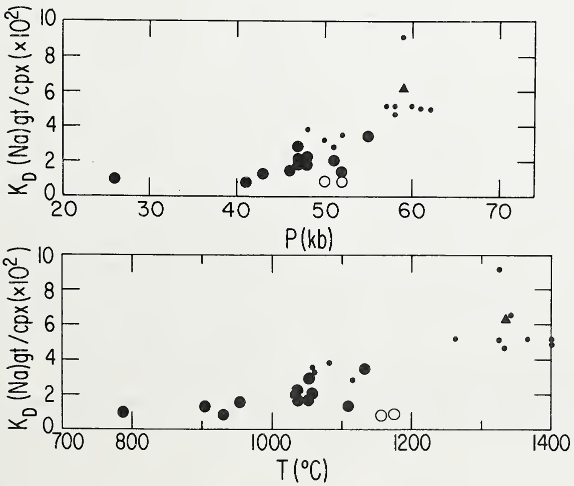

Fig. 2 K_D(Na for garnet/clinopyroxene vs. estimates of pressure and temperature from pyroxenes.