PETROGENESIS OF A NEOGENE SHOSHONITE SUITE, CERRO MOROMORONI, PUNO, SOUTHEASTERN PERU

DANIEL J. KONTAK¹, ALAN H. CLARK, ED FARRAR AND THOMAS H. PEARCE

Department of Geological Sciences, Queen's University, Kingston, Ontario K7L 3N6

DAVID F. STRONG

Department of Earth Sciences, Memorial University, St. John's, Newfoundland A1B 3X5

HALFDAN BAADSGAARD

Department of Geology, University of Alberta, Edmonton, Alberta T6G 2E3

Abstract

The first occurrence of mid-Tertiary basic to intermediate volcanism in the southeastern Peruvian sector of the Inner Arc domain of the Central Andean orogen is documented. The volcanic rocks are of shoshonitic character and crop out near the village of Antauta (Lat. 14°17'17"S, Long. 70°18'14"W). The suite has been dated (K-Ar) at 23.7 \pm 0.6 Ma, coeval with a 24.9 \pm 0.5 Ma old peraluminous monzogranite dyke, in the same area, which contains xenoliths of the shoshonitic rocks. The shoshonitic suite consists of olivine (Fo₈₀₋₈₄) absarokites and orthopyroxene (En78-90) shoshonites proper, which are characterized by several mineralogical features: (i) doublerim compositional profiles in the olivine and orthopyroxene phenocrysts; (ii) aluminous orthopyroxene (up to 5 wt.% Al₂O₃); (iii) sieve-textured plagioclase phenocrysts in the shoshonites proper; (iv) quartz megacrysts with a clinopyroxene corona. The shoshonite suite is subalkaline, with high K₂O contents and K₂O:Na₂O ratios of 0.83 to 1.49. In addition, a bimodal distribution of silica is apparent, with contents of 54 and 58-59 wt.% SiO₂ for, respectively, the absarokites and shoshonites; the rocks have abundant REE (156 to 472 ppm), with strongly fractionated patterns [(La/Yb)_N 6 to 57]. Rb-Sr isotopic analyses define a pseudoisochron for the suite, with an apparent age of ca. 209 Ma and an initial strontium ratio of 0.7061. The shoshonitic suite is thought to have originated by partial melting of a REE- and LILE-enriched garnet peridotite source, as outlined by Dostal et al. (1977a), which resulted from the deep penetration of an easterly dipping subduction-zone. It is suggested that the melts underwent a complex history involving an early period of high-pressure crystallization followed by mixing of the magma with a felsic liquid. The latter liquid, or contaminant, was generated by partial melting of the crust, as a consequence of the basic magmatism, and is represented by the nearby granitic pluton.

Keywords: shoshonites, southeastern Peru, Neogene age, aluminous orthopyroxene, double-rim zoning, magma mixing.

SOMMAIRE

Pour la première fois, on vient de découvrir la présence de volcanisme tertiaire moyen dans le secteur Sud-Est (péruvien) du domaine de l'arc intérieur de l'orogène des Andes centrales. Les roches volcaniques y présentent un caractère shoshonitique et affleurent près du village d'Antauta (lat. 14°17'17"S, long. 70°18'44"W). La série étudié a été datée (K-Ar) à 23.7 \pm 0.6 Ma, contemporaine d'un dyke monzogranitique hyperalumineux, âgé de 24.9 \pm 0.5 Ma, situé dans la même région et qui contient des xénolithes de roches shoshonitiques. La série de spécimens étudiés consiste en absarokites à olivine (Fe₈₀₋₈₄) et shoshonites proprement dites à orthopyroxène (En78-90), qui possèdent plusieurs caractéristiques minéralogiques: (i) les phénocristaux d'olivine et d'orthopyroxène montrent une double bordure dans leur profil de composition; (ii) la teneur en Al_2O_3 de l'orthopyroxène alumineux peut aller jusqu'à 5% en poids; (iii) les shoshonites proprement dites contiennent des phénocristaux de plagioclase à texture d'écumoir; (iv) des mégacristaux de quartz montrent une couronne de clinopyroxène. Les spécimens de la série shoshonitique sont subalcalins, avec forte teneur en K2O et rapport K2O:Na2O variant de 0.83 à 1.49. On note aussi une distribution bimodale de la silice, dont la teneur atteint 54% en poids dans les absarokites et 58-59% dans les shoshonites. Les roches contiennent des TR en abondance (156 à 472 ppm), à tendance fortement fractionnée [(La/Yb)_N de 6 à 57]. Les analyses isotopiques Rb-Sr définissent un pseudo-isochrone pour la série d'échantillons, auxquels on assigne un âge apparent de 209 Ma et un rapport de strontium initial de 0.7061. La suite shoshonitique aurait pris naissance par fusion partielle d'un protolithe de péridotite à grenat enrichi en terres rares et en éléments lithophiles à large rayon (Dostal et al. 1977a), résultat de la pénétration profonde d'une zone de subduction à pendage vers l'Est. Ces magmas auraient ensuite subi une évolution complexe: épisode de cristallisation précoce à haute pression et mélange avec un bain fondu relativement felsique. Ce magma plus siliceux aurait une origine par anatexie de roches crustales due au magmatisme basique, et serait représenté par les roches du pluton granitique voisin.

(Traduit par la Rédaction)

Mots-clés: shoshonites, Sud-Est du Pérou, âge néogène, orthopyroxène alumineux, zonation à double bordure, mélange de magmas.

¹Present address: Nova Scotia Department of Mines and Energy, P.O. Box 1087, 1496 Lower Water Street, Halifax, Nova Scotia B3J 2X1

INTRODUCTION

In recent years, the potassic subalkaline to moderately alkaline volcanic and intrusive rocks assigned to the shoshonite clan by Joplin (1965, 1968; but for discussion, see Nicholls & Carmichael 1969) have assumed significance in tectonic reconstructions of ancient terranes (e.g., Brooks et al. 1982). Several authors (Lefèvre 1973, Dostal et al. 1977a, 1977b, Déruelle 1982) have documented the widespread occurrence of Neogene shoshonitic rocks in the eastern part of the ensialic Central Andean orogen (Main Arc of Clark et al. 1983a, 1984, and see below), prompting the attribution of Andean characteristics to, for example, portions of Archean greenstone belts (Brooks et al. 1982). However, shoshonitic rocks are also represented in continental settings only tenuously related to plate-boundary orogeny (Gest & McBirney 1979, Boccaletti et al. 1978, Clark 1977, Joplin 1968), and in mature island-arcs (Gill 1970, MacKenzie & Chappell 1972, Jakes & White 1969, Keller 1974). Thus, the plate-tectonic significance, as well as the petrogenesis, of the shoshonite clan remains obscure.

The shoshonitic suite described herein was first recognized during the course of a regional reconnaissance study concerned with the magmatic and metallogenetic evolution of the Cordillera de Carabaya region of southeastern Peru (Fig. 1; Kontak 1985). The volcanic rocks were originally assigned to the Permian Mitu Group (Newell *et al.* 1953) on the basis of Rb-Sr dating and field relationships (Kontak *et al.* 1983, 1984a), but a recent K-Ar whole-rock age determination of a sample of absarokite indicates that the suite is of Neogene age. Herein, we document for the first time the occurrence of mid-Tertiary rocks of basic to intermediate composition within the Inner Arc (Clark *et al.* 1983a) setting of the Central Andean orogen, temporally and spatially related to *ca.* 25-Ma-old biotite – cordierite \pm sillimanite monzogranites that host important Sn-Cu-Pb-Zn-Ag mineralization (Clark *et al.* 1983b).

REGIONAL SETTING, AGE AND LOCAL GEOLOGY OF THE SHOSHONITES

On a regional scale, the shoshonitic suite is located in the Inner Arc system of the Central Andean orogen, cospatially with the Cordillera Oriental of Peru and Bolivia (Fig. 1). Within this domain in southeastern Peru, magmatism is characterized by an episodic and mixed mantle- and crust-derived nature, and contrasts with the quasicontinuous, mantle-dominated and subduction-zone-related magmatism of the Main Arc (Clark et al. 1983a, Kontak et al. 1984a). The geological evolution of this region of southeastern Peru, the Cordillera de Carabaya, is considered to reflect its regional tectonic setting between two major terranes, the relatively stable Brazilian craton to the east and the mobile orogen to the west (Kontak 1985). Thus the significance of most magmatic or tectonic events



FIG. 1. Location of the study area in the Cordillera Oriental, southeastern Peru. The shoshonite suite underlies Cerro Moromoroni near the village of Antauta.

within this region is to be sought in the gross relationships between these two terranes.

The geology of the Cordillera de Carabaya region is described elsewhere (Laubacher 1978, Kontak 1985), but a summary is warranted here. The region is underlain by a thick (ca. 10-15 km) succession of pelitic and psammitic rocks of Early Paleozoic (Ordovician - Late Devonian) age, overlain unconformably by ca. 3 km of Upper Paleozoic (Carboniferous - mid-Permian) psammites and carbonates, and less than 3 km of Upper Permian molassoid sediments and alkaline volcanic rocks. Igneous rocks of both mantle and crustal derivation have been episodically emplaced into this stratigraphic succession, at ca. 350, 240-230, 185, 90-70, and 26-8 Ma. Of relevance to this study is the presence of numerous small (less than 2 km²) 26- to 20-Ma-old monzogranitic stocks characterized by the presence of coarse alkali feldspar megacrysts, cordierite and sillimanite. These peraluminous stocks outcrop in the vicinity of the shoshonitic suite.

The shoshonitic volcanic rocks make up a small (4.5 km²), eroded volcanic edifice underlying Cerro Moromoroni, near the village of Antauta (Lat. 14°17'17"S, Long. 70°18'44"W), in northern Puno Department (Fig. 1). The volcanic rocks appear to conformably overlie an Upper Paleozoic sedimentary sequence consisting, from base to top, of quartz sandstones, calcareous sandstones and (fossiliferous) limestones. The contact between the limestones and the volcanic rocks is gradational, the limestones being intercalated with the earlier eruptive units (sills ?). However, the greater part of the volcanic pile is free of interbedded limestones. Cutting the volcanic rocks is a small granitic stock (150 \times 50 m) containing coarse alkali feldspar megacrysts and xenoliths (< 5-6 cm where observed) of the volcanic rocks (Fig. 2).

K-Ar dates have been determined (Table 1) for a whole-rock sample of the volcanic rocks and for a sample of biotite from the granitic intrusive body. The volcanic rock dated is an absarokite that contains 20-30% glass (see below) and shows no alteration. Thus, posteruptive modification of the K-Ar system was minimal, and the date of 23.7 ± 0.6 Ma is considered to be that of eruption. This date is similar to that of 24.9 ± 0.5 Ma obtained for biotite from the granitic body, indicating very close temporal, in addition to spatial, relationships for the volcanic and intrusive rocks.

CLASSIFICATION AND PETROGRAPHY OF THE SHOSHONITES

There is at present no universally adopted nomenclature for the classification of shoshonitic suites. Neither the original absarokite – shoshonite – banakite terminology of Iddings (1895) nor Joplin's



FIG. 2. Inclusion of absarokite (dark) in granite (light). Note the presence of quartz (Q) megacrysts in the absarokite rock and also the sanidine crystal (determined by X-ray diffraction; composition Or_{76}) growing into the xenolith.

TABLE 1. ANALYTICAL RESULTS FOR MATERIAL DATED BY CONVENTIONAL K-AR TECHNIQUE

Sample No.	Material Analyzed	2K	40 Ar(rad) cm STP/g	Z ⁴⁰ Ar (atmos.)	Apparent Age & Error (Ma)
COCA-17	biotite	7.396	0.719×10^{-5}	35.1	24.9 ± 0.5
COCA-22	whole-rock	1.675	0.155×10^{-5}	21.1	21.1 ± 0.6

Analyses by D.J.K. at Queen's University (datails in Kontak 1985). Potassium determined by A.A.S. technique; results represent the average of duplicate analyses. Error is estimated to be 40.7Z (20). The ages were calculated using the constants suggested by Steiger & Jäger (1977); errors represent the analytical precision at 20.

(1968) attempt at a chemical classification has been consistently followed. Instead, most recent authors have resorted to an alternative scheme based on the covariation of potassium and silica (MacKenzie & Chappell 1972, Peccerillo & Taylor 1976). The shoshonitic volcanic rocks of the study area are petrographically and chemically unusual compared to other shoshonitic suites and consequently do not strictly conform to the schemes of nomenclature adopted by others. However, we have chosen to classify the volcanic rocks by using, as much as possible, the mineralogical scheme of Iddings (1895) and Nicholls & Carmichael (1969) for the type-locality rocks from Wyoming. Those rocks containing oli-



FIG. 3. Photomicrographs of absarokites (plane-polarized light): (a) olivine phenocryst with serpentine infilling fractures; (b) matrix containing plagioclase laths (white), unaltered glass (dark), and pyroxene and olivine (high-relief phases).

vine as the dominant, or sole, phenocrystic phase in a two-feldspar – olivine – clinopyroxene – opaque phase \pm glass matrix are termed absarokite. Those in which orthopyroxene \pm plagioclase are the dominant phenocrystic phases in a two-feldspar – orthopyroxene – opaque phase \pm glass matrix are termed shoshonite. More highly evolved representatives of the series (*i.e.*, banakite) have not been observed. Our classification, therefore, is somewhat similar to that used by Hogg (1972) for the shoshonites of west-central Utah.

The *absarokites* display olivine \pm plagioclase and orthopyroxene phenocrysts, generally constituting less than 5% of the mode, in a fine-grained clinopyroxene - olivine - orthopyroxene - plagioclase - opaque phase \pm glass matrix. The olivine phenocrysts (Fig. 3a) are subhedral in form and show a variety of morphologies, probably a reflection of varying cooling history. The olivine grains are widely embayed and fractured, and display incipient alteration to serpentine and carbonate. The grains are compositionally zoned toward their margin, as indicated by the variation in birefringence, and most are free of inclusions. The plagioclase microphenocrysts (0.05-1 mm) are euhedral, tabular crystals generally showing normal zoning (An₄₀₋₈₀), and occur as single, inclusion-free grains. Orthopyroxene microphenocrysts (< 0.05 mm) also occur, but are exceedingly rare. The matrix (Fig. 3b), containing up to 30% brownish glass, has a well-developed pilotaxitic texture, and is remarkably fresh. Qualitative energy-dispersion microprobe analysis confirms the presence of discrete grains of K-feldspar, and also shows that the glass is dominated by K, Si and Al, with lesser amounts of Na, Fe and Ti, and is notably depleted in Ca and Mg.

The *shoshonites* consist of orthopyroxene, plagioclase and olivine phenocrysts in an orthopyroxene – plagioclase – opaque phase \pm glass and car-

bonate matrix. Orthopyroxene (Fig. 4a), the dominant phenocryst phase, is subhedral to euhedral, equant to tabular or, rarely, acicular. The crystals (0.5-4 mm) are inclusion-free and very fresh, and morphologies (e.g., skeletal) suggestive of rapid crystallization are not uncommon. Many grains are brownish, either in part (i.e., the core or rim) or entirely, and these grains (Fig. 4b) show anomalous double-rim profiles of compositional zonation (Kontak et al. 1984b). The rare phenocrysts of olivine (0.5-1 mm) are altered to serpentine-carbonate assemblages, but a few relict cores in some grains, and the well-preserved morphology of others, permit identification. Plagioclase phenocrysts (0.5-2 mm, rarely up to 5-6 mm) are normally zoned, euhedral, tabular crystals of An_{45-70} composition. They are generally larger and more abundant than those in the absarokites; the presence of sieve-like textures (Fig. 4c) suggests a period of disequilibrium (Eichelberger 1978, Sakuyama 1978). These corroded zones are enclosed by a later growth of clear plagioclase, generating euhedral grain-outlines. The matrix (Fig. 4d) is dominated by orthopyroxene and plagioclase, with lesser amounts of an opaque phase, but in some samples brownish glass is the most abundant phase. The presence of K-feldspar has been confirmed by qualitative energy-dispersion microprobe analysis.

Quartz megacrysts also occur in the absarokites and shoshonites in addition to the above phenocrystic phases (Fig. 5). This mineral is present in threequarters of the samples studied, but is far more abundant in the shoshonites, in some cases constituting the predominant megascopic phase. The inclusionfree quartz grains are generally coarser (1–4 mm) than the mafic silicate phenocrysts, and are predominantly anhedral, although rare euhedral crystals indicate that a more idiomorphic assemblage once existed. The grains are characterized by exten-





FIG. 5. Quartz megacrysts in the shoshonites: (a) traces of quartz grains with clinopyroxene coronas (stippled pattern);(b) photomicrograph of quartz megacryst surrounded by clinopyroxene.

Sample No.	22	35	32	33	34	38	39A	40	41	17
\$10,				59.25		59.47		59.43	58.64	68.96
T102	0.93	0.95	0.62	0.64	0.64	0.64	0.63	0.75	0.75	0.30
A1203	16.28	16.21	16.78	16.60	16.50	16.54	16.49	16.08	16.24	15.35
Fe203	1.70	3.47	1.74	3.72	3.96	2.31	1.23	2.65	4.18	0.6
Fe0	6.32	5.00	2.62	1.45	1.24	2.64	3.97	2.48	2.31	1.03
MnO	0.13	0.12	0.07	0.07	0.06	0.07	0.09	0.07	0.09	0.04
MgO	6.43	6.50	4.79	5.23	4.47	4.78	5.69	4.74	5.20	1.20
Ca0	6.45	6.33	4.81	4.40	4.30	4.68	5.04	4.23	440	1.6
Na ₂ 0	2.69	2.57	2.58	2.87	2.58	2.95	2.72	3.35	3.42	3.67
К20	2,24	2.23	3.79	3.78	3.85	3.65	3.41	3.55	3.07	4.2
P205	0.23	0.21	0.25	0.23	0.25	0.25	0.33	0.28	0.21	0.2
Total	97.70	97.50	97.63	98.24	97.44	97.98	98.18	97.61	98.51	97.3
(ppm)										
Nb	14	10	7	10	10	13	21	13	9	. 4
Ba	663	720	878	765	807	823	885	920	625	70
V	124	132	89	92	93	94	97	96	103	23
Cr		292	236	232	253	238	286	208		
Rb	125	111	259	247	252	116	254	219	210	378
Sr	401	380	355	329	341	372	362	370	262	10
Zr	129	133	165	158	162	160	160	166	150	90
Y	23	24	16	17				21		
Ni	40	36	57	61	6.	65		24	13	<1
Cu	42	16	18	14	15	17		12	17	
РЬ	26	21	69	50	57	53		44	44	63
Zn	109		90	79	75	78		81	92	7
K20/Na2	0 0.83	0.87	1.47	1.32	1.49	1.24	1.25	1.06	0.90	1.1

TABLE 2. GEOCHEMISTRY OF NEOGENE SHOSEONITES AND GRANITOID ROCK

All analyses carried out at Quean's University using the X.R.F. technique except for FeO (determined by wet-chemical analysis) and Cu, Fb, Zn and Mi (determined by AA.S. analysis).

Samples analyzed are: absarokites (22,35); shoshonites (32,33,34, 38,39A,40,41); and granite (17).

sive internal fracturing (Fig. 5a), a feature lacking in the mafic phenocrystic phases, thereby precluding abrasion as a possible cause, and by mantles of clinopyroxene (Fig. 5b), a disequilibrium feature shared by quartz megacrysts in andesites (Gill 1980, Sato 1975) and alkali basalts (Strong 1972).

WHOLE-ROCK GEOCHEMISTRY

Chemical analyses of the shoshonitic rocks (Table 2) reveal an unusual composition for the suite, including, for example, a very low CaO/MgO ratio (1.0-0.84) for rocks of this silica content [cf., compositions of shoshonites in Joplin (1965, 1968) and Morrison (1980)], high alkali contents, and elevated K_2O/Na_2O ratios (0.83-1.47). These features are expressed modally by the presence of olivine and orthopyroxene phenocrysts and of matrix K-feldspar. In terms of the more widely adopted classificationdiagrams for shoshonitic rocks based on the covariance of K₂O and SiO₂, the Peruvian data correspond to the shoshonite and latite fields (e.g., MacKenzie & Chappell 1972). The chemical data also define two groupings at ca. 54 and 59 wt.% SiO₂, corresponding to the absarokites and shoshonites,



FIG. 6. Major and trace element variation diagrams of the Cerro Moromoroni shoshonites (open circles) and granitic dyke (cross).

respectively (Fig. 6). We note that this is not a function of sampling since rocks were collected from several different localities.

The shoshonites plot in the subalkaline field in the $(Na_2O + K_2O)$ versus SiO_2 and normative Ol'-Ne'-Q' classification diagrams (Figs. 7a, c) of Irvine & Baragar (1971), and in the latter are shown to correspond to the field defined for shoshonitic suites in general (Kontak 1985). The shoshonitic rocks are markedly Fe-depleted in terms of the AFM plot (Fig. 7b), a universal feature of shoshonites (Jakeš & White 1972), but one that remains unexplained. The suite is distinguished from the tholeiitic rocks using both Miyashiro's (1974) FeO/MgO versus SiO₂ plot (Fig. 7d), and his Ti, Cr, V and Ni plots (Miyashiro & Shido 1975), in addition to the AFM diagram of Irvine & Baragar (1971) (Fig. 7b).

The K_2O versus SiO₂ trend for the Peruvian suite is compared to that of other shoshonitic suites in Figure 8. Although there is a wide spectrum of trends for such rocks, contrasting with, for example, the broadly similar trends shown by low-K calcalkaline suites, it is apparent that most shoshonitic groups show an abrupt rapid increase in K_2O with increasing SiO₂ at low SiO₂ contents, and a decrease in the slope at higher SiO₂ values. The Peruvian data cut across this trend and are generally displaced to higher silica values.

Comparison of the trace-element data with the values compiled by Jakes' & White (1972) for shoshonitic suites indicates that the Peruvian samples have similar Ba and Zr contents, but are enriched in Rb, Ni and Cr and depleted in Sr and V, and have lower K/Rb ratio. These features are consistent with analyses of other Central Andean, Neogene shoshonitic suites with comparable contents of silica (Déruelle 1978, 1982, Dostal *et al.* 1977b, Dupuy & Lefèvre 1974). For the shoshonitic suite under study, we also note that: (i) Ba and Pb increase from the absarokites to the shoshonites, (ii) there are only slight decreases in the abundance of V, Cr and Sr with increasing silica, and (iii) there is some scatter



FIG. 7. Chemical classification diagrams for the Cerro Moromoroni shoshonites. Dividing lines in a, b and c are from Irvine & Baragar (1971), and in d from Miyashiro (1974). Fields for shoshonitic and boninitic suites from Kontak (1985).

for Ni, Cr and Rb in the shoshonites (Fig. 6). Many of these features are not consistent with the "trends" shown by the major elements or with fractionation of the phenocrystic phases present.

The *REE* data (Table 3, Fig. 9) are characterized by enrichment of the *LREE* and a strongly fractionated pattern for the *HREE* [(La/Yb)_N values of 6 to 57]. The *REE* abundances and patterns for these rocks contrast markedly with those of low- to medium-K calcalkaline suites (Jakeš & White 1972, Gill 1980); also, the Peruvian rocks are enriched relative to most shoshonitic suites [see Kontak (1985) for a review], although exceptions occur (*e.g.*, Dostal *et al.* 1977a, Pe-Piper 1980). The *REE* abundances and patterns are instead more similar to those presented by Kay & Gast (1973) for alkali basalts, as Dostal *et al.* (1977a) similarly noted for the Central Andean, Neogene shoshonites that they examined. The latter authors have shown with model calculations that the shoshonites could be derived from a garnet peridotite (< 5% partial melting) with a flat chondrite-normalized *REE* pattern, but with 2-5 times higher absolute *REE* contents. We also note that the decrease of total *REE* content with increasing silica precludes derivation of the shoshonites proper from the associated absarokites by simple fractionation involving olivine, plagioclase and pyroxene, because the K_{ds} for the *REE* in these minerals are all extremely low (Arth 1976). Thus, another mechanism is required.

Rb-Sr isotope data for the shoshonites (Table 4, Fig. 10) define a pseudoisochron age of *ca*. 209 Ma



FIG. 8. Plot of K₂O versus SiO₂, comparing the Cerro Moromoroni shoshonite trend to that of Joplin (1968), and to the trends of shoshonite suites from other regions: 1 Absaroka Mountains, Wyoming, 2 Papua New Guinea, 3 Oxford Lake, Manitoba, 4 Viti Levu, Fiji, 5 Lesbos, Greece, 6 and 12 Srednogorie, Bulgaria, 7 Aeolian Arc, Tyrrhenian Sea, 8 Sierra Nevada, California, 9 west-central Utah, 10 Shebandowan, Ontario, 11 Puerto Rico, 13 Lakmon Mountains, Greece, 14 and 16 Central Andes, 15 southern Peru, Main Arc. Sources of data are found in Kontak (1985).

with a Sr_i of 0.70613 ± 0.00024 . However, a projection of the array defined by the shoshonites extends toward the field outlined by the Tertiary (ca. 25 Ma) peraluminous monzogranites, which are petrographically and chemically similar to the granitic dyke cutting the shoshonitic volcanic suite. The implication of these data is that contamination of the "primary" shoshonitic liquid has occurred; however, the Sr, value is still considered a good approximation of the original initial ratio of the melt prior to contamination. The value of ca. 0.7061 is well above the range of oceanic basalts (Peterman & Hedge 1971) and more "primitive" values obtained for andesitic rocks from the southern volcanic zone of the Andes (Déruelle et al. 1983), but lies well within the range for alkaline rocks in general (Powell & Bell 1974), and is similar to that reported for other shoshonites in, for example, the Aeolian Arc (Cortini 1981) and the Central Andes (McNutt et al. 1975).

MINERAL CHEMISTRY

Mineral compositions were determined with an A.R.L. SEMQ electron microprobe, using wavelength-dispersion analysis and the following operating conditions: accelerating voltage 15 kV, beam current 0.1 μ A and beam width 5 μ m. The raw data were corrected for matrix effects by the method of Bence & Albee (1968) using the alpha factors of

Albee & Ray (1970). A more detailed account of the procedures, including precision and accuracy as determined from analyzing standards, is presented elsewhere (Konťak 1985).

Olivine, analyzed in two of the absarokites (COCA-22 and -35: Table 5, Fig. 11), is markedly zoned, with core compositions falling in the narrow range Fo_{80-84} [except for one analysis (Fo_{77}), which may represent an off-centre section (Pearce 1984a)], and a rim ranging from Fo_{81} to Fo_{66} . This compositional spectrum is comparable to that of olivine in other shoshonitic suites (Déruelle 1982, Hogg 1972, Nicholls & Carmichael 1969); however, the withinsuite variation observed here is unusually large. Part of this is attributed to posteruptive interdiffusion of Fe^{2+} and Mg between the olivine phenocrysts and the groundmass, as demonstrated by Moore & Evans (1967) for olivine basalts from Hawaii.

One of the larger phenocrysts of olivine from an absarokite was studied in detail; its compositional profile, as determined from electron-microprobe analyses and laser interferometry (Pearce 1984b), is shown in Figure 12. The profile shows that the phenocryst has a double rim, in contrast to the simple zoning profiles generally observed in olivine (Kontak *et al.* 1984b, Maaløe & Hansen 1982, Kooten & Buseck 1978).

Orthopyroxene, as a phenocrystic and matrix phase, was analyzed in several of the shoshonites.

Representative compositions are given in Table 6, and the data are presented in Figures 13 and 14. The compositions are those of bronzite: the phenocrysts range from En_{90} to En_{78} , and the matrix pyroxene, from En_{82} to En_{69} . The most notable feature of the phenocryst compositions is their high Al content, in some cases attaining 5 wt.% Al₂O₃. There is a strong negative correlation between Al₂O₃ (expressed as ^{IV}Al) and silica content (Fig. 13). The phenocrysts are also generally richer in aluminum

	3. REE			VOLCANIC			
Sample	22	35	33	40	39A	38	- 17
No.							
La	67.33	102.8	27.32	23.67	113.1	59.7	26.0
Ce	151.2	208.7	73.79	60,99	226.7	123.6	75.9
Pr	16.84	22.25	9.23	8.67	21.4	14.2	7.0
Nd	64.39	89.70	37.03	35.36	78.0	50.4	26.0
Sm	11.84	15.92	7.00	7.47	13.0	9.1	5.6
Eu	1.78	1.73	0.22	1.71	1.90	0.9	0.9
Gđ	9.56	12.78	5.81	6.28	6.3	5.7	3.2
Dy	7.40	10.87	6.71	6.88	4.9	4.3	2.6
Er	2.60	3.97	3.04	4.28	2.6	1.8	1.4
Yb	2.03	3.49	1.18	2.54	1.3	1.1	0.4
	335.20	472.25	171.33	155.85	469.2	270.8	148.9
(La/Yb) _N	22.4	19.4	15.3	6.3	56.9	35.8	41.3

REE elements (ppm) determined at Memorial University by the thin-film X-ray fluorescence method of Fryer (1977). Precision is estimated at \pm 0.2 ppm or 10%, whichever is the greater.

Samples analyzed are: absarokites (22,35); shoshonites (33,40,39A,38); and granite (17).



FIG. 9. Chondrite-normalized [0.8 times Leedey chondrite values of Masuda *et al.* (1973)] *REE* patterns for shoshonites and granite.

than the matrix phenocrysts for a given $Mg/(Mg + Fe^{2+})$ ratio, and there appears to be a positive correlation between increasing Al and Fe²⁺ content (Fig. 13). These observations, coupled with the relationship between Si and ^{IV}Al, suggest that Al substitutes in the orthopyroxene structure according to the scheme $^{IV}Al + ^{VI}Al = Si + Mg$, as would be favored at high pressure owing to the volume decrease and density increase accompanying this exchange (Skinner & Boyd 1964, Boyd & England 1964). Finally, there is a positive correlation between Ca and Fe (Fig. 14), the matrix pyroxene being enriched in both cations. In the same diagram we also note the apparent evidence of both normal and reverse zoning in the phenocrysts, the core and rim compositions showing opposite trends.

An orthopyroxene phenocryst has also been studied in detail using electron-microprobe and laserinterferometry techniques, the results of which have been presented elsewhere (Kontak *et al.* 1984b). As with the olivine profile discussed above, double-rim zoning is developed, albeit in far greater detail than the olivine, owing possibly to the slower rates of diffusion in this mineral (Huebner & Nord 1979, Wilson 1982) than in olivine (Buening & Buseck 1973). The chemical analyses of this phenocryst showed a compositional spectrum from $En_{86.5}$ to $En_{79.6}$ and Al contents ranging from 2.18 to 8.89 wt.% Al₂O₃ (mean 4.5).

The available *plagioclase* data indicate that the absarokites contain microphenocrysts and microlites of An_{70-90} composition, consistent with optical determinations. In contrast, the shoshonites appear to contain two populations of plagioclase, one of composition An_{70} and the other, $An_{33}Ab_{23}Or_{44}$.

DISCUSSION

Any model proposed for the petrogenesis of this shoshonitic suite must explain the salient features of the petrography and whole-rock and mineral chemistry described above. These include: (1) the presence of quartz megacrysts, (ii) the occurrence of a sieve texture in all of the plagioclase "phenocrysts" in the shoshonites proper, (iii) the compositional gap between the absarokites (54% SiO₂) and shoshonites (59% SiO₂) and the trace-element patterns (anomalously high Rb contents, increasing Ba and Pb and only slightly decreasing Sr, V and Cr abundances with increasing silica), (iv) the REE patterns and abundances, (v) Rb-Sr data, (vi) the double-rim compositional profiles for both the olivine and orthopyroxene, (vii) the high Al content of the orthopyroxene, and (viii) the apparent bimodal population of plagioclase phenocrysts in the shoshonites. In addition, the close spatial and temporal association of felsic magmatism must be considered, as well as the regional implications of ca. 25-Ma-old shoshonitic volcanism in the Inner Arc domain of the Central Andean orogen.

Quartz megacrysts and sieve-textured plagioclase

The presence of quartz megacrysts is an unusual feature for shoshonites. Of twenty suites surveyed from the literature (Kontak 1985), only a few are reported to contain quartz. In these instances (Iddings 1895, Hogg 1972, Déruelle 1982), the quartz grains are up to 2–3 mm in size, strongly embayed, and mantled by clinopyroxene. However, none of the authors elaborated on their origin. We consider three possible origins for the quartz grains:

1. High-pressure crystallization. Although quartz has not been recognized as a liquidus phase in experiments on andesitic melts (Green & Ringwood 1968, Green 1972), it does form within 40°C of the liquidus (anhydrous) above 30 kbars. Nicholls *et al.* (1971) have argued on theoretical grounds that quartz should occur as a liquidus phase in basalts and basaltic andesites at 25-27 kbar and 1100°C. The reaction coronas mantling quartz megacrysts and the invariably embayed morphology of quartz grains in andesite (*e.g.*, Smith & Carmichael 1968) may therefore result from disequilibrium at shallow depths. This does not, however, account for the extensive internal fracturing characteristic of the quartz megacrysts.

2. Assimilation of sialic crustal rocks. The absence of xenoliths of granitic composition, or even of quartz-feldspar "glomeroclasts", suggests that if the quartz was derived from assimilation of crustal rocks, then the putative contaminant was a sandstone. Although such rocks outcrop in the immediate vicinity of the study area, forming part of the Carboniferous Ambo Group (Laubacher 1978), they are not considered likely candidates because: (i) the grain size of the quartz clasts is generally smaller than that of the megacrysts, (ii) the quartz megacrysts are morphologically dissimilar to the well-rounded grains in the sandstones, and (iii) the megacrysts occur as single crystals rather than aggregates, and we consider it improbable that only single grains would be widely added to the melt from any precursor.

Magma mixing. Presumably this would have 3. involved a more felsic melt, as has been suggested for the origin of andesites (Eichelberger 1974, 1978). The presence of embayed morphologies (Sakuyama 1978) and clinopyroxene coronas (Eichelberger 1978, MacDonald & Katsura 1965) is cited as evidence favoring a xenocrystic origin for the quartz as a result of magma mixing. The local granitic stock, similar in age to the shoshonitic volcanic rocks and containing quartz phenocrysts, is considered to represent the contaminant. We consider mixing to have occurred while both the end members were predominantly in the liquid state prior to eruption of the volcanic suite. This origin for the quartz megacrysts is also considered to account for their extensive internal fracturing. The abrupt change in temperature from perhaps ca. 750°C (rhyolitic liquid) to ca. 1100°C (shoshonitic liquid) is thought to have resulted in fracturing of the quartz as a consequence of thermal shock. In addition, the presence of morphologies suggestive of a previous idiomorphic shape for the quartz is also accounted for by magma mixing. The grain size of

TABLE 4. Rb-Sr DATA FOR SHOSHONITIC VOLCANIC ROCKS

Sample No.	Rb (ppm)	Sr (ppm)	87 _{Rb} /86 _{Sr} (atomic ratio)	87 _{Sr} /86 _{Sr} (atomic ratio)
COCA-221	39.42	36.44	0.9138	0.70946
COCA-22II	40.34	37.30	0.9140	0.70941
COCA-33	32.90	73.59	2,2111	0.71282
COCA-39	57.03	65.68	1.1386	0.70884

Analyses by H.B., University of Alberta; analytical details are as described in Goff <u>et al</u>. (1982).



FIG. 10. Rb-Sr isochron plot for the shoshonitic suite (absarokite: COCA-22; shoshonites: COCA-33, 39A). The data have been calculated to show the isotopic relations at *ca*. 25 Ma ago. The data for the Tertiary granites are for the nearby San Rafael and Carabaya intrusions (Kontak 1985), of similar age and composition as the dyke rock.

the quartz in the granitic dyke-rock is compatible with this interpretation.

Sieve-textured plagioclase is commonly cited as evidence favoring magma mixing (MacDonald & Katsura 1965, Eichelberger 1978, Gerlach & Grove 1982), and a similar origin is suggested for the textures found in the plagioclase of the shoshonites proper. In this particular case, the core of the sievetextured grains of plagioclase originated from the same felsic liquid that provided the quartz megacrysts. The sieve textures represent the initial state of disequilibrium, whereas the outer euhedral zones of the plagioclase represent a new equilibrium growth.

Whole-rock geochemistry

The most notable feature of the whole-rock chemistry is the compositonal gap between the absarokites and the shoshonites, which we consider to be real and not an artifact of sampling. The petrographic features discussed above have been interpreted in terms of magma mixing, and we ascribe the compositional gap to the same phenomenon. In this regard it is important to note the following: (1)

TABLE 5. REPRESENTATIVE COMPOSITIONS OF OLIVINE PHENOCRYSTS

Sample	10	IR	2C	2R	3C	3R
S10 2	39.04	38.66	38.90	38.63	38.44	36.98
T10 2	0.00	0.06	0.02	0.07	0.09	0.06
Fe0	15.54	18.85	15.69	18.04	17.27	23.89
MgO	44.30	41.90	44.45	42.45	42,95	38.33
Cr203	0.04	0.00	0.02	0.04	0.05	0.03
- •	98.91	99.48	99.08	99.03	98.78	99.28
SI	0.994	0.994	0.989	0.992	0.989	0.978
T1	0.000	0.001	0.000	0.001	0.001	0.001
Fe	0.331	0.405	0.334	0.387	0.371	0.529
Mg	1.680	1.605	1.685	1.625	1.646	1.511
Cr	0.001	0.000	0.000	0.001	0.001	0.000
ZFo	83.6	79.8	83.5	80.7	81.6	74.1

Analyses refer to cores (C) and rims (R); complete list of analyses found in Kontak (1985).

it is the shoshonites proper that contain the sievetextured plagioclase and also host most of the quartz megacrysts, (ii) it has been shown that the shoshonites cannot be derived from the absarokites by fractionation of the crystal phases present (Kontak 1985) and that the compositional data do not correspond to any cotectics in the CMAS projections of O'Hara (1965, Kontak unpubl. data), (iii) the trends of many of the whole-rock data on Harker variation diagrams (Fig. 6) project toward the composition of the granitic stock (its composition is given in Table 2), which is considered to represent the contaminating liquid, and (iv) many of the anomalous trace-element features, including the high contents of Rb and Pb, are accounted for by mixing of the shoshonitic liquid with a contaminant enriched in these elements.

The REE data, in respect of both abundances and patterns, may also reflect in part the phenomenon of magma mixing. The decrease in the total abundance of REE with increasing silica may be explained by mixing of the absarokitic liquid with a felsic liquid that contains lower total REE (ca. 400 ppm versus 150 ppm; see Table 3, Fig. 9). Because of the chondrite-normalized pattern of the postulated contaminant, the effect of mixing is to decrease the LREE more than the HREE. The large negative Eu anomaly for one of the shoshonites (COCA-33) might also be accounted for by this mechanism. However, despite the contamination of the shoshonitic liquid, the REE pattern for some of the volcanic rocks (samples 35 and 39A) probably represents the approximate compositions prior to contamination. Note that sample 39A also appears little modified with respect to the Rb-Sr data (Fig. 10).

Mineral chemistry

Analysis of olivine and orthopyroxene in the absarokites and shoshonites, respectively, has indicated the presence of anomalous, double-rim compositional profiles in both minerals and, in addition, high aluminum contents in the pyroxene. We discuss first the origin of the double-rim zoning, assuming



FIG. 11. Composition of olivine phenocrysts from Neogene absarokites.

that because the minerals show similar profiles, any model must apply to both. Three possible models are presented below:

1. Magma mixing. The zoning profiles in the mafic silicates would require mixing of the olivine- and orthopyroxene-bearing melts with a higher temperature, more mafic magma, for which there is no corroborating evidence. Although such a mechanism may have operated at depth, we instead favor an alternative mechanism discussed below.

A sudden decrease in Fe/Mg ratio of the liquid. 2. There are two ways in which this may be brought about. Firstly, the sudden precipitation of an ironrich phase, such as magnetite, would reduce the Fe/Mg ratio of the melt, stabilizing more magnesian phases. We can exclude this mechanism because there is no evidence to suggest that magnetite coprecipitated with either olivine or orthopyroxene. A second mechanism would be an increase in $f(O_2)$, thereby effectively reducing the amount of Fe²⁺ in the melt. Although this could be accomplished through the dissociation of H₂O, Hamilton & Anderson (1967) and Mueller (1969) pointed out that this is likely to control $f(O_2)$ only if a significant amount of H₂O (*i.e.*, > 1%) is present. The absence of any primary hydrous phase suggests that the H₂O content of the melt was low.

3. A sudden change in K_d due to pressure release. Several authors (Ford *et al.* 1983, Takahashi & Kushiro 1983, Hatton 1984) have recently shown that the crystal/liquid K_d for olivine is sensitive to pressure [*e.g.*, according to Takahashi & Kushiro (1983), $K_d = 0.300 \pm 0.002$ /kbar]. Thus, for polybaric crystallization of olivine, a zoning profile of the double-rim type observed in this study may result [compare to Fig. 5 of Pearce (1984a)]. Whereas there are no comparable experimental results for the orthopyrox-ene/liquid K_d relationship, available data (Frey & Prinz 1978) suggest that the K_d relationships vary sympathetically in these two mineral groups.

The high aluminum contents that we record for the orthopyroxene phenocrysts (3-8 wt. % Al₂O₃, are not unique (Table 7), having been previously reported from a number of geological settings. In virtually all of these instances, the authors favored a high-pressure origin for the orthopyroxene, citing as evidence: (1) disequilibrium with the host rocks, (ii) the coexistence of other high-pressure phases (e.g., pyrope), (iii) the occurrence of less aluminous, second-generation orthopyroxene, and (iv) experimental work carried out on a variety of bulk compositions and systems in which the orthopyroxene phase contains high concentrations of aluminum. The inference that aluminous orthopyroxene represents high-pressure crystallization has been indeed questioned (Anastasiou & Seifert 1972, Danckwerth & Newton 1978, Dymek & Gromet 1984), but we are nevertheless in accord with Duggan & Wilkinson (1973, p. 272), who state that this appraisal ". . . appears to minimize unduly the role of pressure, particularly in view of the increasing Al_2O_3 contents of orthopyroxene crystallizing from polycomponent "natural" systems under conditions of constant temperature and increasing pressure".

Petrogenesis of the shoshonites and regional implications

The evidence presented above is interpreted to record a complex evolution for the Cerro Moromoroni shoshonite suite, involving the following scenario:

1. Generation of subalkaline, or possible moderately alkaline, magma in the upper mantle through partial melting of a garnet peridotite source (see Dostal *et al.* 1977a). We consider the following fea-



FIG. 12. Compositional profile (range of %Fo is 7.5) of olivine phenocryst in an absarokite determined using the electron microprobe and laser interferometry.

COMPOSITIONS	OF	ORTHOPYROXENE
	COMPOSITIONS	COMPOSITIONS OF

Sample	10	2C	3R	4C	5C	6R	7M	8M
S102	53.66	53.21	53.84	52.94	55.22	55.00	52.80	50,57
TiO ₂	0.15	0.15	0,18	0.18	0.14	0.11	0.21	0.47
A1203	3.26	2.92	1.96	5.25	2,02	2.25	1.77	1.78
Fe ₂ 03	0.57	0.09	0.16	0.73	0.21	0.18	1.26	1.85
FeÖ	8.20	9.08	8.37	11.17	6.02	6.17	13.03	17.65
MgO	32.54	33.85	34.48	29,59	33.05	33.29	29.08	25.56
Cr203	0.59	0.47	0.49	0.46	0.73	0.63	0.24	0.11
CaÖ	1.25	0.62	0.71	1.28	1.03	0.89	1.59	2.18
	100.22	100.39	100.19	101.60	98.42	98.52	99.98	100.27
Si Al ^{iv} Al ^{vi}	1.879	1.865	1.886	1.851	1.941	1.932	1.901	1.867
A1	0.121	0.121	0.081	0.149	0.059	0.068	0.075	0.077
Al	0.014	0.000	0.000	0.067	0.024	0.025	0.000	0.000
Ti.	0.004	0.004	0.004	0.004	0.004	0.003	0.006	0.013
Fe	0.015	0.003	0.004	0.019	0.006	0.005	0.034	0.054
T1 Fe ³⁺ Fe ²⁺	0.240	0.266	0.245	0.327	0.177	0.181	0.392	0.545
Mg	1.698	1.768	1.799	1.542	1.731	1.743	1.560	1.406
Cr	0.016	0.013	0.014	0.013	0.020	0.017	0.007	0.003
Ca	0.047	0.023	0.027	0.048	0.039	0.033	0.061	0.086
ZEn	87.6	86.9	88.0	82.5	90.7	90.7	79.9	72.1

Analyses refer to core (C), rim (R) and matrix (M); ferric iron calculated assuming stoichiometry and twelve cationic charges. Complete list of analyses found in Kontak (1985).



FIG. 13. Compositional data for orthopyroxene from Neogene shoshonites.

tures of the magma to be "primary": (i) the *REE*enrichment and strongly fractionated chondritenormalized pattern, with (La/Yb)_N > 20, (ii) the moderate Sr_i (\pm 0.7060), (iii) the high K content (*ca.* 2.0 wt.% K₂O) and enrichment of other largeradius lithophile elements and (iv) the high initial Crcontent (*ca.* 300 ppm). Several of these features are more typical of alkaline, rather than subalkaline, suites.

2. A period of high-pressure crystallization followed by a second period of relatively shallow-level fractionation, resulting in the development of the double-rim compositional profiles observed in the mafic silicates, and also the apparent reverse zoning in several orthopyroxene phenocrysts.

3. Mixing of the shoshonitic melt with a felsic melt, which contained quartz and plagioclase crystals. The clinopyroxene coronas around, and extensive internal fractures within, the quartz megacrysts in the shoshonites are considered disequilibrium features, as is the sieve texture in the plagioclase. Mixing of the two liquids probably occurred in a shallow magma-chamber; we consider the shoshonites proper to represent the mixed component and the absarokites to approximate the uncontaminated melt in composition.

The generation of the shoshonitic volcanic rocks



FIG. 14. Compositional data for orthopyroxenes from Neogene shoshonites plotted in the compositional plane Mg-Fe-Ca.

at ca. 24 Ma coincided with the emplacement of other intermediate to basic magmas along the Inner Arc and Altiplano during the Late Oligocene - Early Miocene. Audebaud et al. (1979) determined K-Ar ages in the range of 23.6 to 28.3 (\pm 1.0) Ma for basalts and trachytic volcanic rocks near the southwestern margin of the Cordillera Oriental in southeastern Peru, and of 22 to 26 Ma for several small stocks of gabbroic to granitic composition in the same general area. Evernden et al. (1977) reported K-Ar ages of 26 Ma and 22 Ma for basaltic rocks near Cherana and Tambo, respectively, in the Altiplano region of northwestern Bolivia, and S.L. McBride (pers. comm. 1984) obtained a K-Ar age of 24.2 \pm 0.6 Ma on the Azurita basalt in the same general area. No geochemical data are available for these rocks; therefore, it is not possible to ascertain the extent of what may be a shoshonitic province, although the gabbros dated by Audebaud et al. (1979) are described as containing a biotiteclinopyroxene assemblage.

The intermediate to basic suites of ca. 28 to 22 Ma age in the Cordillera Oriental and Altiplano regions are coeval with Sn-W mineralized granitic suites in the southeastern Peru and northwestern Bolivia sectors of the Cordillera Oriental (Evernden et al. 1977, Grant et al. 1979, McBride et al. 1983, Clark et al. 1983b). Together, these suites constitute part of the "arc broadening" (Clark et al. 1976, Clark & McNutt 1982) episode of the Central Andean orogen that followed an extended mid-Tertiary period of magmatic quiescence and was sensibly coincident with rejuvenation of the Main Arc system. This expanded arc extended inland for some 500 km, in contrast with the previously narrow, longitudinal, volcano-plutonic belt of the Main Arc, which persisted during much of the Mesozoic and Early Cenozoic.

The presence of shoshonitic rocks along the easternmost limit of the *ca*. 25-Ma-old magmatic province suggests a model involving subduction-zone-related processes to generate these melts of upper-mantle source, thereby implying deep penetration of the subduction zone during this time (*vide* Clark & Zentilli 1972, Clark *et al.* 1976). It is also suggested that these melts caused local melting of the crust to generate the peraluminous felsic suites that host the important reserves of Sn-W and base metals in the tin belt.

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TABLE 7. ALUMINA CONTENTS OF ORTHOPYROXENE IN A VARIETY OF GEOLOGICAL ENVIRONMENTS

Host Lithology	wt.Z Al ₂ 0, in Orthopyroxene	Reference
massif anorthosite	3.9-9.2	Emslie (1975, 1978)
alkaline basalt	3.0-3.6	Green & Hibberson (1970)
alkaline basalt	4.4	Frisch & Wright (1971)
alkaline basalt	8.03	Binns (1969)
alkaline basalt	3.45-8.03	Binns et al. (1970)
subalkaline volcanics	0.5-3.2	Kuno (1964)
tholteiitic andesite	3.7-4.2	Duggan & Wilkinson (1972
Karoo tholeiite	4.0-4.5	Jamieson (1966)
peridotite	5.0-5.5	Green (1963)
peridotite	5.46-6.59	Green (1964)
xenoliths in basalt	1.0-7	White (1966)
peridotite nodules	2.0-5.5	Ross et al. (1954)
xenoliths in basalt	2.31-3.40	Kuno & Aoki (1970)
nodules in alnoite	2.4-4.9	Nixon & Boyd (1979)
ultramafic xenoliths in mafic dykes	2.57-3.46	Leary & Hermes (1979)

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