

Earth and Planetary Science Letters 165 (1999) 45-54

EPSL

Water–rock interactions, orthopyroxene growth, and Si-enrichment in the mantle: evidence in xenoliths from the Colorado Plateau, southwestern United States

Douglas Smith^{a,*}, J.C. Alexis Riter^a, Stanley A. Mertzman^b

^a Department of Geological Sciences, University of Texas, Austin, TX 78712, USA ^b Department of Geosciences, Franklin and Marshall College, P.O. Box 3003, Lancaster, PA 17604-3003, USA

Received 22 July 1998; revised version received 14 October 1998; accepted 14 October 1998

Abstract

Water–rock interactions and consequent orthopyroxene growth are documented by mantle xenoliths from opposite margins of the Colorado Plateau province. The interactions are inferred from a distinctive texture plus composition of orthopyroxene in spinel peridotite, in which porphyroblasts of orthopyroxene with inclusions of resorbed olivine are zoned to interiors exceptionally low in Al₂O₃ (<0.20 wt%). This texture plus composition has been found in xenoliths from Bandera Crater, New Mexico, in the southeastern margin of the Colorado Plateau, extending the known distribution from the northwestern margin (Grand Canyon field). Evidence that Si-enrichment locally accompanied movement of aqueous fluid is provided by an orthopyroxenite xenolith that is about 95% enstatite. The enstatite occurs in curved laths to 25 mm long, and the texture and composition (Al₂O₃ 1 to 2 wt%, Mg/(Mg + Fe) 0.92) are attributed to growth during subsolidus interaction between peridotite and hydrous fluid. Modal orthopyroxene calculated from 4 bulk rock analyses of peridotite xenoliths from the Grand Canyon field ranges from 26 to 29%, more than in comparably depleted oceanic mantle. The mantle root of the Colorado Plateau may have formed from accreted ocean lithosphere and subsequently been enriched in Si by aqueous metasomatism at widely distributed sites. Similar fluid–rock interaction may have contributed to the orthopyroxene-enrichment characteristic of some mantle xenoliths from roots of Archaean cratons. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: water-rock interaction; orthopyroxene; mantle; xenoliths; Colorado Plateau

1. Introduction

Xenoliths in Colorado Plateau occurrences provide an opportunity to investigate the possibilities that rock-water interactions can be widespread in cool continental mantle and that consequent aqueous metasomatism can cause orthopyroxene growth and silica enrichment. Although aqueous fluids have long been considered of possible importance as metasomatic agents in the mantle, particularly above subduction zones, most evidence for these fluids is equivocal. In the Navajo field on the Colorado Plateau, however, xenoliths have been described with chlorite and other hydrous minerals attributed to subsolidus mantle hydration [1,2]. In xenoliths

^{*} Corresponding author. Tel.: +1 512 471 4261; Fax: +1 512 471 9425; E-mail: doug@maestro.geo.utexas.edu

⁰⁰¹²⁻⁸²¹X/99/\$ – see front matter O 1999 Elsevier Science B.V. All rights reserved. PII: S0012-821X(98)00251-9

from the Grand Canyon field on the Plateau, pyroxene textures and compositions have been interpreted as consequences of mantle–water interactions [3,4], and Alibert [4] suggested that the interactions were accompanied by Si metasomatism. Schneider and Eggler [5] determined that hydrous fluids equilibrated with peridotite have high Si/Mg, and they noted that rock–water reactions in the mantle could lead to orthopyroxene enrichment.

The distribution and possible effects of aqueous mantle metasomatism are explored here in two ways. First, the regional distribution of evidence for mantle rock-water reactions below the Plateau has been investigated by study of xenoliths from Bandera Crater near the southeastern margin of the Colorado Plateau, the margin opposite the Grand Canyon occurrence described by Smith and Riter [3] and Alibert [4]. Second, the formation of orthopyroxene-rich mantle has been investigated by study of textures and mineral chemistry in a xenolith of orthopyroxenite. Bulk compositions of xenoliths from the Grand Canyon field also have been analyzed, and these and other Colorado Plateau xenoliths have been compared to compositions of abyssal peridotites and of xenoliths from the Kaapvaal and Siberian cratons.

Comparisons of peridotite from contrasting geologic provinces are pertinent to hypotheses about the evolution of continental mantle. The Plateau crust and mantle lithosphere record ages of about 2 Ga and younger, as summarized by Esperanca et al. [6]. The xenolith population from older, cratonic mantle has distinctive characteristics [7-12]. For instance, some peridotite xenoliths from the Kaapvaal cratonic mantle have ratios of orthopyroxene to olivine higher than that of comparably depleted oceanic lithosphere, and the mineralogic distinction is mirrored by bulk rock enrichment in Si relative to Mg [8,13]. The causes of the relative enrichment in Si remain controversial, but appeals have been made to processes primarily operative in the Archaean, such as komatiite extraction [8]. In contrast, Kesson and Ringwood [14] suggested that the orthopyroxenerich nature of cratonic mantle is a consequence of Si transport by aqueous fluids released from subducting slabs, and xenoliths from the Colorado Plateau mantle provide an opportunity to investigate this process.

2. Textural and mineralogic evidence in Colorado Plateau xenoliths

2.1. Evidence for rock–water reactions and known distribution in the Plateau mantle

In the interior of the Plateau, mantle xenoliths are found only in minettes and serpentinized ultramafic microbreccias of the Navajo field [15,16] (Fig. 1). In these ultramafic microbreccias, many peridotite xenoliths contain hydrous minerals such as chlorite and tremolite, and a few of the eclogite xenoliths contain chlorite; these minerals have been attributed to mantle hydration [1,2,17]. Rare chlorite-rich Navajo xenoliths contain enstatite, diopside, and titanian chondrodite that appear to be products of hydration reactions at contacts between peridotite and mafic rock [17]. It is unclear whether this evidence for hydration is relevant to mantle below other regions, however, because the extraordinary Navajo host rocks and unusual mineral assemblages are difficult to relate to host rocks and xenoliths elsewhere.

Xenoliths of Cr-diopside spinel peridotite also have been described in four of the basaltic fields within the Plateau margins (Fig. 1). The host rocks are commonplace alkalic basalts in these fields, in contrast to the host rocks of the Navajo field. Most of the xenoliths have the assemblage of olivineorthopyroxene-clinopyroxene-spinel with rare pargasite and phlogopite [15], as is typical of basalthosted peridotite xenoliths worldwide. The evidence for mantle-water reactions is based primarily on pyroxene textures and compositions in these otherwise typical xenoliths. The unusual pyroxene previously was recognized only in peridotites of the Grand Canyon suite in the western margin of the Plateau. The orthopyroxene occurs in porphyroblasts with partly resorbed inclusions of olivine [3,4,18], a texture that Alibert [4] suggested could be due to metasomatism by a silica-rich aqueous fluid. Smith and Riter [3] found that some of these orthopyroxene porphyroblasts have interiors unusually low in Al and Cr: they interpreted the textures and composition as evidence that protoliths contained mantle talc and chlorite eliminated by prograde reactions.

Xenoliths at Bandera Crater, New Mexico, in the Zuni-Bandera field near the opposite margin of the Plateau (Fig. 1), were chosen to investigate the re-



Fig. 1. Outline of the Colorado Plateau and included volcanic fields from which xenoliths of Cr-diopside peridotite have been described. In the Navajo field, these xenoliths are hosted by minette and by ultramafic diatremes [16]. In the four other fields, the xenoliths are basalt-hosted. Xenoliths with evidence for mantle-water reactions are from the Grand Canyon, Zuni-Bandera, and Navajo fields.

gional extent of similar hydration histories. The key texture, elongate orthopyroxene porphyroblasts containing numerous olivine inclusions with resorbed grain boundaries, is present in some but not all of the Bandera peridotite inclusions. Orthopyroxene in the interiors of such porphyroblasts is extraordinarily low in Al and Cr (Analysis 1, Table 1), like that in some Grand Canyon xenoliths but distinct from that in typical spinel peridotite (Fig. 2). Orthopyroxene in rims of porphyroblasts and in irregular interior domains typically is more aluminous (Analyses 2 and 3, Table 1). Spinel grains in porphyroblast interiors associated with low-Al orthopyroxene are relatively Al-poor and Cr-rich relative to matrix spinel. These textures, low-Al orthopyroxene compositions, and zonations are identical to those interpreted as evidence of heating and metamorphism of hydrous chlorite-bearing protoliths [3]. Mineral compositions that represent 4-phase equilibrium assemblages are difficult to identify conclusively in Bandera xenoliths with low-Al orthopyroxene, because intragranular zonation of orthopyroxene and intergranular zonation of all minerals is complex. One intergrowth of orthopyroxene-olivine-spinel (Analyses 2, 4, and 5, Table 1) yields a temperature of 800°C with the thermometer of Witt-Eickschen and Seck [19]. Temperatures calculated by various methods for four Bandera peridotite xenoliths range from about 800 to 950°C; this range overlaps that reported for the Grand Canyon samples but is cooler than the ranges for typical Basin and Range localities [20].

Nearly identical distinctive textures, orthopyroxene compositions, and equilibration histories now have been recognized in basalt-hosted xenoliths from opposite margins of the Colorado Plateau (Fig. 1). The peridotite and eclogite xenoliths in Navajo ultramafic diatremes are evidence for mantle hydration below the Plateau interior. Rock–water reactions therefore appear to have been widespread in the upper mantle of the province.

2.2. Orthopyroxenite S-100: evidence of a fluid–orthopyroxene link

Additional evidence that rock-water reactions can form orthopyroxene-rich mantle is provided by an orthopyroxenite xenolith (sample S-100) from the Grand Canyon field. The sample was collected by M.G. Best (personal communication) from alluvium at $113^{\circ}06'18''W$, $36^{\circ}21'58''N$, in weathered debris from a basaltic flow 5.7 km SSE of Mount Trumbull. The rock has an irregular shape and a maximum dimension of ~7 cm. Coarse crystals of enstatite comprise about 95% of the sample (Fig. 3). The remainder consists of fine-grained clusters of inter-

Rock: Phase:	Spinel peridotite Wi-35-02, Bandera Crater, New Mexico						Orthopyroxenite S-100, Grand Canyon field, Arizona					
	1 Opx	2 Opx	3 Opx	4 Ol	5 Sp	6 Cpx	7 Opx	8 Opx	9 Ol	10 Cpx	11 Glass	12 Amph
SiO ₂	58.5	56.5	56.9	40.3	0.04	54.7	58.5	57.8	42.5	54.5	57.7	52
TiO ₂	0.03	0.03	0.07	0.02	0.25	0.05	0.02	0.02	_	_	_	_
Al_2O_3	0.19	1.67	2.66	0.02	34.3	2.18	0.96	1.91	0.02	3.7	20.8	9.4
Cr_2O_3	0.04	0.23	0.30	0.01	31.3	0.13	0.07	0.03	_	_	_	_
Fe as FeO	6.27	6.14	6.37	10.6	17.6	2.50	5.41	5.41	5.61	1.75	2.6	3.3
MnO	0.18	0.15	0.17	0.17	0.22	0.07	0.13	0.17	_	_	_	_
MgO	34.8	34.2	33.8	48.2	14.4	17.4	35.6	35.3	52.4	18.19	4.16	23
CaO	0.26	0.33	0.46	0.03	0.02	23.1	0.51	0.54	0.21	20.43	9.2	9.7
Na ₂ O	0.01	0.06	0.03	0.00	0.00	0.40	0.01	0.02	0.01	0.52	3.78	1.7
K_2O	_	_	_	-	_	_	_	_	_	0.01	0.98	0.4
NiO	_	-	-	-	-	-	0.05	0.09	-	-	-	-
Total	100.3	99.2	100.7	99.5	98.1	100.6	101.2	101.3	100.7	99.1	99.2	

Table 1 Representative compositions of phases in two xenoliths from the Colorado Plateau

Electron microprobe as described by Ref. [3]. 1, low-Al orthopyroxene in interior of porphyroblast; 2–3, other points in the same porphyroblast; 4–6, other grains; 7 and 8, lowest-Al and highest-Al orthopyroxene analyzed in the rock; 9–11, phases in intergrowth formed by decompression melt of amphibole; 12, calculated amphibole composition.

grown glass (30%), vesicles (26%), olivine (23%), clinopyroxene (21%), and a trace of spinel: these phase proportions were calculated from back-scattered electron images using the public domain NIH Image program (developed at the U.S. National Institutes of Health). Analyses of the clinopyroxene, olivine, and glass combine in modal proportions to yield a calculated bulk composition appropriate for amphibole (Table 1). The large volume of vesicle space (26%) in the mineral-glass clusters is consistent with low-pressure vapor separation from melt produced during decompression melting of amphibole. Similar textures are common in spinel peridotite xenoliths at the locality [18].

Enstatite textures and compositions in the orthopyroxenite are unlike those in most pyroxenite xenoliths. Long dimensions of enstatite grains range to 25 mm. Part of the rock is made of a cluster of anhedral but elongate subparallel enstatite grains, some of which have twin boundaries subparallel to their elongation (Fig. 3). Some of these elongate grains are gently curved. No exsolution lamellae were observed in the pyroxene. Contents of Al_2O_3 and Cr_2O_3 in all analyses of S-100 enstatite are lower than those of orthopyroxene in spinel peridotite xenoliths from the Basin and Range and Rio Grande rift (Fig. 2a). The pyroxene is enstatite (En₉₂Fs₈), and mg values and TiO_2 are at the low extremes of the compared populations (Fig. 2b). CaO (0.5 wt%, Table 1) also is near the low end of the range of 0.4 to 2.5 wt% CaO in orthopyroxene from these provinces. Inasmuch as the orthopyroxene is without exsolution lamellae, and volumetrically minor amphibole was the only other significant phase, the orthopyroxene composition is unlikely to have been modified by exsolution.

The distinctive composition and texture of the enstatite constrain petrogenetic hypotheses. The low contents of Al, Cr, Ti, and Ca are inconsistent with equilibration with spinel lherzolite at high mantle temperatures; such orthopyroxene would be richer in Ca, Al, and Cr, as in Basin and Range xenoliths (Fig. 2a). Orthopyroxene equilibrated with basalt magma also would be richer in Fe and Ti, and the low mg-values (Fig. 2b) establish that if the pyroxene equilibrated with any melt, that melt must have been more magnesian than basalt. Even orthopyroxene in equilibrium with komatiite melt is more enriched in minor and trace elements; for instance, in the experiments of Canil [21], orthopyroxene present with magnesian komatiite-like melt contained 2.6 to 3.9 wt% Al_2O_3 , 0.32 to 0.5 wt% Cr_2O_3 , and 1.6 to 2.7 wt% CaO. Hence, the orthopyroxenite is not a melt crystallization product. The pyroxene textures (Fig. 3) are unlike those common in products of



Fig. 2. Orthopyroxene in spinel peridotite xenoliths and in orthopyroxenite S-100. Points are shown for analyses of cores of zoned orthopyroxene porphyroblasts in two spinel peridotite xenoliths, one from the Grand Canyon field [3], and one from Bandera Crater (Table 1). Seven points are shown for enstatite in orthopyroxenite S-100. Each other point represents orthopyroxene equilibrated in a spinel peridotite assemblage within a xenolith from the Colorado Plateau, Basin and Range, and Rio Grande rift provinces: these data are from Riter (in preparation), Smith (in preparation), and various literature sources. (a) Plot of Al₂O₃ vs. Cr₂O₃; these components are sensitive to temperature and bulk composition in spinel lherzolite assemblages. (b) Plot of TiO₂ and mg = $100 \times Mg/(Mg + Fe)$; these are more sensitive to bulk composition than temperature.

solid-state recrystallization, and the most comparable textures are in vein deposits. Subarc xenoliths from near Papua New Guinea contain orthopyroxenite veins with fibrous, radiating crystals of enstatite



Fig. 3. Photomicrograph of a large-size thin section of rock S-100, taken with crossed polars. The long dimension of this section is 6.5 cm.

(0.30 wt% Al₂O₃), attributed to subsolidus reaction between peridotite and slab-derived hydrous fluid [22]. Enstatite-talc veins in metamorphic forsterite– enstatite–anthophyllite rock also contain large radiating orthopyroxene crystals, and some veins have enstatite margins [23]. Because the pyroxene composition does not appear to have been altered by exsolution and is unlike that expected from melt crystallization, and because similar textures have been described in veins, orthopyroxenite S-100 is interpreted as a vein deposit formed during interaction of a hydrous fluid and peridotite wallrock.

3. Comparisons of relative Si-enrichment in mantle peridotite

Three spinel peridotite xenoliths from the Grand Canyon field, selected for their large sizes and apparent freedom from host contamination, were analyzed to evaluate possible enrichment in silica. The three analyses, together with the only other bulk analysis of a Grand Canyon xenolith, are in Table 2. Textural classifications of these xenoliths using the criteria of Best [18] are as follows: ME8, Type G; VT45, Type M; VT44, Type M to Type G; VT19, Type P.

Table 2 Analyses and modes of spinel peridotite xenoliths from the Grand Canyon field, Arizona

Rock, analyst ^a :	VT44, 1	ME8, 1	VT45, 1	VT19, 2
SiO ₂	44.94	45.21	44.78	45.26
TiO ₂	0.03	0.03	0.02	0.008
Al_2O_3	2.48	2.66	1.43	1.87
Fe ₂ O ₃	0.95	1.04	0.89	-
FeO	6.85	6.74	6.62	-
Fe as FeO	7.70	7.68	7.42	7.32
MnO	0.12	0.12	0.11	0.106
MgO	40.81	40.59	43.09	44.14
CaO	2.60	2.43	1.71	1.20
Na ₂ O	0.12	0.13	0.04	0.08
K ₂ O	0.007	0.006	0.006	0.00
P_2O_5	0.01	0.02	0.01	0.018
LOI	0.49	0.61	0.6	-
Total	99.41	99.59	99.31	(100)
ppm				
Sc	14	15	10	6
V	64	61	45	33
Cr	2808	3009	2775	2768
Co	115	137	118	-
Ni	2152	2059	2308	2401
Cu	13	7	13	11
Zn	51	52	48	43
Ga	2.1	1.9	1.1	2
Sr	25	11	13	18
Zr	7	8	7	7
Nb	2	2.3	1.6	3.1
Ba	17	19	14	nd
wt% mode				
Olivine	60	60	64	64
Orthopyroxene	28	26	28	29
Clinopyroxene	10	7.4	6.7	4.5
Spinel	1.9	1.1	1.3	1.8
Amphibole	tr?	4.9	tr?	nd
Mg/(Mg + Fe)				
Bulk rock	90.4	90.4	91.2	91.5
Olivine	90.1	90.2	91.2	91.8

^a 1 = Analyses by S.A. Mertzmann. Modes calculated using mineral analyses (**EPSL Online Background Dataset** http://www.elsevier.nl/locate/epsl, mirror site: http://www. elsevier.com/locate/epsl, Table 1). 2 = Analysis by Washington State University GeoAnalytical Laboratory. Major elements and mode from Ref. [3]. nd, not detected.

The low-Al compositions diagnostic of equilibration in chlorite-facies peridotite have been found only in relict volumes in interiors of large orthopyroxene porphyroblasts in Type P xenoliths, but large orthopyroxene porphyroblasts also characterize Type M. Smith and Riter [3] deduced that the low-Al orthopyroxene compositions and porphyroblastic textures are eliminated during mantle heating, but that the porphyroblasts themselves persist longer than do the distinctive compositions. Three of the four analyzed rocks do contain large orthopyroxene porphyroblasts. Alibert [4] found high Sr/Nd in both Type P and Type G rocks and attributed the high ratios to Sr metasomatism by aqueous fluids. The four analyzed rocks from The Grand Canyon field may have common histories of hydration.

Three populations of peridotite analyses were selected to compare with the analyses from the Grand Canyon field. A compilation of analyses of 52 samples (EPSL Online Background Dataset¹, Table 1) from other Colorado Plateau localities, most in the Navajo field, represents the mantle of the province. Xenoliths from cratonic mantle hosted by kimberlites in southern Africa [7] and Siberia [12] were selected to compare relative Si enrichment; the 65 analyses are of large-volume samples and are by the same analyst (S.A. Mertzman) as the new data for Grand Canyon rocks in Table 2. Abyssal peridotites are also compared, as Boyd [8] suggested that they define an evolutionary trend distinct from that of cratonic mantle but like that of young continental mantle. The database for abyssal peridotites contains 170 analyses calculated from mineral analyses and modes [24,25].

Mg/Si, one guide to orthopyroxene/olivine, is plotted against Al/Si, an indicator of fertility, in Fig. 4a. Jagoutz et al. [26] found that compositions of selected xenoliths define a 'geochemical fractionation' line on that diagram, and the line is shown for reference in Fig. 4a. Samples from the Colorado Plateau cluster about a linear trend displaced to lower Mg/Si than the line, implying higher orthopyroxene/ olivine. The abyssal peridotite population is more olivine-rich (higher Mg/Si) than both the reference line and the Colorado Plateau xenoliths at Al/Si greater than 0.05. The comparison establishes that neither the 'geochemical fractionation' line nor the trend for abyssal peridotites adequately represents the more orthopyroxene-rich Plateau mantle.

¹ http://www.elsevier.nl/locate/epsl, mirror site:

http://www.elsevier.com/locate/epsl



Fig. 4. Comparisons of peridotite compositions. (a) Colorado Plateau xenoliths compared to a population from the Kaapvaal and Siberian cratons [7,12] and to calculated compositions of abyssal peridotites [24,25]. The line is the 'geochemical fractionation' trend [26]. (b) Colorado Plateau xenoliths compared to a population from the Kaapvaal and Siberian cratons [7,12].

Xenolith compositions from the Colorado Plateau also are compared to the population from the Kaapvaal and Siberian kimberlites in Fig. 4. The field for Colorado Plateau xenoliths overlaps much of the field for the cratonic xenoliths in Fig. 4a, although cratonic mantle is more heavily represented by low Mg/Si points. The distinctive nature of part of the cratonic population is clear in Fig. 4b, where mg $[100 \times Mg/(Mg + Fe)]$ is used as an index of depletion and (Mg + Fe)/Si is used as an alternative index of orthopyroxene/olivine. Some cratonic peridotites both are unusually magnesian and unusually silicarich relative to their depleted nature, as emphasized by Boyd [8] and many others. In the mg range where they overlap, the Colorado Plateau and the cratonic populations define similar, large ranges of (Mg + Fe)/Si. The four samples from the Grand Canyon field plot in the more orthopyroxene-rich portion of that range.

Calculated modal orthopyroxene confirms distinctions evident in Fig. 4. The four Grand Canyon samples have 26 to 29 wt% orthopyroxene and mg from 90.4 to 91.5 (Table 2). In contrast, Boyd [8] calculated 12.5 wt% orthopyroxene and mg of 90.8 for average abyssal peridotite. In the more recent database of Niu et al. [25], abyssal samples average 21% orthopyroxene and an mg of 90.2. Average abyssal peridotite not only contains less orthopyroxene than peridotite from kimberlites on the Archaean Kaapvaal craton, as emphasized by Boyd [8], but also less orthopyroxene than xenoliths from the Grand Canyon field with comparable mg.

4. Discussion

Precipitation during reaction between aqueous solutions and peridotite is the most satisfactory explanation for the texture and composition of orthopyroxene in rock S-100, and the orthopyroxenite appears to have formed as a vein filling. The origin of rock S-100 provides insight into processes associated with the distinctive orthopyroxene–olivine textures observed in rocks from the Bandera and Grand Canyon xenolith suites. These textures have been interpreted either as caused directly by aqueous fluid infiltration [4], or as consequences of dehydration reactions of previously infiltrated peridotite [3]. Metasomatic addition of Si during such fluid interaction not only explains the olivine resorption textures in the spinel peridotites, but it is also consistent with the hypothesis that orthopyroxenite S-100 formed by peridotite–water reactions. Silicate melts more commonly have been proposed as metasomatic agents to enrich orthopyroxene in peridotite (e.g., [27,28]), but judging from the evidence in Colorado Plateau xenoliths, aqueous fluids also cause orthopyroxene enrichment. The Plateau was underlain by a subducted slab in late Mesozoic and early Cenozoic time [29], and that slab is one possible water source.

The Grand Canyon xenoliths (Table 2) and others from the Plateau contain relatively higher orthopyroxene/olivine than both the 'geochemical reference' line of Jagoutz et al. [26] and the fertile abyssal peridotites (Fig. 4a). Olivine/orthopyroxene ratios and Al contents of melting residues depend upon the pressure and composition of the melting region [11,30], and hence the different trends in Fig. 4a could indicate that the Plateau root formed in a different pressure range than abyssal peridotite. Nonetheless, Roden and Shimizu [31] proposed that the mantle root of the Colorado Plateau did form by accretion of Proterozoic oceanic lithosphere. The variable orthopyroxene enrichment of Plateau mantle may have been partly imposed after accretion; the dispersed (Mg + Fe)/Si values of Plateau xenoliths (Fig. 4b) are consistent with a process characterized by small-scale variations, and fracture-controlled metasomatism is such a process.

Similar Si-metasomatism may have caused local orthopyroxene-enrichment in Archaean mantle, as suggested by Kesson and Ringwood [14]. Water likely was introduced into the mantle below southern Africa during early stages of craton formation [32]. Metasomatism is unlikely to have been uniform or pervasive, consistent with the wide range of orthopyroxene/olivine and Mg/Si in Kaapvaal mantle [8,13]. Populations of peridotite xenoliths from some cratons are not as Si-rich as those from the Kaapvaal [11,33,34], and so high orthopyroxene/ olivine does not appear to be a result of a process intrinsic to formation of depleted cratonic roots.

The hypothesis that Si-metasomatism in aqueous fluid [14] was a significant process in the evolution of Kaapvaal craton mantle has been questioned for several reasons. Canil [21] noted that a large fluid/rock ratio would be required to convert dunite to harzburgite with 30 wt% orthopyroxene, and that such fluid/rock ratios were unlikely. Protoliths, however, may have been harzburgites rather than dunites, and aqueous metasomatism need not have been the sole process. Boyd et al. [12] noted that the orthopyroxene content of cratonic xenoliths does not appear to be related to depth, as Si enrichment in Kaapvaal spinel peridotites is similar to that of underlying garnet peridotite. The vertical mantle column beneath the cratons, however, may consist of tectonically juxtaposed volumes that evolved over a range of depths [32,35]. If so, a systematic relationship with depth is not required for the hypothesis to be correct.

5. Conclusions

Xenoliths from the Colorado Plateau provide evidence that mantle-water interactions can be widespread in continental lithosphere and that orthopyroxene enrichment can result from these interactions. Direct evidence is provided by an orthopyroxenite with orthopyroxene compositions and textures unlike those expected from magmatic crystallization and subsequent cooling but consistent with aqueous precipitation. Indirect evidence is provided by peridotite in which orthopyroxene unusually poor in Al forms large porphyroblasts that include resorbed olivine. These orthopyroxene textures and compositions have been recognized in peridotite xenoliths from basaltic fields within opposite margins of the Colorado Plateau province. Although the mantle root of the Plateau has been proposed to have formed from accreted oceanic lithosphere [31], bulk compositions of the peridotite xenoliths are relatively though unevenly orthopyroxene-rich compared to those of abyssal peridotite. The orthopyroxene enrichment may have been imposed by aqueous metasomatism, consistent with the hypothesis of Kesson and Ringwood [14] that aqueous fluids introduce Si into continental mantle.

Acknowledgements

M.G. Best and his geology class collected orthopyroxenite S-100, recognized its importance, and contributed it to this investigation. Some Bandera Crater samples were made available by the Division of Petrology and Volcanology, Department of Mineral Sciences, Smithsonian Institution from a contribution by H.G. Wilshire; others were collected with permission of David Candeleria. C.T. Herzberg and F.R. Boyd provided helpful preprints. Herzberg and M.F. Roden constructively criticized ms versions. Most support for this investigation was furnished by the Geology Foundation of the University of Texas at Austin; it was begun with support from National Science Foundation grant 9218864. [FA]

References

- D. Smith, Hydrous minerals and carbonates in peridotite inclusions from the Green Knobs and Buell Park kimberlitic diatremes on the Colorado Plateau, in: F.R. Boyd, H.O.A. Meyer (Eds.), Proc. 2nd International Kimberlite Conf. 2, American Geophysical Union, Washington, D.C., 1979, pp. 345–356.
- [2] H. Helmstaedt, D.J. Schulze, Garnet clinopyroxenitechlorite eclogite transition in a xenolith from Moses Rock: further evidence for metamorphosed ophiolites under the Colorado Plateau, in: F.R. Boyd, H.O.A. Meyer (Eds.), Proc. 2nd International Kimberlite Conf. 2, American Geophysical Union, Washington, D.C., 1979, pp. 357–365.
- [3] D. Smith, J.C.A. Riter, Genesis and evolution of low-Al orthopyroxene in spinel peridotite xenoliths, Grand Canyon field, Arizona, USA, Contrib. Mineral. Petrol. 127 (1997) 391–404.
- [4] C. Alibert, Peridotite xenoliths from western Grand Canyon and The Thumb: A probe into the subcontinental mantle of the Colorado Plateau, J. Geophys. Res. 99 (1994) 21605– 21620.
- [5] M.E. Schneider, D.H. Eggler, Fluids in equilibrium with peridotite minerals: implications for mantle metasomatism, Geochim. Cosmochim. Acta 50 (1986) 711–724.
- [6] S. Esperanca, R.W. Carlson, S.B. Shirey, D. Smith, Dating crust–mantle separation: Re–Os isotopic study of mafic xenoliths from central Arizona, Geology 25 (1997) 651– 654.
- [7] F.R. Boyd, S.A. Mertzman, Composition and structure of the Kaapvaal lithosphere, southern Africa, in: B.O. Mysen (Ed.), Magmatic Processes: Physicochemical Principles, Spec. Publ. 1, The Geochemical Society, University Park, PA, 1987, pp. 13–24.
- [8] F.R. Boyd, Compositional distinction between oceanic and cratonic lithosphere, Earth Planet. Sci. Lett. 96 (1989) 15– 26.
- [9] W.F. McDonough, Constraints on the composition of the continental lithospheric mantle, Earth Planet. Sci. Lett. 101 (1990) 1–18.

- [10] C.T. Herzberg, Lithosphere peridotites of the Kaapvaal craton, Earth Planet. Sci. Lett. 120 (1993) 13–29.
- [11] C.T. Herzberg, Formation of cratonic mantle as plume residues and cumulates, Submitted to the Boyd Symposium Volume (1998).
- [12] F.R. Boyd, N.P. Pokhilenko, D.G. Pearson, S.A. Mertzman, N.V. Sobolev, L.W. Finger, Composition of the Siberian cratonic mantle: evidence from Udachnaya peridotite xenoliths, Contrib. Mineral. Petrol. 128 (1997) 228–246.
- [13] D.G. Pearson, R.W. Carlson, S.B. Shirey, F.R. Boyd, P.H. Nixon, Stabilization of Archaean lithospheric mantle: a Re– Os isotope study of peridotite xenoliths from the Kaapvaal craton, Earth Planet. Sci. Lett. 134 (1995) 341–357.
- [14] S.E. Kesson, A.E. Ringwood, Slab-mantle interactions: 2. The formation of diamonds, Chem. Geol. 78 (1989) 97– 118.
- [15] H.G. Wilshire, C.E. Meyer, J.K. Nakata, L.C. Calk, J.W. Shervais, J.E. Nielson, E.C. Schwarzman, Mafic and ultramafic xenoliths from volcanic rocks of the western United States, U.S. Geol. Surv. Prof. Pap. 1443 (1988) 179 pp.
- [16] M.F. Roden, Origin of coexisting minette and ultramafic breccia, Navajo volcanic field, Contrib. Mineral. Petrol. 77 (1981) 195–206.
- [17] D. Smith, Chlorite-rich ultramafic reaction zones in Colorado Plateau xenoliths: recorders of sub-Moho hydration, Contrib. Mineral. Petrol. 121 (1995) 185–200.
- [18] M.G. Best, Contrasting types of chromium-spinel peridotite xenoliths in basanitic lavas, western Grand Canyon, Arizona, Earth Planet. Sci. Lett. 23 (1974) 229–237.
- [19] G. Witt-Eickschen, H.A. Seck, Solubility of Ca and Al in orthopyroxene from spinel peridotite: An improved version of an empirical geothermometer, Contrib. Mineral. Petrol. 106 (1991) 431–439.
- [20] J.C.A. Riter, D. Smith, Xenolith constraints on the thermal history of the mantle below the Colorado Plateau, Geology 24 (1996) 267–270.
- [21] D. Canil, Orthopyroxene stability along the peridotite solidus and the origin of cratonic lithosphere beneath southern Africa, Earth Planet. Sci. Lett. 111 (1992) 83–95.
- [22] B. McInnes, Fluid-peridotite interactions in mantle wedge xenoliths, Eos 77 (1996) S282.
- [23] B.R. Frost, Contact metamorphism of serpentinite, chloritic blackwall and rodingite at Paddy-Go-Easy Pass, central Cascades, Washington, J. Petrol. 16 (1975) 272–313.
- [24] M. Seyler, E. Bonatti, Regional-scale melt–rock interactions in lherzolitic mantle in the Romanche Fracture Zone (Atlantic Ocean), Earth Planet. Sci. Lett. 146 (1997) 273– 287.
- [25] Y. Niu, C.H. Langmuir, R.J. Kinzler, The origin of abyssal peridotites: a new perspective, Earth Planet. Sci. Lett. 152 (1997) 251–265.
- [26] E. Jagoutz, H. Palme, H. Baddenhausen, K. Blum, M. Cendales, G. Dreibus, B. Spettel, V. Lorenz, H. Wanke, The abundances of major, minor, and trace elements in the earth's mantle as derived from primitive ultramafic nodules, Proc. Lunar Planet. Sci. Conf. 10 (1979) 2031–2050.
- [27] P.B. Kelemen, H.J.B. Dick, J.E. Quick, Formation of

harzburgite by pervasive melt/rock reaction in the upper mantle, Nature 358 (1992) 635–641.

- [28] I.E. Ertan, W.P. Leeman, Metasomatism of Cascades subarc mantle: Evidence from a rare phlogopite orthopyroxenite xenolith, Geology 24 (1996) 451–454.
- [29] W.R. Dickenson, W.S. Snyder, Plate tectonics of the Laramide orogeny, in: V. Matthews (Ed.), Laramide folding associated with basement block faulting in the western United States, Geol. Soc. Mem. 151 (1978) 355–366.
- [30] R.J. Kinzler, Melting of mantle peridotite at pressures approaching the spinel to garnet transition: Application to mid-ocean ridge basalt petrogenesis, J. Geophys. Res. 102 (1997) 853–874.
- [31] M.F. Roden, N. Shimizu, Ion microprobe analyses bearing on the composition of the upper mantle beneath the Basin and Range and Colorado Plateau provinces, J. Geophys.

Res. 98 (1993) 14091-14108.

- [32] M.J. de Wit, R.A. Hart, Earth's earliest continental lithosphere, hydrothermal flux and crustal recycling, Lithos 30 (1993) 309–335.
- [33] S. Bernstein, P.B. Kelemen, C.K. Brooks, Depleted spinel harzburgite xenoliths in Tertiary dykes from East Greenland: restites from high degree melting, Earth Planet. Sci. Lett. 154 (1998) 221–235.
- [34] N.J. Pearson, W.L. Griffin, B.J. Doyle, S.Y. O'Reilly, E. van Achterbergh, K. Kivi, Xenoliths from kimberlite pipes of the Lac de Gras area, Slave Craton, Canada, submitted for publication, Proceedings International Kimberlite Conference (1998).
- [35] R.J. Hart, M. Tredoux, M.J. deWit, Refractory trace elements in diamond inclusions: Further clues to the origins of the ancient cratons, Geology 25 (1997) 1143–1146.