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CH₄ inclusions in orogenic harzburgite: Evidence for reduced slab fluids and implication for redox melting in mantle wedge

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Abstract

Fluids released from the subducting oceanic lithosphere are generally accepted to cause mantle wedge peridotite melting that produces arc magmas. These fluids have long been considered to be dominated by highly oxidized H₂O and CO₂ as inferred from erupted arc lavas. This inference is also consistent with the geochemistry of peridotite xenoliths in some arc basalts. However, the exact nature of these fluids in the mantle wedge melting region is unknown. Here, we report observations of abundant $CH_4 + C + H_2$ fluid inclusions in olivine of a fresh orogenic harzburgite in the Early Paleozoic Oilian suture zone in Northwest China. The petrotectonic association suggests that this harzburgite body represents a remnant of a Paleozoic mantle wedge exhumed subsequently in response to the tectonic collision. The mineralogy, mineral compositions and bulk-rock trace element systematics of the harzburgite corroborate further that the harzburgite represents a high-degree melting residue in a mantle wedge environment. Furthermore, existing and new C, He, Ne and Ar isotopes of these fluid inclusions are consistent with their being of shallow (i.e., crustal vs. deep mantle) origin, likely released from serpentinized peridotites and sediments of the subducting oceanic lithosphere. These observations, if common to subduction systems, provide additional perspectives on mantle wedge melting and subduction-zone magmatism. That is, mantle wedge melting may in some cases be triggered by redox reactions; the highly reduced ($\sim \Delta FMQ$ -5, i.e., 5log units below the fayalite-magnetite-quartz oxygen fugacity buffer) CH₄-rich fluids released from the subducting slab interact with the relatively oxidized ($\sim \Delta FMQ-1$) mantle wedge peridotite, producing H₂O and CO₂ that then lowers the solidus and incites partial melting for arc magmatism. The significance of slab-component contribution to the geochemistry of arc magmatism would depend on elemental selection and solubility in highly reduced fluids, for which experimental data are needed. We do not advocate the above to be the primary mechanism of arc magmatism, but we do suggest that the observed highly reduced fluids are present in mantle wedge peridotites and their potential roles in arc magmatism need attention.

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1. INTRODUCTION

The ocean crust is hydrothermally altered during its accretion at ocean ridges and pervasively weathered subsequently on the seafloor. It is widely accepted that this hydrated ocean crust that is atop the subducting slab endures the greatest extents of dehydration in subduction

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zones. Fluids released from this dehydration lower the solidus of the overlying mantle wedge, which then melts to produce "primary" arc magmas (Gill, 1974, 1981; Tatsumi et al., 1986; McCulloch and Gamble, 1991; Hawkesworth et al., 1991, 1993; Arculus, 1994; Stolper and Newman, 1994; Pearce and Peate, 1995; Tatsumi and Eggins, 1995; Peacock, 1996). This perception has led to the acceptance that fluids in the subduction-zone system are dominated by highly oxidized H_2O and CO_2 as inferred from erupted arc lavas (Arculus, 1994; Stolper and Newman, 1994). This inference is also consistent with the more oxidized

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geochemistry of mantle xenoliths in some arc basalts (Parkinson and Arculus, 1999).

Previous fluid inclusion studies have shown that H₂O and CO₂ are the major fluid species in upper mantle rocks from various tectonic settings (Ertan and Leeman, 1999; Andersen and Neumann, 2001), which is consistent with the estimated redox state of the upper mantle ($\sim \Delta FMQ$ or $\sim \Delta FMQ-1$, i.e., close to or about 1 logunit below the favalite-magnetite-quartz oxygen fugacity buffer) (Christie et al., 1986; Wood et al., 1990; Lee et al., 2003, 2005). The consistent oxidized state of erupted arc lavas and mantle xenoliths they carry led to the conclusion that the mantle wedge is more oxidized than elsewhere in the mantle source regions of basalts (Parkinson and Arculus, 1999). By comparing V/Sc (vs. Fe^{3+}/Fe^{2+}) ratios in arc basalts and MORB melts, however, Lee et al. (2003, 2005) conclude that the redox state in the sub-arc melting region is essentially the same as beneath ocean ridges (i.e., $\sim \Delta FMQ$ or $\sim \Delta FMQ-1$). They also conclude that the apparently oxidized character of mantle xenoliths carried in arc basalts reflects the effects of metasomatic modifications of the sub-arc lithosphere (Lee et al., 2003, 2005). That is, these mantle xenoliths are not from the mantle wedge magma source region, but from the sub-arc lithosphere of complex history. In this context, it should be noted that some intra-oceanic arc mantle lithosphere may in fact be slivers of continental margin lithosphere before the initiation and evolution of back-arc basins (see Niu et al., 2003). Direct information on redox state of the mantle wedge melting region is unknown because of the inaccessibility and because mantle wedge materials, if ever exhumed, have not been recognized (Ballhaus and Frost, 1994) or proved not useful because they often do not survive from serpentinization or other forms of alteration in the crustal levels or under near surface conditions.

In this paper, we report the presence of abundant $CH_4 + C + H_2$ fluid inclusions in olivine of a very fresh orogenic harzburgite body, the Yushigou harzburgite that is most consistent with being a remnant section of a mantle wedge melting residue, trapped and exhumed in the Early Paleozoic Qilian suture zone in Northwest China. The presence of highly reduced fluids in a mantle wedge is unexpected, but requires an explanation that must be consistent with the petrological and geochemical data as well as the tectonic context. Of all the conceivable possibilities, our best explanation, in brief, is that the reduced fluids originate from serpentinized peridotites and sediments in the subducting/subducted oceanic lithosphere, and are incorporated in the mantle wedge olivine through incongruent melting in the spinel peridotite stability field for arc magmas. It is our intention that this paper will serve as a stimulus for further studies and discussion.

2. GEOLOGIC CONTEXT OF THE YUSHIGOU HARZBURGITE

The Yushigou harzburgite is a $\sim 25 \text{ km}^2$ fault-bounded block in the North Qilian Early Paleozoic suture zone (Fig. 1) (Song et al., 2004, 2006, 2007a,b), and was previously interpreted as a unit of a highly dismembered ophio-

lite (Song and Su, 1998; Su et al., 1999; Zhang et al., 2003). It is noteworthy that every mafic or ultramafic assemblage along the Oilian Orogenic belt, as is in other orogenic belts in China, has been interpreted as dismembered ophiolite (Zhang et al., 2003). The pervasive deformation and fault contacts among all the lithologies (e.g., harzburgite, gabbros, pillow lavas, arc volcanics, and blueschist-eclogite high pressure metamorphic rocks) within the suture zone (Fig. 1) make it difficult to reveal the true affinity of the harzburgite without uncertainties. However, its spatial association with arc volcanics and subduction-zone complex suggest its possible close affinity with the subduction zone. Furthermore, the unusual freshness of the harzburgite (see below) distinguishes it from serpentinized oceanic lithospheric mantle (Dick, 1989; Niu and Hékinian, 1997a). These observations and inference together with its petrology and geochemistry (see below) argue that the Yushigou harzburgite represents a remnant of a fossil mantle wedge exhumed in response to continental collision during the Caledonian Qilian Orogeny, and to the continued uplifting and unroofing as a result of India-Asia collision and continued convergence since the Tertiary. The precise age of the Yushigou harzburgite is unknown, but the SHRIMP zircon U-Pb dating yields an age of 550 ± 17 Ma for the spatially associated gabbros (Shi et al., 2004) and an age of 466 ± 10 Ma for the high pressure (1.8-2.6 GPa) blueschist/eclogites (Song et al., 2004) (see Fig. 1).

3. BRIEF PETROLOGY AND GEOCHEMISTRY OF THE YUSHIGOU HARZBURGITE

The Yushigou harzburgite is very fresh (Fig. 2) and contains minor (<2 vol %) dunite veins. The harzburgite (Fig. 2a) shows coarse-grained inequigranular textures, and comprises olivine (\sim 70–85 vol %), orthopyroxene (Opx, \sim 10–25 vol %), minor clinopyroxene (Cpx, <2– 3 vol %) and Cr-rich spinel (Spl, \leq 1.0 vol %). The dunite (Fig. 2b) mainly consists of >95 vol % olivine with minor clinopyroxene and spinel.

It is worth to note that olivine crystals from both harzburgite (Fig. 2a) and dunite (less obvious in Fig. 2b) show preferentially orientated kink-bands. These kink-bands are diffusion-controlled (100) dislocation, and have been demonstrated both experimentally and in natural samples to have resulted from solid-state plastic flow at the mantle temperatures (~1000 °C) (Raleigh, 1968; Kirby and Raleigh, 1976; Nicolas and Poirier, 1976; Fleet, 1978). Such deformation fabric is consistent with the harzburgite being of mantle origin with mantle olivine compositions (Fo_{91.07-} 93.2 in harzburgite and Fo_{89.7-90.1} in dunite; see Fig. 3 and Table 1, where $Fo = 100 \times Mg/[Mg + Fe^{2+}]$ as expected. Most Opx crystals in harzburgite contain abundant Cpx exsolution lamellae that can be as much as 5-6 vol % (see Fig. 2d and e), which, together with the Opx composition (i.e., $Mg^{\#} = 90.9-93.1$; Table 2), is again consistent with the Opx, hence the bulk-rock harzburgite, being of mantle origin. No Opx was found in the dunite. Cpx is a minor phase in both harzburgite and dunite (Fig. 2b and c). Opx lamellae are also observed in some larger Cpx grains



Fig. 1. Geological map of the central portion of the North Qilian Mountain, indicating the Yushigou peridotite (harzburgite). The interpreted ophiolite comprises metamorphosed pillow lavas and dikes (Song and Su, 1998; Su et al., 1999; Song et al., 2004, 2006, 2007a,b). The high-pressure rocks refer to blueschist and eclogites with calculated peak metamorphic pressures of 1.8–2.6 GPa (Song et al., 2004, 2006, 2007a,b). The map is simplified from Song et al. (2004).

(not shown). In addition, the low Al₂O₃ content in the harzburgite Opx (0.71-1.67 wt%, Table 2) and Cpx (1.02-1.91 wt%; Table 3) is consistent with harzburgite being a residue of high extent of melt extraction, which is also corroborated by the high $Cr^{\#}$ (= Cr/[Cr + Al], 0.58–0.67; Table 4) of the spinel in the harzburgite. The slightly lower olivine Fo (89.7-90.1; Table 1), higher Cpx Al₂O₃ (2.86-3.51 wt%; Table 3) and lower spinel $Cr^{\#}$ (0.41–0.50; Table 4) of the dunite veins is consistent with the dunite being a cumulate crystallized from a mantle melt. The presence of Cpx (vs. plagioclase) in the dunite is consistent with crystallization from a wet basaltic melt (i.e., subduction-zone magmas; see Niu, 2005) or at high pressures (>8 kbar; Langmuir et al., 1992) or both. Oxybarometric calculation using Ol-Opx-Sp equilibrium of O'Neill and Wall (1987) yields oxygen fugacity (fO₂) from 0 to -1.47 log units below the QFM buffer at 15 kbar (Table 5), which is within the range of normal asthenospheric mantle values (Christie et al., 1986; Wood et al., 1990; Lee et al., 2003, 2005).

Compared with abyssal peridotites (AP) from midocean ridges (Dick, 1989; Niu and Hékinian, 1997a,b), the Yushigou harzburgite is much more depleted than the most depleted AP samples (Fig. 3), resembling highly depleted forearc harzburgites (see Niu et al., 2003). Fig. 3 shows that the Yushigou harzburgite has (1) olivine that is more depleted with higher Fo (91–93) and Ni than AP olivine (Fo < 91) (Fig. 3a), (2) Opx and Cpx that are both highly depleted in Al₂O₃ (<2 wt%) than AP Opx and Cpx (Al₂O₃ >2 wt%) (Fig. 3b and c), and (3) spinel that is highly depleted in Al_2O_3 with much higher $Cr^{\#} = Cr/[Cr + Al]$ (0.58–0.67) than the most depleted AP (<0.60) (Fig. 3b–d). These data (also see Tables 1–4) are consistent with the Yushigou harzburgite being a melting residue of very high extent of melting and melt extraction, much higher than beneath the fast-spreading East Pacific Rise and beneath ridges thermally influenced by hotspots (Niu and Hékinian, 1997b), pointing to fluid-enhanced melting in a mantle wedge environment (see Niu et al., 2003).

As expected, bulk-rock compositions of the Yushigou harzburgite samples (Table 6) are highly depleted with high MgO (~46 wt%) and FeO (7.13-8.35 wt%) and extremely low TiO_2 (<0.01 wt%), Al_2O_3 (0.40–0.65 wt%), CaO (0.30-0.54 wt%) and Na₂O (<0.05 wt%). Chondrite-normalized rare earth element (REE) and primitive mantle-normalized multi-element diagrams (Fig. 3e-f) show that all the harzburgite samples under this study have similar trace element compositions with characteristic U-shaped REE patterns. The U-shaped REE patterns are consistent with these rocks being highly depleted melting residues overprinted with light REE enrichments (e.g., Niu and Hékinian, 1997a; Niu, 2004). All these, plus the overall large ion lithophile element (LILE) enrichments (Fig. 3f), in particular the spikes of the fluid-mobile elements Cs, U and Pb corroborate the argument that the Yushigou harzburgite represents mantle wedge melting residues refertilized by a later percolating melt component.



Fig. 2. Photomicrographs of the Yushigou harzburgite from the North Qilian Early Paleozoic suture zone (Fig. 1). (a) Textual overview of the harzburgite with kink-bands in olivine. (b) Granoblastic texture of dunite; note that clinopyroxene (Cpx) and spinel (Sp) occur in the triple-junctions of olivine crystals. (c) Presence of minor Cpx grains in harzburgite. (d) Cpx exsolution lamellae in orthopyroxene (Opx) from harzburgite. (e) Back-scattered electronic image showing Cpx exsolutions in the host Opx. (f) Back-scattered electronic image showing Opx exsolutions in the minor Cpx.

4. FLUID INCLUSIONS IN OLIVINE OF THE YUSHIGOU HARZBURGITE

Abundant fluid inclusions were observed in olivine crystals of the Yushigou harzburgite (Su et al., 1999). These fluid inclusions can be divided into three types (Fig. 4): *Type-I* inclusions are most abundant. They are large $(5-10 \,\mu\text{m})$, dominantly liquid-phase (only a few with small vapor bubbles), colorless, and exhibit spherical to subspherical shapes. Some of these inclusions take the negative crystal forms of the host olivine (Fig. 4a). They are usually surrounded by even finer $(1-2 \,\mu\text{m})$ spherical inclusions as clusters towards edges of olivine crystals (Fig. 4a and b). Some of the *Type-I* inclusions are re-distributed or cut by kink-bands of the host olivine (Fig. 4c). *Type-II* inclusions are tubular, colorless, and distributed along some annealed planes that do not extend across grain boundaries (Fig. 4d). *Type-III* inclusions are variable in size, vapor-dominated, and distributed as planes along annealed fractures. Olivine crystals that occur as inclusions in spinel also contain tubular (*Type-II*) fluid inclusions. The occurrence of these inclusions, in particular the *Type-I* with *negative crystal forms of the host olivine and those reformed by the kink-bands*, indicates unequivocally that they are trapped during crystallization of olivine and spinel at magmatic temperatures ($T \ge 1200$ °C). However, no fluid inclusions are found in Opx and Cpx crystals.

Compositions of fluid inclusions were analyzed *in situ* using laser Raman micro-spectroscopy (Ranishaw RM-1000) with the 514.5 nm line of an Ar-ion laser at Peking University, which is the most robust technique for analyzing single fluid inclusions (Burke, 2001). The laser beam was focused by using a $50 \times$ objective lens to a spot size of approximately 2 µm through a microscope. The whole



Fig. 3. Geochemistry of the Yushigou harzburgite. (a) NiO vs. Fo (Mg/[Mg + Fe]) of olivine from the Yushigou harzburgite in comparison with those from abyssal peridotites (AP) of mid-ocean ridge (MOR) environment (Dick, 1989). (b–d) Comparison with AP (Dick, 1989; Niu and Hékinian, 1997a,b) from the Mid-Atlantic Ridge (MAR), Indian Ocean Ridge (IOR) and East Pacific Rise (EPR) to show that the Yushigou harzburgite is much more depleted than the most depleted AP from ridges affected by hotspots and from the fast-spreading EPR in having low Al_2O_3 in Opx, Cpx and spinel (i.e., high $Cr^{\#}(Cr/[Cr + Al])$. (e) Chondrite (Sun and McDonough, 1989) normalized REE patterns of the Yushigou harzburgite. (f) Primitive mantle (PM; Sun and McDonough, 1989) normalized multi-element diagram of the Yushigou harzburgite (see data in Table 6).

spectrum was scanned from 100 to 5000 cm⁻¹ with a resolution better than 1.3 cm^{-1} . The host olivine was also scanned in order to exclude its influence. Raman spectra of *Type-I* inclusions show (1) extremely strong peaks of liquid CH₄ at bands of 2911–2913 cm⁻¹ (minor peaks at ~3000 and 3065 cm⁻¹ also are detectable); the vapor bub-

bles are too small to be analyzed, (2) weak bands of liquid N₂ (2328 cm⁻¹), H₂S (2580 cm⁻¹) and H₂ (4156 cm⁻¹), and (3) very weak but detectable bands of C₂H₆, C₃H₈, and H₂O (Fig. 5a and b). That is, liquid methane is the dominated phase in all *Type-I* inclusions with very high liquid/vapor ratios. *Type-II* tubular inclusions are mixture of gas

Table 1	
Representative analyses of olivine from harzburgite (HB) and dunite by electron microprobe.	

Sample	ZQ6a-1	ZQ6a-2	ZQ6a-4	ZQ11-1	ZQ11-	2	ZQ12-1	ZQ12-2	ZQ13-1	ZQ13-2	ZQ18-1	ZQ18-2	ZQ19-1	ZQ24-1
Rock	HB	HB	HB	HB	HB		HB							
SiO ₂	40.92	40.44	40.58	40.75	40.83		40.80	41.23	41.25	41.05	40.92	40.74	40.92	40.86
TiO ₂	0.02	0.00	0.01	0.00	0.02		0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Al_2O_3	0.00	0.00	0.00	0.00	0.00		0.00	0.03	0.08	0.09	0.05	0.00	0.00	0.01
Cr_2O_3	0.00	0.04	0.00	0.00	0.02		0.00	0.01	0.03	0.27	0.03	0.03	0.06	0.02
FeO	8.36	8.17	8.77	8.02	8.05		8.32	8.35	7.43	7.06	8.09	8.15	8.36	8.21
MnO	0.09	0.08	0.11	0.12	0.03		0.19	0.13	0.11	0.07	0.14	0.05	0.14	0.10
NiO	0.43	0.47	0.42	0.43	0.34		0.43	0.44	0.49	0.44	0.38	0.36	0.42	0.41
MgO	50.32	50.23	50.17	50.68	50.67		50.37	50.69	50.66	50.61	50.87	50.28	50.48	50.23
CaO	0.01	0.04	0.03	0.01	0.07		0.02	0.01	0.04	0.03	0.07	0.08	0.00	0.01
Na ₂ O	0.00	0.01	0.00	0.01	0.03		0.03	0.00	0.02	0.00	0.10	0.01	0.01	0.00
K ₂ O	0.01	0.00	0.00	0.00	0.01		0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.01
Total	100.16	99.48	100.09	100.02	99.16		100.17	100.89	100.12	99.63	100.67	99.91	100.70	99.86
Calculate	ed on the basi.	s of 4 oxygen												
Si	0.996	0.992	0.991	0.993	0.993		0.994	0.996	1.000	0.999	0.991	0.995	0.994	0.997
Ti	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.000	0.000	0.000	0.000	0.000		0.000	0.001	0.002	0.003	0.001	0.000	0.000	0.000
Cr	0.000	0.001	0.000	0.000	0.000		0.000	0.000	0.001	0.005	0.001	0.001	0.001	0.000
Fe	0.170	0.168	0.179	0.163	0.164		0.169	0.169	0.151	0.144	0.164	0.166	0.170	0.168
Mn	0.002	0.002	0.002	0.002	0.001		0.004	0.003	0.002	0.001	0.003	0.001	0.003	0.002
Ni	0.008	0.009	0.008	0.008	0.007		0.008	0.009	0.010	0.008	0.007	0.007	0.008	0.008
Mg	1.826	1.836	1.827	1.840	1.838		1.829	1.826	1.831	1.836	1.836	1.831	1.829	1.827
Ca	0.000	0.001	0.001	0.000	0.002		0.001	0.000	0.001	0.001	0.002	0.002	0.000	0.000
Na	0.000	0.000	0.000	0.000	0.001		0.001	0.000	0.001	0.000	0.005	0.000	0.000	0.000
Κ	0.000	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum	3.004	3.008	3.009	3.008	3.007		3.007	3.003	2.999	2.997	3.010	3.005	3.005	3.003
Fo	91.48	91.64	91.07	91.85	91.82		91.52	91.54	92.40	92.74	91.81	91.67	91.50	91.60
Sample	ZO24-2	ZO25-1	ZO25-2	ZO25-3	ZO25-4	Y52-1	Y52-2	Y52-3	ZO49-2	ZO49-3	ZQ56-1	ZO56-2	ZQ56-3	ZO56-4
Rock	HB	HB	HB	HB	HB	HB	HB	HB	Dunite	Dunite	Dunite	Dunite	Dunite	Dunite
SiO ₂	40.74	41.60	41.27	40.99	41.12	40.64	40.86	40.85	40.33	40.84	40.77	40.47	40.33	40.84
TiO ₂	0.01	0.00	0.06	0.00	0.00	0.04	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.03
Al_2O_3	0.01	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.00
Cr_2O_3	0.00	0.00	0.12	0.00	0.02	0.00	0.02	0.02	0.04	0.01	0.01	0.00	0.04	0.01
FeO	8.08	8.06	6.69	8.04	7.84	7.86	7.91	7.95	10.02	9.76	9.89	9.71	10.02	9.76
MnO	0.11	0.13	0.04	0.14	0.15	0.12	0.07	0.14	0.15	0.10	0.18	0.16	0.15	0.10
NiO	0.41	0.50	0.46	0.39	0.38	0.36	0.44	0.36	0.37	0.35	0.29	0.33	0.37	0.35
MgO	50.29	51.36	51.64	50.78	50.89	50.13	50.78	50.16	49.08	48.86	49.93	49.67	49.08	48.86
CaO	0.17	0.04	0.01	0.03	0.02	0.04	0.00	0.01	0.15	0.14	0.13	0.14	0.15	0.14
Na ₂ O	0.17	0.01	0.03	0.07	0.03	0.00	0.00	0.05	0.04	0.01	0.01	0.03	0.04	0.01
$\tilde{K_2O}$	0.02	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00
Total	100.30	100.72	100.32	100.13	100.46	99.21	99.78	99.54	100.19	100.09	101.24	100.52	100.19	100.09

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Calculati	ed on the basi	s of 4 oxygen												
Si	0.994	0.996	0.996	0.994	0.996	7997	0.994	0.999	0.990	1.001	0.989	0.989	0.990	1.001
Ξ	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
AI	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
Cr	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000
Fe	0.165	0.161	0.135	0.163	0.159	0.161	0.161	0.163	0.206	0.200	0.201	0.198	0.206	0.200
Mn	0.002	0.003	0.001	0.003	0.003	0.002	0.001	0.003	0.003	0.002	0.004	0.003	0.003	0.002
ïz	0.008	0.010	0.009	0.008	0.007	0.007	0.009	0.007	0.007	0.007	0.006	0.006	0.007	0.007
Mg	1.828	1.833	1.857	1.836	1.837	1.833	1.841	1.828	1.797	1.785	1.806	1.809	1.797	1.785
Ca	0.004	0.001	0.000	0.001	0.001	0.001	0.000	0.000	0.004	0.004	0.003	0.004	0.004	0.004
Na	0.008	0.000	0.001	0.003	0.001	0.000	0.000	0.002	0.002	0.000	0.000	0.001	0.002	0.000
K	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Sum	3.010	3.004	3.003	3.008	3.005	3.003	3.006	3.003	3.010	2.999	3.010	3.012	3.010	2.999
Fo	91.73	91.91	93.23	91.84	92.05	91.92	91.97	91.84	89.73	89.92	90.00	90.12	89.73	89.92
Fo = 100	- Mg/(Mg - 0)	+ Fe); total F	e as Fe ²⁺ .											

phase methane (2914–2915 cm⁻¹) and graphite (Fig. 5c). *Type-III* inclusions are dominated by gas phase methane with minor graphite and N₂ (Fig. 5d). We interpret Type-II and III inclusions as resulting from within-crystal redistribution in response to subsolidus deformation (Song and Su, 1998). No oxidized forms of fluids such as CO₂, CO or SO₂ have been detected in any of these fluid inclusions from any of the harzburgite samples we studied.

Carbon isotopes (δ^{13} C) in these fluid inclusions range from -12.5% to -29.5% (PDB) (Hu et al., 2007), which is far too negative to be of asthenospheric mantle origin (typically -3% to -7%; Mattey et al., 1984; Exley et al., 1986; Deines, 2002), but is consistent with the carbon being of crustal (sediments) origin (Eiler et al., 1998; Hu et al., 2007). We also analyzed noble gas isotopes of He, Ne and Ar (Table 7) on gasses extracted from olivine and Opx mineral separates using a noble gas mass spectrometer (VG5400) at the Earthquake Research Institute of the University of Tokyo, Japan (Lai et al., 2005). The very low ${}^{3}\text{He}/{}^{4}\text{He}$ ratio (0.38 \pm 0.02R/Ra, 0.43 \pm 0.06R/Ra), very low 20 Ne/ 22 Ne ratio (9.93 ± 0.08, 9.97 ± 0.04) and variably high ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratio (3952 ± 66, 6483 ± 284) also are consistent with the fluids being of shallow origin (e.g., crustal environments) rather than of deep mantle origin.

The above interpretation that the Yushigou harzburgite represents a residue of high-degree melting in a mantle wedge environment together with the chemical and isotopic compositions of the fluid inclusions indicate that the Yushigou harzburgite may record a "snapshot" of subduction factory processes from oceanic lithosphere subduction, fluid transport to the mantle wedge, mantle wedge melting, and melt percolating/extraction.

5. WHY ARE THE FLUIDS ONLY TRAPPED IN OLIVINE OF THE YUSHIGOU HARZBURGITE?

The observation why the fluids are trapped only in olivine crystals (not pyroxene crystals) is intriguing, but is consistent with the incongruent melting relationship in the spinel peridotite stability field (i.e., $a \operatorname{Cpx} + b \operatorname{Opx} + c$ spinel = 1.00 melt + d olivine (Baker and Stolper, 1994; Niu, 1997). That is, during melting, pyroxenes melt whereas olivine, as a peritectic product, precipitates. This explains why olivine that is crystallizing during melting traps the fluids that are available whereas Opx and Cpx that are being melted preserve no fluids. It is also possible that pyroxenes may initially have fluid inclusions, but lost during subsolidus equilibration. However, there is no petrographic observation in favor of this speculation.

6. ORIGIN OF FLUIDS

Some researchers suggest that C–H–O vapor phases in mantle-derived magmas originate from deep mantle degassing (Green et al., 1987; Taylor and Green, 1988; Ballhaus and Frost, 1994). CH₄-bearing fluid inclusions have also been observed in ophiolitic dunite and post-collisional mafic–ultramafic intrusions, which were interpreted as being derived from ancient reduced asthenospheric mantle (Liu and Fei, 2006). This is probably true in the source regions

Sample Rock	ZQ6a HB	ZQ11 HB	ZQ12 HB	ZQ16-1 HB	ZQ16-2 HB	ZQ18 HB	ZQ19-1 HB	ZQ19-2 HB	ZQ24 HB	ZQ25-1 HB	ZQ25-2 HB	ZQ25-3 HB	Y52-1 HB	Y52-2 HB	Ү52-3 НВ
SiO ₂	56.51	56.35	56.45	56.92	57.15	57.02	57.90	56.72	56.32	56.85	57.12	58.31	56.92	56.75	57.22
TiO ₂	0.03	0.01	0.00	0.04	0.05	0.03	0.00	0.00	0.00	0.00	0.02	0.00	0.01	0.03	0.03
Al_2O_3	1.22	1.57	1.67	1.33	1.41	1.18	0.71	1.29	1.19	1.31	1.48	0.70	1.33	1.35	1.29
Cr_2O_3	0.51	0.47	0.62	0.50	0.71	0.66	0.18	0.36	0.64	0.52	0.93	0.64	0.53	0.58	0.54
FeO	6.02	5.53	5.88	5.28	5.24	5.57	5.77	5.44	5.51	5.39	5.42	4.72	5.23	5.15	5.39
MnO	0.08	0.12	0.16	0.10	0.22	0.18	0.12	0.19	0.21	0.19	0.07	0.13	0.14	0.12	0.14
NiO	0.10	0.10	0.12	0.14	0.09	0.09	0.19	0.11	0.12	0.11	0.07	0.11	0.11	0.08	0.13
MgO	33.57	34.08	34.04	34.52	33.68	34.81	35.71	34.62	33.96	34.23	33.67	35.70	34.27	33.98	34.62
CaO	1.84	1.14	0.95	1.13	1.84	0.77	0.13	0.65	1.34	1.08	1.33	0.42	1.26	1.28	0.85
Na ₂ O	0.04	0.00	0.06	0.05	0.10	0.00	0.00	0.03	0.00	0.03	0.12	0.01	0.04	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.02	0.02	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.00
Total	99.91	99.37	99.95	100.04	100.51	100.32	100.71	99.42	99.29	99.72	100.24	100.74	99.85	99.31	100.20
Calculated	on the basis d	of 6 oxygen													
Si	1.959	1.956	1.951	1.961	1.963	1.960	1.977	1.964	1.960	1.965	1.965	1.983	1.964	1.967	1.966
Ti	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.001
Al	0.050	0.064	0.068	0.054	0.057	0.048	0.029	0.053	0.049	0.053	0.060	0.028	0.054	0.055	0.052
Cr	0.014	0.013	0.017	0.014	0.019	0.018	0.005	0.010	0.018	0.014	0.025	0.017	0.014	0.016	0.015
Fe	0.175	0.160	0.170	0.152	0.151	0.160	0.165	0.157	0.160	0.156	0.156	0.134	0.151	0.149	0.155
Mn	0.002	0.004	0.005	0.003	0.006	0.005	0.003	0.006	0.006	0.006	0.002	0.004	0.004	0.004	0.004
Ni	0.003	0.003	0.003	0.004	0.002	0.002	0.005	0.003	0.003	0.003	0.002	0.003	0.003	0.002	0.003
Mg	1.735	1.763	1.754	1.773	1.725	1.784	1.818	1.787	1.762	1.764	1.727	1.810	1.763	1.756	1.773
Ca	0.068	0.042	0.035	0.042	0.068	0.028	0.005	0.024	0.050	0.040	0.049	0.015	0.047	0.048	0.031
Na	0.003	0.000	0.004	0.003	0.007	0.000	0.000	0.002	0.000	0.002	0.008	0.001	0.003	0.000	0.000
K	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum	4.010	4.006	4.008	4.007	4.001	4.007	4.006	4.006	4.007	4.003	3.996	3.995	4.003	3.997	4.000
Mg [#]	0.909	0.917	0.912	0.921	0.920	0.918	0.917	0.919	0.917	0.919	0.917	0.931	0.921	0.922	0.920

 Table 2

 Representative analyses of orthopyroxene from harzburgite (HB) and dunite by electron microprobe.

 $Mg^{\#} = Mg/(Mg + Fe)$; total Fe as Fe^{2+} .

Table 3 Representative analyses of clinopyroyene from harzburgite (HR) and dunite by electron microprobe

Sample	ZO6A	ZO11	ZO12	ZO19	ZO24	ZO25-1	ZO25-2	Y52-1	Y52-2	Y52-3	ZO49	ZO56-1	ZO56-2
Rock	НВ	НВ	НВ	HB	НВ	НВ	НВ	HB	HB	HB	Dunite	Dunite	Dunite
SiO ₂	53.73	53.58	53.60	53.25	53.64	53.92	54.20	53.67	53.68	55.01	52.86	52.92	52.86
TiO ₂	0.00	0.04	0.00	0.00	0.05	0.11	0.00	0.03	0.04	0.01	0.10	0.10	0.11
Al_2O_3	1.60	1.91	1.79	1.58	1.84	1.60	1.14	1.28	1.44	1.02	2.86	3.51	3.30
Cr_2O_3	0.80	0.99	0.94	0.95	1.04	0.80	1.19	0.66	0.80	0.76	0.98	0.96	0.73
FeO	2.49	2.15	2.38	2.18	2.04	2.03	1.92	1.98	2.06	1.64	2.36	2.33	2.20
MnO	0.06	0.07	0.12	0.07	0.00	0.14	0.05	0.08	0.10	0.12	0.08	0.08	0.10
NiO	0.09	0.12	0.09	0.02	0.01	0.10	0.07	0.15	0.05	0.06	0.10	0.10	0.02
MgO	17.69	17.57	18.93	18.61	16.37	17.84	17.86	18.28	18.02	17.11	16.56	16.53	16.24
CaO	23.03	23.40	22.83	22.22	24.20	23.46	23.76	22.89	22.88	24.73	23.76	23.43	23.55
Na ₂ O	0.20	0.17	0.09	0.27	0.26	0.20	0.18	0.17	0.21	0.22	0.30	0.30	0.31
K ₂ O	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02
Total	99.69	100.01	100.77	99.15	99.45	100.2	100.38	99.18	99.29	100.67	99.96	100.25	99.44
Calculate	ed on the ba	usis of 6 oxy	vgen										
Si	1.958	1.946	1.933	1.947	1.961	1.954	1.962	1.961	1.960	1.983	1.926	1.919	1.931
Ti	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.001	0.001	0.000	0.003	0.003	0.003
Al	0.069	0.082	0.076	0.068	0.079	0.068	0.049	0.055	0.062	0.043	0.123	0.150	0.142
Cr	0.023	0.028	0.027	0.027	0.030	0.023	0.034	0.019	0.023	0.022	0.028	0.027	0.021
Fe	0.076	0.065	0.072	0.067	0.062	0.062	0.058	0.060	0.063	0.049	0.072	0.071	0.067
Mn	0.002	0.002	0.004	0.002	0.000	0.004	0.002	0.002	0.003	0.004	0.002	0.002	0.003
Ni	0.003	0.004	0.003	0.001	0.000	0.003	0.002	0.004	0.001	0.002	0.003	0.003	0.001
Mg	0.961	0.952	1.018	1.014	0.892	0.964	0.964	0.996	0.981	0.919	0.900	0.894	0.884
Ca	0.899	0.911	0.882	0.870	0.948	0.911	0.921	0.896	0.895	0.955	0.928	0.910	0.922
Na	0.014	0.012	0.006	0.019	0.018	0.014	0.013	0.012	0.015	0.016	0.021	0.021	0.022
K	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Sum	4.004	4.004	4.019	4.015	3.992	4.005	4.003	4.007	4.004	3.992	4.006	4.000	3.996
Mg [#]	0.927	0.936	0.934	0.938	0.935	0.940	0.943	0.943	0.940	0.949	0.926	0.927	0.929

 $Mg^{\#} = Mg/(Mg + Fe)$; total Fe as Fe^{2+} .

of mid-ocean ridge basalts (MORB) and intraplate ocean island basalts (OIB). However, the C-H-O fluids in the mantle wedge for arc magmatism may largely result from devolatilization of the subducting oceanic lithosphere. This reasoning is logical because (1) the asthenospheric mantle may have already highly degassed before flowing subhorizontally (e.g., from beneath back-arc basin) to the mantle wedge, (2) in the case of the Yushigou harzburgite, the reduced volatile species are trapped in olivine (not pyroxenes), that is consistent with the incongruent melting taking place in the spinel peridotite stability field in the mantle wedge where olivine crystallizes (~1200-1300 °C; see above), and thus traps whatever volatiles available, (3) C, He, Ne and Ar isotope data demonstrate that these CH₄-rich fluids are ultimately of crustal origin, and (4) the subducting oceanic lithosphere potentially carries much more abundant reduced fluids such as $CH_4 + C + H_2$ than we have so far recognized (see below).

Serpentization is known to be an important process that produces CH_4 (as well as H_2 , Fe–Ni alloys) (Kelley and Früh-Green, 1999; Sleep et al., 2004) and a significant (>2 km) portion of the oceanic lithospheric mantle beneath the crust is largely serpentinized as represented by abyssal peridotites (Dick, 1989; Niu and Hékinian, 1997a; Niu, 2004), which is thus an important CH_4 reservoir (Kelley and Früh-Green, 1999). Furthermore, serpentinization may occur and reach the depth of ~50 km of the oceanic lithosphere at the trench-outer rise (Dobson et al., 2002; Ranero et al., 2003). Moreover, some seafloor sediments contain abundant "gas hydrates" with enormous amounts of CH₄ (Kastner et al., 1988; Kvenvolden, 1993; Hesse, 2003). All these suggest that the oceanic lithosphere is an immense CH₄ reservoir, and can provide reduced fluids in subduction zones to the mantle wedge. Such reduced fluids must have C–He–Ne–Ar isotopic signatures of shallow (vs. deep mantle) origin as is the case for the Yushigou harzburgite.

7. THE EFFECT OF REDUCED FLUIDS ON MANTLE WEDGE MELTING – REDOX MELTING

To invoke the presence of highly reduced fluids in the mantle wedge source region of arc volcanism is in conflict with the common view that the mantle wedge should be oxidized as inferred from arc lavas and mantle xenoliths they carry (Wood et al., 1990; Carmichael, 1991; Arculus, 1994). If the subducting oceanic lithosphere is the important source of reduced fluids with abundant $CH_4 + H_2 + C$ as we reason, this would also be at odds with the standard concept of "slab dehydration-induced mantle wedge melting for arc magmatism". This is because $CH_4 + H_2$ fluids do not reduce the solidus temperature significant enough to induce wet melting directly (Green et al., 1987; Wyllie, 1987; Taylor and Green, 1988; Wyllie and Ryabchikov,

T 1 1 4

Table 4						
Representative analy	yses of spinel	l from harzburg	gite (HB) a	nd dunite by	electron micro	probe.

	-			-									
Sample	ZQ6A	ZQ11	ZQ12	ZQ16	ZQ18	ZQ19	ZQ24	ZQ25-1	ZQ25-2	Y52	ZQ56	ZQ49-1	ZQ49-2
Rock	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	Dunite	Dunite	Dunite
SiO ₂	0.10	0.03	0.02	0.02	0.03	0.00	0.02	0.29	0.00	0.02	0.04	0.04	0.03
TiO ₂	0.05	0.00	0.00	0.01	0.04	0.03	0.00	0.00	0.01	0.04	0.16	0.14	0.12
Al_2O_3	17.13	21.16	21.70	16.18	17.49	18.24	18.80	21.31	17.89	18.38	30.37	28.26	26.13
Cr_2O_3	49.19	47.03	45.36	48.09	48.43	49.57	47.13	47.04	49.60	49.66	33.39	36.2	38.38
FeO	23.07	18.82	20.21	25.17	21.28	19.69	20.88	19.03	20.23	18.98	20.86	21.2	21.99
MnO	0.46	0.49	0.39	0.66	0.51	0.38	0.56	0.43	0.40	0.42	0.38	0.41	0.5
NiO	0.03	0.04	0.12	0.11	0.11	0.10	0.10	0.11	0.03	0.02	0.17	0.12	0.12
MgO	10.65	12.16	13.13	9.49	12.14	12.44	12.49	11.44	12.08	11.61	13.79	13.6	12.28
CaO	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.01	0.04	0.02	0.04	0.02	0.00	0.33	0.00	0.00	0.00	0.04	0.00
K_2O	0.01	0.01	0.00	0.02	0.01	0.00	0.01	0.03	0.02	0.00	0.01	0.00	0.00
Total	100.68	99.75	100.98	99.78	100.08	100.48	99.99	100.05	100.26	99.13	99.17	100.01	99.56
Calculate	ed on the ba	sis of 4 oz	xvgen										
Si	0.003	0.001	0.001	0.001	0.001	0.000	0.001	0.009	0.000	0.001	0.001	0.001	0.001
Ti	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001	0.004	0.003	0.003
Al	0.639	0.775	0.779	0.615	0.648	0.671	0.692	0.779	0.662	0.688	1.065	0.993	0.938
Cr	1.230	1.156	1.093	1.226	1.203	1.223	1.163	1.153	1.230	1.246	0.785	0.853	0.924
Fe ³⁺	0.126	0.068	0.127	0.159	0.147	0.106	0.144	0.059	0.108	0.065	0.140	0.147	0.130
Fe ²⁺	0.484	0.421	0.388	0.520	0.412	0.408	0.401	0.435	0.423	0.439	0.379	0.382	0.430
Mn	0.012	0.013	0.010	0.018	0.014	0.010	0.015	0.011	0.011	0.011	0.010	0.010	0.013
Ni	0.001	0.001	0.003	0.003	0.003	0.003	0.003	0.003	0.001	0.001	0.004	0.003	0.003
Mg	0.502	0.564	0.597	0.456	0.569	0.579	0.581	0.529	0.565	0.549	0.612	0.605	0.558
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.001	0.002	0.001	0.002	0.001	0.000	0.020	0.000	0.000	0.000	0.002	0.000
Κ	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000
Cr [#]	0.66	0.60	0.58	0.67	0.65	0.65	0.63	0.60	0.65	0.64	0.42	0.46	0.50
$Mg^{\#}$	0.51	0.57	0.61	0.47	0.58	0.59	0.59	0.55	0.57	0.56	0.62	0.61	0.56

 Fe^{3+} was calculated using charge balance. $Cr^{\#} = Cr/(Cr + Al)$, $Mg^{\#} = Mg/(Mg + Fe^{2+})$.

2000). However, the highly reduced $CH_4 + H_2$ fluids ($\sim \Delta FMQ$ -5) (e.g., French, 1966; Wood et al., 1990; Green and Falloon, 1998; Kadik et al., 2004) will necessarily react with the relatively more oxidized ($\sim \Delta FMQ$ -1) asthenospheric mantle wedge peridotite (see Table 5 and above), producing H₂O and CO₂ that then lower the solidus and incite melting for arc magmatism. Such redox processes, for example, can be explained in terms of standard oxidation reactions such as:

$$CH_4 + O_2 \rightarrow 2H_2O + C_{Graphite} \tag{1}$$

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \tag{2}$$

Table 5 Oxygen fugacity calculation using Ol–Opx–Sp oxygen geobarometry

but more likely by reactions involving Fe^{2+}/Fe^{3+} redox in the forms of

$$CH_4 + 6Fe_2O_3 \rightarrow 2H_2O + 4Fe_3O_4 + C_{Graphite}$$
(3)

$$6Fe_2O_3 + C_{Graphite} \rightarrow CO_2 + 4Fe_3O_4 \tag{4}$$

where Fe_2O_3 and Fe_3O_4 are components in spinel to illustrate the concept, and there are many other forms to express the redox relations involving metal, carbonate and silicate phases (O'Neill and Wall, 1987; Bryadzia and Wood, 1990; Wood et al., 1990; Blundy et al., 1991). This reasoning suggests that redox melting mechanism (Green et al., 1987; Taylor and Green, 1988; Green and Falloon,

			0			
Sample	T in K (Ol/Sp)	lna(Fe ₃ O ₄)	lna(Fe ₂ SiO ₄)	$ln\alpha(SiO_2)$	$\Delta log 10 fO_2 (QFM)$	<i>T</i> in K (BNK90)
ZQ6A	1006	-4.23	-1.95	-1.34	-0.34	1219
ZQ11	1008	-5.47	-1.99	-1.30	-1.28	1179
ZQ12	1081	-4.29	-1.99	-1.22	-0.13	1279
ZQ19	1096	-4.92	-1.99	-1.13	-0.56	1281
ZQ24	1095	-4.20	-2.00	-1.20	0.01	1167
ZQ25	1058	-4.77	-2.02	-1.23	-0.48	1177
Y52	1019	-5.77	-2.00	-1.28	-1.47	1233

The calculation is based on Ol–Opx–Sp oxygen geobarometry of O'Neill and Wall (1987) except with the new thermodynamic data for $Mg_2SiO_4 + SiO_2 = Mg_2Si_2O_6$ from Holland and Powell (1998). Temperature was calculated from Ol–Sp Fe–Mg geothermometry and pressure was assumed 15 kb. Temperature was also calculated using Cpx–Opx thermometer of Brey and Koehler (1990).

1998) is perhaps important for mantle wedge melting although fluid release from the subducting slab remains the ultimate cause of the subduction-zone magmatism.

The abundance levels of CH_4 in serpentinized peridotites are unknown, but we do know that there could be as much as 13 wt% H₂O in serpentines (i.e., complete serpentinization). It is intriguing again why only $CH_4 + H_2$, not H₂O,

Table 6 Whole-rock compositions for the Yushigou peridotite.

would release during oceanic lithosphere subduction implicit in our foregoing interpretation. The reason may actually be straightforward. As serpentines are stable up to 7 GPa (at T < 750 °C) (Williams and Hemley, 2001) before being transformed to dense hydrous magnesium silicate phases at even greater pressures (~5–50 GPa) (Williams and Hemley, 2001), serpentine dehydration is likely to be incomplete

Sample Rock	Y92-51 Harzburgite	Y92-52 Harzburgite	ZQ6a Harzburgite	ZQ16 Harzburgite	ZQ56 Dunite
Majon and with	an alamant avidas (manzourgite		Turzouigite	Dunit
Major ana min	or element oxides $(W1\%)$	44.08	44.44	42.22	20.06
310 ₂ TiO	44.79	44.26	44.44	43.55	39.90
110 ₂	0.01	0.01	0.01	0.01	0.01
AI_2O_3	8.40	7.02	0.05	0.47	0.57
MnO	0.12	0.13	0.12	9.28	0.14
MaQ	46.42	45.07	45.05	46.62	47.99
CaO	40.42	43.97	43.93	40.02	47.88
Na-O	0.05	0.03	0.03	0.03	0.17
K O	0.05	0.03	0.05	0.05	0.21
R ₂ O	0.01	0.02	0.01	0.01	0.01
	0.16	0.45	0.08	0.07	0.01
	100.42	100.57	100.20	100.24	100.00
Total	100.43	100.57	100.26	100.34	100.06
Mg ⁿ	91.55	92.00	91.41	90.87	89.38
Trace element	analyses (ppm)				
Li	1.6936	1.7552	1.7299	1.2359	1.1752
Be	0.0008	0.0088	0.0061	0.0023	0.0081
Sc	8.1704	8.2419	10.5112	9.1031	6.2000
V	25.2351	26.5713	32.3249	31.9568	25.7140
Cr	2530	2585	2157	2978	3299
Со	141	144	138	138	157
Ni	2069	2097	2014	2111	2707
Cu	8.8045	8.9479	2.1907	2.8214	324.2030
Zn	37.1075	37.8402	36.6822	38.7825	43.2106
Ga	0.4492	0.5135	0.5259	0.4716	0.9193
Ge	0.9343	0.9324	0.9863	0.9760	0.8937
Rb	0.0730	0.1878	0.1269	0.0665	0.1809
Sr	0.5230	1.1946	0.1762	0.3870	0.9782
Y	0.0948	0.1236	0.2670	0.0807	0.3349
Zr	0.0925	0.1961	0.1820	0.0622	0.2346
Nb	0.0267	0.0342	0.0210	0.0183	0.0400
Cs	0.0151	0.0198	0.0308	0.0084	0.0140
Ba	1.3168	2.1149	0.7451	0.8165	1.7202
La	0.0244	0.0671	0.0110	0.0094	0.0568
Ce	0.0520	0.1271	0.0240	0.0200	0.1194
Pr	0.0046	0.0149	0.0027	0.0017	0.0110
Nd	0.0175	0.0502	0.0104	0.0087	0.0474
Sm	0.0033	0.0088	0.0017	0.0013	0.0072
Eu	0.0008	0.0026	0.0009	0.0005	0.0018
Gd	0.0024	0.0092	0.0037	0.0009	0.0081
Tb	0.0007	0.0013	0.0006	0.0002	0.0009
Dy	0.0062	0.0100	0.0078	0.0036	0.0094
Но	0.0015	0.0023	0.0026	0.0008	0.0020
Er	0.0055	0.0075	0.0105	0.0042	0.0073
Tm	0.0012	0.0017	0.0029	0.0013	0.0017
Yb	0.0110	0.0152	0.0298	0.0120	0.0187
Lu	0.0025	0.0025	0.0064	0.0030	0.0041
Hf	0.0061	0.0117	0.0085	0.0085	0.0161
Та	0.0524	0.0530	0.0427	0.0372	0.0293
				(acertine	und on mout man

(continued on next page)

Sample Rock	Y92-51 Harzburgite	Y92-52 Harzburgite	ZQ6a Harzburgite	ZQ16 Harzburgite	ZQ56 Dunite
Pb	1.0452	1.1022	1.1050	1.1757	1.7387
Th	0.0072	0.0155	0.0051	0.0042	0.0111
U	0.0040	0.0067	0.0015	0.0017	0.0074

Table 6 (continued)

Bulk-rock major elements were analyzed using a RIX-2100 X-ray fluorescence (XRF) spectrometer on fused glass disks at Northwest University of China. Calibrated against Chinese rock reference standard GBW07105, the reproducibility of major elements in these rocks is better than 2% for Si, Mg, Fe, better than 10% for Al and Ca, and better than 20% for Ti, Mn and Na. Analytical detail is described in Song et al. (2007a,b). $Mg^{\#} = 100 \times Mg/(Mg+Fe)$; total Fe as Fe^{2+} . Bulk-rock trace elements were analyzed using an Elan 6100-DRC inductively coupled plasma mass spectrometry (ICP-MS) at Guangzhou Institute of Geochemistry of China. Fifty milligrams of sample was dissolved in equal mixture of subboiling distilled superpure HF and HNO₃ with a Teflon digesting vessel on a hot-plate for 24 h. This procedure was repeated using smaller amounts of acids for a further 12 h. After digestion, the sample was evaporated to incipient dryness, refluxed with 6 N HNO₃, and heated again to incipient dryness. The sample was then dissolved in 2 ml of 3 N HNO₃ and diluted with Milli-Q water (18 MΩ) to a final dilution factor of 2000. Two USGS rock reference materials BCR-1 and BHVO-1 were used to monitor the analytical accuracy and precision. Analytical accuracy, as indicated by relative difference (RE) between measured and recommended values is better than 10% for most elements, ranging between 10% and 13% for Cu, Sc, Nb, Er, Th, and U, and between 11% and 20% for Ta, Tm, and Gd. Analytical detail is described in Song et al. (2007a,b).

in subduction zones (Niu, 2004, 2005), but CH₄ that is structurally unbounded in serpentines can be largely released. If redox melting is a possible melting mechanism in the mantle wedge as we infer, then H₂O and CO₂ as the products of the redox reactions would have similar chances to be trapped in the crystallizing olivine crystals. The fact that we do not observe such oxidized species (CO, CO₂, H₂O) but reduced forms (e.g., CH₄, H₂, C, C₂H₆, etc.) encourages us to speculate that the high solubilities of H₂O and CO₂ (vs. CH₄, C₂H₆) (Holloway and Jacobsson, 1986; Green et al., 1987) in silicate melts would have efficiently removed H₂O and CO₂ with the melt by the process of fractional or near-fractional melting and melt separation. This explains why the crystallizing olivine during the incongruent melting traps only the reduced and melt-insoluble species like CH₄.

8. WHY ARE ERUPTED ARC LAVAS MORE OXIDIZED?

The redox melting mechanism explains why arc magmas are rich in H₂O and CO₂ (vs. CH_4). The arc magmas can be further oxidized during ascent by two combined processes: (1) decreasing pressure (small effect on the order of 0.6-0.8 log fO₂ unit increase per GPa decompression) (Ballhaus and Frost, 1994; Woodland and Koch, 2003), and more significantly (2) hydrogen loss during degassing (e.g., $2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2\uparrow$). Christie et al. (1986) showed that relatively slowly-cooled interiors of MORB pillows are much more oxidized ($\sim 1-3\log fO_2$ units) in terms of Fe³⁺/Fe²⁺ ratio than rapidly quenched MORB glass rinds. Obviously, the more oxidized nature of the slowly-cooled pillow interiors is a surface effect of hydrogen loss achieved by reaction of H₂O with ferrous iron in the melt. Holloway (2004) argues that the hydrogen loss is primarily due to crystallization of magnetite-ulvospinel in rapidly crystallized MORB. The latter is indeed consistent with our MORB petrographic observations. This surface and near-surface hydrogen loss will not affect V/Sc ratio (Lee et al., 2003, 2005). Therefore, the apparently oxidized nature of arc lavas in terms of Fe³⁺/Fe²⁺ ratio cannot be used to infer redox conditions in the mantle wedge source region.

Mantle xenoliths carried in arc magmas are unlikely materials from the mantle wedge melting region, but from sub-arc lithosphere with complex history of metasomatism and are thus necessarily metasomatized (e.g., Brandon and Draper, 1996; Ertan and Leeman, 1999; Lee et al., 2003, 2005). Hence, mantle xenoliths from arc magmas cannot be used to infer mantle wedge redox conditions either. Addition of ~0.5–1.0% of "arc" melts percolating through the advanced residues along grain boundaries is adequate to produce the observed bulk-rock LREE and LILE enrichments (Fig. 3e and f) (see Niu and Hékinian, 1997a; Niu, 2004).

9. DISCUSSION AND IMPLICATIONS

We are confident that the Yushigou harzburgite represents a fragment of a fossil mantle wedge. This interpretation is most consistent with the petrotectonic association in the field, and is corroborated by the detailed petrology and geochemistry of the rock. However, like many geological interpretations, there is no hard proof that this interpretation is definitely correct. On the other hand, there is no other tectonic setting on earth that we can logically reason to record incongruent melting in the spinel peridotite facies with the peritectic olivine entrapping highly reduced fluids of shallow crustal origin as revealed from C, He, Ne and isotopes. The fact that some primary *Type-I* fluid inclusions take *negative crystal forms of host olivine* indicates unequivocally that they are trapped during crystallization of the host olivine at magmatic temperatures.

One may argue that this fresh harzburgite could be of metamorphic origin from recrystallization of serpentines, which could then have fluid inclusions with negative crystal forms. It is important to note, however, that serpentinization is practically a process that transforms mostly olivine (and others) to Fe-poor serpentines, with Fe forming trails of fine-grained magnetite dispersed along original grain boundaries or between serpentine domains. Recrystallization of serpentinized harzburgites will retain such features with magnetite aggregate trails and metamorphic olivine of very high Fo content (i.e., Fo_{94-97}) (Bruce et al., 2008). However, the Yushigou harzburgite does not



Fig. 4. Photomicrographs of fluid inclusions in olivine crystals from the Yushigou harzburgite. (a) Type-I negative crystal liquid CH_4 inclusions (arrowed) with a small gas bubble. (b) Type-I spherical (some negative crystal) single-phase inclusions. (c) orientated CH_4 -dominated inclusions. (d) CH_4 inclusions occurring along the growth planes of olivine. (e) CH_4 -dominated colorless inclusions; some brown-colored graphite- CH_4 inclusions were re-distributed along the kink-bands (KB). (f) Type-II irregular or tubular colorless CH_4 -graphite inclusions. (g) type-II inclusions in olivine hosted in spinel (Sp). (h) trails of Type-III vermicular inclusions.

100 µm

have such variably high Fo metamorphic olivine nor magnetite trails, but is texturally and compositionally straightforward depleted harzburgitic melting residue. In this context, it is necessary to emphasize that the crustal (shallow level) origin of the fluids (in olivine inclusions) as revealed by their C-He-Ne-Ar isotopes does not mean in any way at all that the host harzburgite is of crustal origin. Petrologically, spinel peridotite can only be formed and stable under pressures in excess of >10 kbar (or >30 km in the mantle) and the compositionally depleted spinel harzburgite must be residues of melting and melt extraction under similar mantle conditions. The subsolidus equilibration temperature of >900 °C calcu-



Fig. 5. Raman spectra of fluid inclusions in olivine crystals of the Youshigou harzburgite. (a) Liquid (L) CH_4 -dominanted fluids with minor N_2 , H_2 , H_2S and H_2O in Type-I inclusions (Fig. 4a). (b) Liquid (L) CH_4 -dominanted fluids with minor N_2 , H_2 , H_2S and H_2O in Type-I inclusions (Fig. 4a). (c) Graphite (Grp) + gaseous CH_4 (G) in type-II inclusions (Fig. 4d). (d) Gaseous CH_4 (G) in type-III inclusions (Fig. 4f). The unlabeled tiny peaks at 3000 and 3065 cm⁻¹ in the insets of (a) and (b) are those of CH_4 .

lated using Opx–Opx geothermometry (Table 5) is also consistent with mantle (vs. crustal) conditions. The deformation kink-bands that postdates the entrapment of the fluid inclusions recorded in olivine also require subsolidus mantle (vs. crustal) temperatures of ~1000 °C (see above). It should also be noted that fluids of crustal (shallow level) origin are not uncommon in mantle xenoliths (see Zhang et al., 2007). Hence, the Yushigou harzburgite is the best candidate for a fossil mantle wedge that records a "snapshot" of subduction factory processes from oceanic lithosphere subduction, fluid transport to the mantle wedge, mantle wedge melting, and melt percolating/extraction. It is possible that the fluids trapped in olivine were originally H_2O and CO_2 , and they may have reacted with the host olivine during the slow cooling of the harzburgite to produce the more reduced forms, i.e., CH_4 and H_2 . These hypothetical reactions are actually serpentinization processes that convert olivine, $(Fe,Mg)_2SiO_4$, into serpentine, $(Fe,Mg)_3Si_2O_5(OH)_4$. As the reduction of C^{4+} (in CO_2) and H^+ (in H_2O) into C^{4-} (in CH_4) and H^0 (in H_2), respectively, is accompanied by oxidation of Fe^{2+} (in olivine) into Fe^{3+} (in magnetite: $Fe_2^{3+}O_3 \cdot Fe^{2+}O$), the following Fe-rich end-member reactions are conceptually straightforward:

Table 7Nobel gas analyses of olivine and orthopyroxene separates in Yushigou harzburgite sample ZQ-25.

Sample	Phase	Weight (g)	4 He 1.00 × 10^{-7} cc/g	³ He/ ⁴ He R/Ra	Error	20 Ne 1.00 × 10^{-11} cc/g	²⁰ Ne/ ²² Ne	Error	$^{40} m Ar~1.00 imes 10^{-7}~cc/g$	⁴⁰ Ar/ ³⁶ Ar	Error
ZQ-25A	Oliv	0.7604	15.5	0.43	0.06	2.7	9.97	0.04	6.2	6483	284
ZQ-25B	Opx	0.6976	4.1	0.38	0.02	1.2	9.93	0.08	5.1	3952	66

 $Ra = the atmospheric ratio; ZQ25A = (0.43/1.4) \times 10^{-6} = 0.31 \times 10^{-6}; and ZQ25B = (0.38/1.4) = 0.27 \times 10^{-6}.$ Analytical techniques are described in Lai et al. (2005), and sample preparation and analytical details are described below.

Olivine (Oliv) and orthopyroxene separates of 0.4–0.8 mm grain size were hand-picked and washed ultrasonically in 2 N–HNO₃ for 10 min, and then in distilled water, acetone and ethanol for 5 min, respectively. The dried samples were weighed (usually ~1 g used for analysis) before set into crushers. The whole system was baked out (about 150 °C) overnight to remove adsorbed atmospheric noble gases. Noble gases extracted by crushing at 250 °C. The evolved noble gases were purified using two Ti–Zr getters activated at about 800 °C. He fraction was separated from Ar–Kr–Xe fraction using two charcoal traps at liquid N₂ temperature and from Ne fraction using another trap chilled down to 26 K with a cryogenic refrigerator. He, Ne and Ar–Kr–Xe fractions were sequentially admitted into a sector-type mass spectrometer (VG5400) at the Earthquake Research Institute of the University of Tokyo, Japan (Lai et al., 2005). Air was used as a standard gas to determine noble gas sensitivities and mass discrimination. Measurement of noble gas isotopes was carried out by the peak comparison between unknown samples and air. Faraday detector was used for noble gas isotopes with high abundances such as ⁴He, ⁴⁰Ar, while either Daly photo multiplier or electron multiplier was used for other isotopes with low abundances. Blank levels of ⁴He, ²⁰Ne, ⁴⁰Ar, ³⁶Ar are (3–5) × 10⁻¹⁰, 2 × 10⁻¹², 2 × 10⁻⁹ and 6 × 10⁻¹² cm³ (STP), respectively. For the analysis of Ne isotopes, ²⁰Ne and ²²Ne have been calibrated from the interference of ⁴⁰Ar²⁺ and ⁴⁴CO²²⁺, respectively. Errors for noble gas abundances are estimated to be ~5%.

The data show that ${}^{3}\text{He}/{}^{4}\text{He}$ ratios are lower than air, ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios are much higher than air (295.5). The neon isotopic data show that they are indistinguishable from the atmospheric neon. The low ${}^{3}\text{He}/{}^{4}\text{He}$ and high ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios could be due to radiogenic ingrowth, but this is unlikely the case because U and Th contents in olivine and Opx are very low (higher in Opx than in olivine), yet the isotopic ratios are indistinguishable. We interpret the data to represent "primary" values during the petrogenesis of the rock. The data are inconsistent with mantle origin, but consistent with shallow crustal/surface origin.

$$\begin{split} & 6Fe_2SiO_4^{[faylite]} + 7H_2O \rightarrow 3Fe_3Si_2O_5(OH)_4^{[serpentive]} \\ & + Fe_3O_4^{[magnetite]} + H_2 \end{split} \tag{5}$$

$$& 24Fe_2SiO_4 + 26H_2O + CO_2 \rightarrow 12Fe_3Si_2O_5(OH)_4 \end{split}$$

$$+4Fe_3O_4 + CH_4 \tag{6}$$

where serpentine and magnetite are necessary reaction products, yet neither serpentine nor magnetite is found in any of the fluid inclusions (both Type-I primary and Type-II and Type-III secondary) despite careful scrutiny. Therefore, CH_4 and H_2 are primary fluid species entrapped in olivine during incongruent melting process under magmatic conditions.

We cannot rule out the possibility that the Yushigou harzburgite is a special case where subducted CH_4 is preserved in an arc melting region (asthenosphere), and may not have global significance. However, given the volumetric significance of serpentines in the subducting oceanic lithosphere (Dobson et al., 2002; Ranero et al., 2003; Niu, 2004) and likely subduction of deep sea sediments with abundant CH_4 (formerly gas hydrates; Kastner et al., 1988; Kvenvolden, 1993; Hesse, 2003) prior to subduction, it is essential that we examine seriously the physical and chemical consequences of reduced fluids on subduction-zone magmatism. Such efforts will also facilitate improved understanding of C–H–O recycling and origin of mantle volatiles.

If highly reduced species such as $CH_4 + C + H_2$ (vs. oxidized H_2O and CO_2) are important in fluids released from the subducting slab, and if redox reactions are important in triggering mantle wedge melting, then the implications are profound: (1) the "slab component" may have limited elemental contribution to arc magmatism because of the overall limited elemental solubility in highly reduced fluids (vs. H_2O and CO_2) although solubil-

ity experiments for specific elements are needed; (2) mantle wedge and recycled sediments may be the principal source materials controlling the geochemistry of arc magmatism as has been advocated (Morris et al., 1990; Hawkesworth et al., 1993; Plank and Langmuir, 1993, 1998; Elliott et al., 1997; Elliot, 2003); and (3) the geochemical "arc signature" (i.e., the relative depletion of Nb, Ta and Ti and enrichment of Ba, Rb, U, Pb, etc.) in arc magmas may be largely inherited from sediments, particularly land-derived sediments (Plank, 2005).

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REFERENCES

Andersen T. and Neumann E.-R. (2001) Fluid inclusions in mantle xenoliths. *Lithos* 55, 301–320.

- Arculus R. J. (1994) Aspects of magma genesis in arcs. *Lithos* 33, 189–208.
- Baker M. B. and Stolper E. M. (1994) Determining the composition of high-pressure mantle melts using diamond aggregates. *Geochim. Cosmochim. Acta* 58, 2811–2827.
- Ballhaus C. and Frost B. R. (1994) The generation of oxidized CO₂-bearing basaltic melts from reduced CH₄bearing upper mantle sources. *Geochim. Cosmochim. Acta* 58, 4931–4940.
- Blundy J. D., Brodholt J. P. and Wood B. J. (1991) Carbon-fluid equilibria and the oxidation state of the upper mantle. *Nature* **349**, 321–324.
- Brandon A. D. and Draper D. S. (1996) Constraints on the origin of the oxidation state of mantle overlying subduction zones: an example from Simcoe, Washington, USA. *Geochim. Cosmochim. Acta* 60, 1739–1749.
- Brey G. P. and Koehler T. (1990) Geothermobarometry in fourphase lherzolites II: new thermobarometers and practical assessment of existing thermobarometers. J. Petrol. 31, 1353– 1378.
- Bruce M. C., Niu Y. L., Harbort T. A. and Holcombe R. J. (2000) Petrological, geochemical and geochronological evidence for a Neoproterozoic ocean basin recorded in the Marlborough terrane of the northern New England Fold Belt. *Aust. J. Earth Sci.* 47, 1053–1064.
- Bryadzia L. T. and Wood B. J. (1990) Oxygen thermobarometry of abyssal spinel peridotites: the redox state and C–O–H volatile composition of the earth's sub-oceanic upper mantle. *Am. J. Sci.* 290, 1093–1116.
- Burke E. A. J. (2001) Raman microspectrometry of fluid inclusions. *Lithos* 55, 139–158.
- Carmichael I. S. E. (1991) The redox states of basic and silicic magmas – A reflection of their source regions. *Contrib. Mineral. Petrol.* 106, 129–141.
- Christie D. M., Carmichael I. S. E. and Langmuir C. H. (1986) Oxidation states of mid-ocean ridge basalt glasses. *Earth Planet. Sci. Lett.* 79, 397–411.
- Deines P. (2002) The carbon isotope geochemistry of mantle xenoliths. *Earth Sci. Rev.* 58, 247–278.
- Dick H. J. B. (1989) Abyssal peridotites very slow spreading ridges and ocean ridge magmatism. In *Magmatism in the Ocean Basins*, vol. 42 (eds. A. D. Saunders and M. J. Norry). Geol. Soc. Spec. Publ., pp. 71–105.
- Dobson D. P., Meredith P. G. and Boon S. A. (2002) Simulation of subduction zone seismicity by dehydration of serpentine. *Science* 289, 1407–1410.
- Eiler J. M., McUnnes B., Valley J. W., Graham C. M. and Stolper E. M. (1998) Oxygen isotope evidence for slab-derived fluids in the sub-arc mantle. *Nature* **393**, 777–781.
- Elliot T. (2003) Tracers of slab. In *Inside the subduction factory*, vol. 138 (ed. J. Eiler). Geophys. Monogr., pp. 23–46.
- Elliott T., Plank T., Zindler A., White W. and Bourdon B. (1997) Element transport from slab to volcanic front at the Mariana Arc. J. Geophys. Res. **102**, 14991–15019.
- Ertan I. E. and Leeman W. P. (1999) Fluid inclusions in mantle and lower crustal xenoliths from the Simcoe volcanic field, Washington. *Chem. Geol.* **154**, 83–95.
- Exley R. A., Mattey D. P., Clague D. A. and Pillinger C. T. (1986) Carbon isotope systematics of a mantle "hot spot": a comparison of Loihi Seamount and MORB glasses. *Earth Planet. Sci. Lett.* **78**, 189–199.
- Fleet M. E. (1978) Origin of olivine subgrain boundaries in mantle peridotites. *Nature* 275, 48–50.
- French B. M. (1966) Some geological implications of equilibrium between graphite and a C–H–O gas phase at high temperatures and pressures. *Rev. Geophys.* 4, 223–253.

- Gill J. B. (1974) Role of underthrust oceanic crust in genesis of a fijian calc-alkaline suite. *Contrib. Mineral. Petrol.* 43, 29–45.
- Gill J. B. (1981) Orogenic Andesites and Plate Tectonics. Springer-Verlag, Berlin, 390pp.
- Green D. H. and Falloon T. J. (1998) Pyrolite: a ringwood concept and its current expression. In *The Earth's Mantle–Composition*, *Structure, and Evolution* (ed. I. Jackson). Cambridge University Press, Melbourne, pp. 311–380.
- Green D. H., Falloon T. J. and Taylor W. R. (1987) Mantlederived magmas – roles of variable source peridotite and variable C–H–O fluid compositions. *Geochem. Soc. Spec. Publ.* 1, 121–138.
- Hawkesworth C. J., Hergt J. M., Ellam R. M. and Mcdermott F. (1991) Element fluxes associated with subduction related magmatism. *Phil. Trans. Roy. Soc. Lond.* 335, 393–405.
- Hawkesworth C. J., Gallagher K., Hergt J. M. and Mcdermott F. (1993) Mantle and slab contributions in arc magmas. *Ann. Rev. Earth Planet. Sci.* 21, 175–204.
- Hesse R. (2003) Pore water anomalies of submarine gas-hydrate zones as tool to assess hydrate abundance and distribution in the subsurface what we have learned in the past decade? *Earth Sci. Rev.* **61**, 149–179.
- Holland T. J. B. and Powell R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. J. Metamorph. Geol. 16, 309–343.
- Holloway J. R. (2004) Redox reactions in seafloor basalts: possible insights into silicic hydrothermal systems. *Chem. Geol.* 210, 225–230.
- Holloway J. R. and Jacobsson S. (1986) Volatile solubilities in magmas: transport of volatiles from mantles to planet surfaces. J. Geophys. Res. 91, 505–508.
- Hu P., Zhang M. J., Tang Z. L., Li C. S. and Wang J. (2007) Chemical and stable isotopic compositions of volatiles in mantle peridotites of the Yushigou ophiolite in Qilian orogenic belt, western China. *Acta Petrol. Sin.* 23, 169–197.
- Kadik A., Pineau F., Litvin Y., Jendrzejewski N., Martinez I. and Javoy M. (2004) Formation of carbon and hydrogen species in magmas at low oxygen fugacity. J. Petrol. 45, 1297–1310.
- Kastner M., Kvenvolden K. A. and Lorenson T. D. (1988) Chemistry, isotopic composition, and origin of a methane– hydrogen sulfide hydrate at the Cascadia subduction zone. *Earth Planet. Sci. Lett.* **156**, 173–183.
- Kelley D. S. and Früh-Green G. L. (1999) Abiogenic methane in deep-seated mid-ocean ridge environments: insights from stable isotope analyses. J. Geophys. Res. 104, 10439–10460.
- Kirby S. H. and Raleigh C. B. (1976) Mechanisms of hightemperature, solid-state flow in minerals and ceramics and their bearing on the creep behavior of the mantle. *Tectonophysics* 151, 1–26.
- Kvenvolden K. A. (1993) Gas hydrates–geological perspective and global change. *Rev. Geophys.* 31, 173–187.
- Lai Y., Liu Y., Huang B. and Chen Y. (2005) The characteristics of noble gases in mantle-derived xenoliths in Wudalianchi and Kuandian, NE China: MORB-like mantle and metasomatized mantle. *Acta Petrol. Sin.* 21, 1373–1381.
- Langmuir C. H., Klein E. M. and Plank T. (1992) Petrological systematics of mid-ocean ridge basalts: constraints on melt generation beneath ocean ridges. In *Mantle Flow and Melt Generation at Mid-ocean Ridges*, vol. 71 (eds. J. Phipps Morgan, D. K. Blackman and J. M. Sinton). Am. Geophys. Union Monogr., pp. 183–280.
- Lee C.-T., Brandon A. D. and Norman M. (2003) Vanadium in peridotites as a proxy for paleo-fO2 during partial melting: prospects, limitations, and implications. *Geochim. Cosmochim. Acta* 67, 3045–3064.

- Lee C.-T. A., Leeman W. P., Canil D. and Li Z.-X. A. (2005) Similar V/Sc systematics in MORB and arc basalts: implications for the oxygen fugacities of their mantle source regions. J. Petrol. 46, 2313–2336.
- Liu W. and Fei P. X. (2006) Methane-rich fluid inclusions from ophiolitic dunite and post-collisional mafic–ultramafic intrusion: the mantle dynamics underneath the Palaeo-Asian Ocean through to the post-collisional period. *Earth Planet. Sci. Lett.* 242, 286–301.
- Mattey D. P., Exley R. A. and Pillinger C. T. (1984) Isotope composition of CO₂ and dissolved carbon species in basalt glasses. *Geochim. Cosmochim. Acta* 52, 2377–2386.
- McCulloch M. T. and Gamble J. A. (1991) Geochemical and geodynamical constraints on subduction zone magmatism. *Earth Planet. Sci. Lett.* **102**, 358–374.
- Morris L., Leeman W. P. and Tera F. (1990) The subducted component is island arc lavas: constraints from Be isotopes and B–Be systematics. *Nature* 344, 31–36.
- Nicolas A. and Poirier J. P. (1976) *Crystalline Plasticity and Solid State Flow in Metamorphic Rocks*. Wiley, London, 444 pp.
- Niu Y. L. (1997) Mantle melting and melt extraction processes beneath ocean ridges: evidence from abyssal peridotites. J. Petrol. 38, 1047–1074.
- Niu Y. L. (2004) Bulk-rock major and trace element compositions of abyssal peridotites: implications for mantle melting, melt extraction and post-melting processes beneath ocean ridges. J. Petrol. 45, 2423–2458.
- Niu Y. L. (2005) Generation and evolution of basaltic magmas: some basic concepts and a hypothesis for the origin of the Mesozoic–Cenozoic volcanism in eastern China. *Geol. J. China Univ.* **11**, 9–46.
- Niu Y. L. and Hékinian R. (1997a) Basaltic liquids and harzburgitic residues in the Garrett Transform: a case study at fastspreading ridges. *Earth Planet. Sci. Lett.* 146, 243–258.
- Niu Y. L. and Hékinian R. (1997b) Spreading-rate dependence of the extent of mantle melting beneath ocean ridges. *Nature* 358, 326–329.
- Niu Y. L., O'Hara M. J. and Pearce J. A. (2003) Initiation of subduction zones as a consequence of lateral compositional buoyancy contrast within the lithosphere: a petrologic perspective. J. Petrol. 44, 851–866.
- O'Neill H. St. C. and Wall V. J. (1987) The olivine-spinel oxygen geobarometer, the nickel precipitation curve and the oxygen fugacity of the upper mantle. J. Petrol. 28, 1169–1192.
- Parkinson I. J. and Arculus R. J. (1999) The redox state of subduction zones: insights from arc-peridotites. *Chem. Geol.* 160, 409–423.
- Peacock S. M. (1996) Thermal and petrologic structure of subduction zones. In *Subduction top to bottom*, vol. 96 (eds. G. E. Bebout, D. W. Scholl, S. H. Kirby and L. P. Platt). Geophys. Monogr., pp. 119–133.
- Pearce J. A. and Peate D. W. (1995) Tectonic implications of the composition of volcanic arc magmas. *Ann. Rev. Earth Planet. Sci.* 23, 251–285.
- Plank T. (2005) Constraints from Thorium/Lanthanum on sediment recycling at subduction zones and the evolution of continents. J. Petrol. 46, 921–944.
- Plank T. and Langmuir C. H. (1993) Tracing trace elements from sediment input to volcanic output at subduction zones. *Nature* 362, 739–743.
- Plank T. and Langmuir C. H. (1998) The chemical compositions of subducting sediments and its consequences for the crust and mantle. *Chem. Geol.* 145, 325–394.
- Raleigh C. B. (1968) Mechanisms of plastic deformation of olivine. J. Geophys. Res. 73, 5391–5406.

- Ranero C. R., Phipps Morgan J., McIntosh K. and Reichert C. (2003) Bending-related faulting and mantle serpentinization at the Middle America trench. *Nature* 425, 367–373.
- Shi R. D., Yang J. S. and Wu C. L. (2004) The evidence of SHRIMP formed Late Sinina of Yushigou ophiolite in North Qilian Mountain. *Acta Geol. Sin.* 78, 649–657.
- Sleep N. H., Meibom A., Fridriksson T., Coleman R. G. and Bird D. K. (2004) H₂-rich fluids from serpentinization: geochemical and biotic implications. *Proc. Natl. Acad. Sci. USA* **101**, 12818– 12823.
- Song S. and Su L. (1998) Plastic rheology of the Yushigou mantle peridotite and implications for dynamics of Paleo-Plate movement in the North Qilian Mountains. *Acta. Geol. Sin.* 72, 131– 141.
- Song S., Zhang L., Niu Y. L., Song B., Zhang G. and Wang Q. (2004) SHRIMP ages of ultra-high pressure eclogites from North Qilian Orogeny and tectonic significance. *Chin. Sci. Bull.* 49, 592–595.
- Song S., Zhang L., Niu Y. L., Su L., Song B. and Liu D. Y. (2006) Evolution from oceanic subduction to continental collision: a case study of the Northern Tibetan Plateau based on geochemical and geochronological data. J. Petrol. 47, 435–455.
- Song S., Su L., Niu Y. L. and Zhang L. (2007a) Petrological and geochemical constraints on the origin of garnet peridotite in the North Qaidam ultrahigh-pressure metamorphic belt, Northwestern China. *Lithos* 96, 243–265.
- Song S., Zhang L., Niu Y. L., Wei C., Liou J. G. and Shu G. M. (2007b) Eclogite and carpholite-bearing meta-pelite in the North Qilian suture zone, NW China: implications for Early Paleozoic cold oceanic subduction. J. Metamorph. Geol. 25, 547–563.
- Stolper E. M. and Newman S. (1994) The role of water in the petrogenesis of Mariana trough magmas. *Earth Planet. Sci. Lett.* **121**, 293–325.
- Su L., Song S. and Wang Z. (1999) CH₄-rich fluid inclusions in the Yushigou mantle peridotite and their implications, North Qilian Mountains China. *Chin. Sci. Bull.* 44, 1992–1995.
- Sun S.-S. and McDonough W. F. (1989) Chemical and isotopic systematics of oceanic basalt: implications for mantle composition and processes. In *Magmatism in the Ocean Basins*, vol. 42 (eds. A. D. Saunders and M. J. Norry). Geol. Soc. Spec. Publ., pp. 313–345.
- Tatsumi Y. and Eggins S. (1995) Subduction Zone Magmatism. Blackwell Science, Cambridge, MA, 211pp.
- Tatsumi Y., Hamilton D. L. and Nesbitt R. W. (1986) Chemical characteristics of fluid phase from a subducted lithosphere and origin of arc magmas: evidence from high-pressure experiments and natural rocks. J. Volcanol. Geoth. Res. 29, 293–309.
- Taylor W. R. and Green D. H. (1988) Measurement of reduced peridotite–C–O–H solidus and implications for redox melting of the mantle. *Nature* 332, 349–352.
- Williams Q. and Hemley R. J. (2001) Hydrogen in the deep earth. Ann. Rev. Earth Planet. Sci. 29, 365–418.
- Wood B. J., Bryndzia L. T. and Johnson K. E. (1990) Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science* 248, 337–345.
- Woodland A. B. and Koch M. (2003) Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth Planet. Sci. Lett.* **214**, 295–310.
- Wyllie P. J. (1987) Transfer of subcratonic carbon into kimberlites and rare earth carbonatites. *Geochem. Soc. Spec. Publ.* 1, 107– 119.
- Wyllie P. J. and Ryabchikov I. D. (2000) Volatile components, magmas, and critical fluids in upwelling mantle. J. Petrol. 41, 1195–1206.

- Zhang Q., Zhou C. and Wang Y. (2003) The distribution of time and space of Chinese ophiolites and their tectonic settings. *Acta Petrol. Sin.* **19**, 1–8.
- Zhang G. B., Song S. G., Zhang L. F. and Niu Y. L. (2008) The subducted oceanic crust within continental-type UHP metamorphic belt in the North Qaidam, NW China: evidence from petrology, geochemistry and geochronology. *Lithos* 104, 99– 118.
- Zhang M. J., Hu P. Q., Niu Y. L. and Su S. G. (2007) Chemical and stable isotopic constraints on the origin and nature of volatiles in sub-continental lithospheric mantle beneath eastern China. *Lithos* **96**, 55–66.

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