Geochemical and petrological evidence for a suprasubduction zone origin of Neoarchean (ca. 2.5 Ga) peridotites, central orogenic belt, North China craton

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ABSTRACT

The 2.55–2.50 Ga Zunhua and Wutaishan belts within the central orogenic belt of the North China craton contain variably metamorphosed and deformed tectonic blocks of peridotites and amphibolites that occur in a sheared metasedimentary matrix. In the Zunhua belt, dunites comprise podiform chromitites with high and uniform Cr-numbers (88). Peridotites and associated picritic amphibolites are characterized by light rare earth element (LREE)–enriched patterns and negative high field strength element (HFSE: Nb, Zr, and Ti) anomalies. They have positive initial ε_{HF} values (+7.9 to +10.4), which are **consistent with an extremely depleted mantle composition. Mass-balance calculations indicate that the composition of the 2.55 Ga man-** **tle beneath the Zunhua belt was enriched in** $\rm SiO_2$ and $\rm FeO_T$ compared to modern abyssal **peridotites. These geochemical signatures are consistent with a suprasubduction zone geodynamic setting. Metasomatism of the subarc mantle by slab-derived hydrous melts and/or** fluids at ca. 2.55 Ga is likely to have been the **cause of the subduction zone geochemical signatures in peridotites of the Zunhua belt.**

In the Wutaishan belt, chromitite-hosting harzburgites and dunites display U-shaped rare earth element (REE) patterns and have high Mg-numbers (91.1–94.5). These geochemical characteristics are similar to those of Phanerozoic forearc peridotites. The dunites might have formed by dissolution of orthopyroxene in reactive melt channels, similar to those in modern ophiolites. However, they differ in detail, and they might be residues of Archean komatiites. Following the initiation of an intra-oceanic subduction zone, **they were trapped as a forearc mantle wedge between the subducting slab and magmatic** arc. Slab-derived hydrous melts infiltrating **through the mantle wedge metasomatized the depleted mantle residue, resulting in U-shaped rare earth element (REE) patterns.**

Keywords: Archean, peridotite, suprasubduction, picrite, spinel, trace element, North China craton.

INTRODUCTION

Geochemical and structural characteristics of magmatic rocks in Archean greenstone-granitoid terranes have been shown to be useful in providing significant new insights concerning the geodynamic origin of Archean greenstone belts and the evolution of the Archean mantlecrustal system (Sylvester et al., 1997a; Condie, 1994, 1998; Dostal and Mueller, 1997; Polat

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et al., 1998; Kusky and Polat, 1999; Polat and Hofmann, 2003; Dostal et al., 2004). In this study, we report the following new data from peridotites occurring in the 2.55–2.50 Ga Zunhua structural and Wutaishan greenstone belts of the central orogenic belt in the North China craton (Fig. 1): (1) whole-rock major-element data and inductively coupled plasma–mass spectrometer (ICP-MS) trace-element data (12 samples); (2) microprobe mineral majorelement data (e.g., chromite, olivine, pyroxene, spinel; over 1000 measurements); and (3) whole-rock multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS) Lu-Hf isotope data (10 samples). On the basis of the new geochemical data and field observations, we characterize the Archean mantle composition beneath the central orogenic belt, discuss the petrogenetic processes, and interpret the geodynamic history of peridotites. Existing models are also revisited.

The central orogenic belt is one of the largest Neoarchean-Paleoproterozoic orogenic belts in the world, extending over 1500 km from northeast to southwest in the North China craton (Fig. 1). The arc-shaped central orogenic belt separates the craton into the Eastern and Western continental blocks (Fig. 1). The central orogenic belt is composed mainly of variably metamorphosed and multiply deformed supracrustal rocks, peridotites, gabbros, granitoids, high-grade gneisses, and granulites facies metamorphic rocks (Kusky and Li, 2003; Huang et al., 2004; Kusky et al., 2004a, 2004b). These rocks have been interpreted to represent a collage of 2.55–2.50 Ga oceanic arcs, subductionaccretion complexes, backarcs, and foreland basins (Wang et al., 1996; Kusky et al., 2001; Kusky and Li, 2003; Li et al., 2004; Wang et al., 2004; Kröner et al., 2005; Polat et al., 2005).

According to the definition used in the first Penrose Conference (Anonymous, 1972), an ophiolite is a distinctive assemblage of mafic to ultramafic rocks that are believed to represent the oceanic crust and upper mantle formed at oceanic spreading centers. However, most ophiolites typically occur as dismembered, allochthonous units in accretionary and collisional orogenic belts (Coleman, 1977; Moores, 1982; Şengör, 1990; Kusky and Bradley, 1999; Dilek, 2003a, 2003b; Şengör and Natal'in, 2004). Geological data accumulated from the studies of ophiolites and oceanic crust in the Ocean Drilling Program over the last two decades suggest that there are diverse types of ophiolites with different lithological, structural, petrological, and geochemical characteristics (Dilek, 2003a, 2003b). Accordingly, it is now widely accepted that ophiolites originate in a variety of ways in several different tectonic settings, including mid-ocean ridges, oceanicisland arcs, forearcs, backarcs, and oceanic plateaus (Dewey, 2003; Dilek, 2003a; Kusky, 2004; Şengör and Natal'in, 2004).

The presence of ophiolites in Archean orogenic belts remains controversial, given that little is known about Archean oceanic crust (Sylvester et al., 1997b; Condie, 1997; Kusky and Polat, 1999; Dilek, 2003a; Kusky, 2004). The question of whether the Archean geological record shows the existence of ophiolites remains unresolved (Bickle et al., 1994; Abbott, 1996; Kusky, 2004; Zhao et al., 2005). There are two possible reasons for this uncertainty. Geologists working in Archean orogenic belts have been looking for a Penrose-type complete ophiolite section (see Dilek, 2003a; Kusky, 2004; Şengör and Natal'in, 2004). Given several generations of deformation and multiple episodes of metamorphism, finding an intact Penrose-type ophiolite in the Archean geological record is unlikely. Second, if Archean oceanic crust was thicker due to potentially higher mantle temperatures (Sleep and Windley, 1982; McKenzie and Bickle, 1988), then it is possible that only the crustal section was obducted or accreted, and the ultramafic sections were subducted. Dilek (2003a) suggested that thick basaltic sequences, with or without komatiites, which occur in many Archean greenstone belts, likely represent the remnants of Caribbean-type oceanic-plateau ophiolites.

Notwithstanding these problems, partial sections of Archean ophiolites have tentatively been identified (de Wit, 2004; Shchipansky et al., 2004). Ultramafic rocks in the Wutaishan

Figure 1. Tectonic map of the North China craton (NCC), showing the locations of study areas in the central orogenic belt (modified after Li et al., **2002).**

belt have been interpreted as remnants of Late Archean oceanic lithosphere, scraped off from a westerly dipping oceanic slab and accreted as slices in a subduction-accretion complex (Wang et al., 1996). Similarly, Kusky et al. (2001) interpreted ultramafic to mafic rocks in the Dongwanzi area of the central orogenic belt as a dismembered Neoarchean ophiolite. Li et al. (2002) documented the presence of peridotites, gabbros, pillow basalts, and podiform chromitites in the Zunhua structural belt, which is located along strike approximately 70 km to the southwest of the Dongwanzi area (Fig. 2). However, given the structural and magmatic complexity of the region, it is not clear whether ultramafic rocks in the Dongwanzi, Zunhua, and Wutaishan areas represent fragments of the same magmatic assemblage. Results of recent structural analyses and geological mapping have revealed that the rocks of the central orogenic belt contain oceanic assemblage rocks with strong early tectonic fabrics overprinted by later collisional fabrics and several generations of magmatism and metamorphism (Kusky et al., 2004a, 2004b, 2006).

REGIONAL GEOLOGY

Zunhua Belt

The North China craton is traditionally divided into two major continental blocks, the Western and Eastern blocks, which are separated by the Neoarchean-Paleoproterozoic central orogenic belt that extends across the craton (Fig. 1). The Western block contains a thick platform-type sedimentary cover intruded by a narrow belt of 2.55–2.50 Ga arc plutonic rocks along its eastern margin. The Eastern block contains a variety of 3.8–2.5 Ga gneisses and greenstone belts, which are locally covered by 2.6–2.5 Ga sandstones and carbonates, which have been interpreted by Kusky and Li (2003) to represent a passive margin–foreland basin sequence. Geochronological studies indicate that some supracrustal assemblages and intrusive rocks, including rhyolites, amphibolites, and granitoids, in the central orogenic belt formed between 2.6 and 2.5 Ga (Liu et al., 1985; Wu et al., 1998; Wilde et al., 2002; Zhao et al., 2002; Wilde et al., 2005).

The Zunhua structural belt is characterized by blocks of dismembered ultramafic rocks dispersed in a sheared paragneissic matrix (Fig. 2; Li et al., 2002; Huang et al., 2004; Kusky et al., 2004a). The blocks consist mainly of metamorphosed dunites, harzburgites, lherzolites, olivine pyroxenites, podiform chromitites, gabbros, and amphibolites possibly of a pillow basalt origin (Fig. 2). The belt is mainly metamorphosed to amphibolite facies, and is

separated from an Archean granulite-gneiss dome of the Eastern block by a major NE-striking thrust zone (Kusky et al., 2004a). Granulites occur to the west and north of the belt (Fig. 2A). The thrust zone contains tectonically intercalated tonalite-trondhjemite-granodiorite (TTG) and garnet-bearing gneisses, mafic volcanic rocks, banded iron formations (BIF), and granites (Kusky et al., 2001; Wu et al., 1998; Wu and Zhong, 1998; Fang et al., 1998). More than 1000 peridotite boudins, ranging from several meters to several kilometers in length, have been recognized (Li et al., 2002; Huang et al., 2004). Re-Os isotopic analyses of podiform chromitites occurring in the dunites have yielded an age of 2547 ± 10 Ma (Kusky et al., 2004b). The mafic and ultramafic boudins occur in a fine-grained biotite-gneiss matrix, and are interpreted as tectonic blocks in an ophiolitic mélange complex (Fig. 2; Li et al., 2002). Many parts of the mélange were intruded by the 2.5–2.4 Ga tonalites and granodiorites, and were deformed again in the Proterozoic. The Zunhua structural belt was intruded by mafic dikes and granites in the Paleoproterozoic (Wu and Geng, 1991). The belt is overlain unconformably by unmetamorphosed Mesoproterozoic sedimentary sequences.

Wutaishan Belt

The 2.55–2.50 Ga Wutaishan greenstone belt, also known as the Wutai Complex in the literature, is located in the central part of the orogenic belt (Fig. 1; see Wang et al., 1996, 2004; Kusky and Li, 2003). It is composed mainly of 2533– 2513 Ma mafic to felsic bimodal volcanic rocks, and siliciclastic sedimentary rocks, and volcanogenic massive sulfide deposits and banded iron formations are present (Li et al., 2004; Wilde et al., 2005). It is structurally underlain by a mélange complex, consisting mainly of chromitite-hosting harzburgite and dunite blocks dispersed in a sedimentary matrix (Wang et al., 1996; Kusky and Li, 2003). An excellent review of the evolution of pre- to postvolcanic (relative to Wutaishan felsic to intermediate volcanic rocks) granitoids in the Wutaishan Complex is given by Wilde et al. (2005). They recognized two major phases of granitoid magmatism, one in the Late Archean ranging in age from 2560 Ma to 2515 Ma, and the other one in the Early Proterozoic, between 2170 and 2120 Ma (Wilde et al., 2005; Wilde and Zhao, 2005). Prevolcanic granitoids were emplaced between 2560 and 2545 Ma, whereas synvolcanic granitoids were intruded between 2540 and 2515 Ma (Liu et al., 2004; Kröner et al., 2005; Wilde et al., 2005; Wilde and Zhao, 2005). Contacts between granitoids and greenstones are generally sheared,

obscuring the original relationships (Wilde et al., 2005).

The Wutaishan greenstone belt is located between two high-grade gneissic terranes, the Hengshan Complex to the northwest (western block) and the Fuping Complex to the southeast (eastern block). The Hengshan Complex is composed mainly of 2.7–2.5 Ga amphibolite to granulite facies orthogneisses (Zhao et al., 2001, 2002). The Fuping Complex is characterized dominantly by amphibolite-grade TTG gneisses (Guan et al., 2002; Zhao et al., 2002). Both complexes were intruded by granitoids between 2520 and 2480 Ma (Kröner et al., 2005). The gneisses contain numerous inclusions of mafic granulites and amphibolites, and record polyphase deformation and multiple events of metamorphism.

The Wutaishan greenstone belt has been structurally divided into lower, middle, and upper subgroups (Tian, 1991; Kusky and Li, 2003, and references therein). The lower group is composed of mafic to felsic volcanic rocks, and stable continental-margin sedimentary rocks, collectively at amphibolite facies. Volcanogenic massive sulfide (VMS)-hosting volcanic rocks occur as tectonic slices of a mélange complex within a sedimentary matrix (Wang et al., 1996; Kusky and Li, 2003; Li et al., 2004). The middle group consists of mafic to felsic volcanic rocks and banded iron formations at greenschist facies. The upper group includes quartzites, siltstones, and phyllites at sub–greenschist facies. Given discontinuities of metamorphic grade between the subgroups, these are likely tectonic slices.

PETROGRAPHY

Peridotites in the Zunhua belt are largely tectonized serpentinites from harzburgite and lherzolite protoliths. The petrography of seven samples discussed next consists of serpentine + picotite-magnetite spinel \pm brucite \pm amphibole \pm orthopyroxene \pm augite. Olivine is extremely rare and, where present, is metamorphic in origin, as are orthopyroxene and clinopyroxene. Pentlandite, barite, and chlorite are accessory minerals.

Pyroxenes in olivine pyroxenites are partly replaced by amphiboles. Given deformation and metamorphism, no primary volcanic textures and minerals have been preserved in amphibolites. Amphibolites are dominantly actinolite, with minor amounts of opaque minerals. Amphibolite samples from low-strain zones are characterized by prismatic crystals, whereas counterparts from high-strain zones show a fibrous texture. Podiform chromitite pods are encased in a matrix of serpentine and magnetite (Fig. 3). They contain an abundance of inclusions of ser p entine + talc \pm chlorite \pm tremolite.

Figure 2. Geological maps of the Zunhua area (modified after Li et al., 2002). TTG—tonalite-trondhjemite-granodiorite.

Peridotites in the Wutaishan belt are mainly harzburgites and dunites. The four samples discussed next were originally dunites and consist of fresh olivine + serpentine + magnetite \pm chlorite \pm amphibole. As discussed next, there is some indication that the olivines formed by metamorphism of a serpentinite protolith, but more work is needed to evaluate this possibility. Pentlandite, barite, calcite, and ilmenite are accessory minerals.

GEOCHEMICAL RESULTS

Mineral Chemistry

Clinopyroxene

Diopside occurs in Zunhua samples ZU02-07, ZU02-08, and ZU02-14 (Table $DR1¹$). They are compositionally uniform at MgO = 17.2–17.6 wt%, FeO = $2.1 - 2.6$ wt%, CaO = $24.0 - 24.6$ wt%, $SiO_2 = 53.9 - 54.6$ wt%, and Mg-number = 92.2–93.6 (see Table DR1). They have moderate variations in Al_2O_3 (0.79–1.6 wt%) and TiO₂ $(0.02-0.06 \text{ wt\%})$ concentrations, and are compositionally similar to clinopyroxenes in peridotites from active subduction zones, such as Izu-Bonin-Mariana (Mg-number = 94.6–96.1; Ishii et al., 1992; Parkinson and Pearce, 1998) and the Lesser Antilles (Mg-number = 91.0–93.5; Parkinson et al., 2003). They are also similar to clinopyroxenes from the peridotite section of the Oman ophiolite (Mg-number = 92–94; Takazawa et al., 2003).

Orthopyroxene

Samples ZU02-04 and ZU02-08 contain enstatite (Table DR1, see footnote 1). The composition of this mineral is homogeneous in Mgnumber (89.0–89.8), CaO (0.26–0.29 wt%), MgO (33.6–34.2 wt%), and SiO_2 (56.3–57.0 wt%). Compositions of coexisting augite and orthopyroxene in sample ZU02-08 yield 774– 789 °C at 3–10 kgbars using the thermometer of Brey and Köhler (1990), which is consistent with upper amphibolite facies temperatures.

Olivine

Serpentinization of the Zunhua peridotites is pervasive, and olivines are only rarely present. One sample was found to have olivine $(Mg-number = 94.5)$ surrounded by serpentine and magnetite; the extremely high Mg-number indicates that it might be metamorphic in origin, formed by amphibolite facies metamorphism of pre-existing serpentine.

The Wutaishan dunites are unique in having an abundance of fresh olivines with very high Mg-numbers (94.0–95.6; Table DR2, see footnote 1). Olivine Mg-numbers vary by about ± 2 at the 2σ level within individual samples, and a value of 97.0 has been reliably obtained in samples 2002-88 and 2002-89. These olivine compositions generally reflect the high Mgnumbers of the whole rocks (Polat et al., 2005), but the range might have arisen by metamorphism of serpentinite protoliths. Olivines with these compositions are not commonly found in modern peridotites. They compare with Mg-numbers of 89.5–91.5 for olivines in most abyssal peridotites (Dick, 1989; Seyler and Bonatti, 1997), 90.5–91.9 for olivines in Oman peridotites (Takazawa et al., 2003), 90.4–92.1 for olivines from the peridotite section of the Bay of Islands ophiolite (Suhr and Edwards, 2000), and 92.6–92.9 for olivines in the Pozanti-Karsanti dunites (Parlak et al., 2002). They are significantly higher even than 93.2, which is the value from olivines that occur in some peridotites from the Izu-Bonin-Mariana arc (Parkinson and Pearce, 1998). Wutaishan whole rocks and olivines are comparable, however, to some dunite fossil melt channels in the Bay of Islands and Luobusa ophiolites (Suhr et al., 2003; Zhou et al., 2005). They are also similar to olivine phenocryst phases in komatiites of Archean age (e.g., Nisbet et al., 1993; Renner et al., 1994), and to model residues of Al-undepleted komatiites (Herzberg, 2004).

Spinel and Magnetite

Most Zunhua peridotites contain two spinel phases. The most abundant phase is referred to as the host spinel; they are picotites, with Mgnumbers in the 10.3–47.7 range and Cr-numbers in the 36.0–72.3 range (Table DR1, see footnote 1). The less abundant phase occurs with two distinct textures and compositions (Table DR1). The first type is small, round Cr- and Al-rich magnetite inclusions dispersed throughout the host spinel found in peridotites ZU02-4, ZU02- 05, ZU02-08; these are clearly associated with the host spinel and are of exsolution or redox origin. The second is nearly pure magnetite that is distributed throughout the sample and is fortuitously associated with the host spinel as rims and cracks (ZU02-01, ZU02-02, ZU02-07); we interpret these as mobilized magnetite after serpentinization of primary olivine.

The relative abundances of host and inclusion spinels were determined by modal analysis of backscatter scanning-electron microscope (SEM) images. This permitted an estimate to be made of the bulk spinel composition prior to exsolution by integrating host and inclusion spinel compositions according to their masses

Figure 3. Polished surfaces of podiform chromitites.

(Table DR1, see footnote 1). All Zunhua peridotite host and bulk spinel compositions have much lower Mg-numbers and higher Fe³⁺ contents than spinels from peridotites in modern ophiolites, abyssal ocean basins, and subduction zones (Barnes and Roeder, 2001; Parkinson and Pearce, 1998; Kamenetsky et al., 2001). Spinels in the Zunhua peridotites more closely resemble spinels found in continental mafic intrusions (Barnes and Roeder, 2001), indicating that they were a late-phase addition to the Zunhua peridotites.

All Wutaishan dunite samples contain grains of Cr-rich magnetite with an average Cr-number of 98.6 (Table DR2, see footnote 1). They have variably low Al_2O_3 (0.01–0.68 wt%), TiO₂ (0.01–0.45 wt%), and Mg-numbers (10–16). They are unlike chromium spinels in dunite melt channels from the Bay of Islands ophiolite (Suhr et al., 2003).

¹ GSA Data Repository item 2006118, mass balance calculations, is available on the Web at http:// www.geosociety.org/pubs/ft2006.htm. Requests may also be sent to editing@geosociety.org.

Amphibole

Amphiboles in the Zunhua peridotites (Table DR1, see footnote 1) are hornblende to pargasite in composition. Amphiboles in the Wutaishan peridotites (Table DR2, see footnote 1) have higher Mg-numbers and lower $AI₂O₃$ (0.44–0.50 versus 9.5–12.3 wt%) contents than Zunhua counterparts; these differences are controlled in part by substantial differences in whole-rocks compositions.

Podiform Chromites

Podiform chromites occur only in the Zunhua belt. Mg-numbers vary widely from 30 to 70, but Cr-numbers are remarkably uniform at 88 (Table DR3, see footnote 1). Samples ZZ-45 and CM10-1 contain large, disseminated chromite pods with an average Mg-number of 55, and with an average Cr-number of 88 (Table DR3). Smaller grains of chromite surrounding the large chromite pods have Mgnumbers as low as 31, with no change in Crnumber (Table DR3). Samples ZZ-56 and 1692 contain smaller clustered chromite pods with Mg- and Cr-numbers that average 50 and 88, respectively.

Major and Trace Elements

Geochemical data presented in this section represent only the least altered samples. These were selected from a larger population on the basis of alteration screening criteria outlined in Polat and Hofmann (2003). Major- and traceelement compositions of the Wutaishan peridotites were presented in Polat et al. (2005); accordingly, they are only summarized here.

Peridotites of the Zunhua belt are compositionally uniform at 37.3–41.6 wt% MgO, 40.8– 44.5 wt% SiO_2 , 11.7–15.9 wt% Fe_2O_3 , 130–160 Co ppm, and Mg-number $= 83-87$ (Table DR4, see footnote 1). They possess moderately variable Al_2O_3 (1.3–5.8 wt%), Ti (340–1020 ppm), CaO (0.1–3.0 wt%), Cr (5300–28400 ppm), Ni (1450–3300 ppm), and V (40–138 ppm) abundances (Table DR4). Ratios of $\text{Al}_2\text{O}_3/\text{TiO}_2$ $(19-44)$ and Ti/Zr $(58-213)$ range from subchondritic to super-chondritic, whereas Zr/Y (2.4–7.7) ratios are super-chondritic. In addition, they have the following geochemical features: (1) LREE-enriched patterns $(La/Sm_{n} =$ 2.1–2.9; Gd/Yb_n = 1.3–2.4); (2) negative Nb $(Nb/Nb^* = 0.10 - 0.25)$ and Ti $(Ti/Ti^* = 0.50 -$ 0.80; except sample ZU02-02) anomalies; and (3) and depletion of Zr and Hf relative to Nd and Sm, generating negative Zr and Hf anomalies ($Zr/Zr* = 0.21-0.68$; Hf/Hf^{*} = 0.23-0.81) (Fig. 4A; Table DR4). REE contents increase from dunites through harzburgites to lherzolites, whereas Ni displays the opposite trend.

Only one pyroxenite sample was analyzed (Table DR4, see footnote 1). This sample has 54 wt% SiO_2 , 0.11 wt% TiO_2 , 19 wt% MgO, 800 ppm Ni, and 3330 ppm Cr. Like peridotites, it is characterized by an LREE-enriched and HFSE-depleted primitive mantle–normalized trace-element pattern (Fig. 4; La/Sm_{cn} = 1.2; $Gd/Yb_{on} = 2.9$, $Nb/Nb^* = 0.03$, $Ti/Ti^* = 0.41$, $Zr/Zr^* = 0.51$, $Hf/Hf^* = 0.61$).

Amphibolites are characterized by 50.7–51.3 wt% SiO_2 , 0.42–0.44 wt% TiO_2 , 19.1–19.7 wt% MgO, 6.8–7.0 wt% Al_2O_3 , and 10.0 wt% Fe_2O_3 . There are small variations in Ni (796–869 ppm), Cr (2500–2960 ppm), Co (63–65 ppm), V (129– 138), Zr (49–55 ppm), Y (9–11 ppm), and REE concentrations (e.g., $La = 11-12$ ppm; Table DR4). $\text{Al}_2\text{O}_3/\text{TiO}_2$ (15–17) and Ti/Zr (48–49) ratios are sub-chondritic, whereas Zr/Y (4.6–6.9) ratios are higher than the chondritic value of 2.4 (see Sun and McDonough, 1989). MgO, Ni, and Cr concentrations are consistent with an ultramafic composition. In addition, they have the following trace-element characteristics: (1) LREE-enriched patterns $(La/Sm_{n} = 2.6-2.7,$ La/Yb_{cn} = 8.0–8.7, Gd/Yb_{cn} = 2.0–2.2); and (2) large negative Nb (Nb/Nb^{*} = $0.17-0.20$), Zr $(Zr/Zr^* = 0.53-0.64)$, Hf (Hf/Hf^{*} = 0.58-0.66), and Ti (Ti/Ti $* = 0.37 - 0.43$) anomalies (Fig. 4B; Table DR4, see footnote 1).

Dunites and harzburgites in the Wutaishan belt have narrow ranges of SiO_2 (40–42 wt%), TiO₂ (0.02–0.05 wt%), and MgO (47–52 wt%), and moderate ranges of Al_2O_3 (0.16–1.17 wt%), Cr (1300–1900 ppm), and Ni (1200–3000 ppm) concentrations (Polat et al., 2005). They have extremely low REE and HFSE concentrations $(e.g., La = 0.09 - 0.25$ ppm; $Ce = 0.20 - 0.50$ ppm; $Y = 0.31 - 2.2$ ppm; $Zr = 1 - 11$ ppm). On a chondrite-normalized diagram, they display concaveup REE patterns (Fig. 4C; La/Sm_{cn} = $0.81-1.92$; $Gd/Yb_{m} = 0.19-0.74$.

Hafnium Isotope Compositions

Lu-Hf measurements were performed using the MC-ICP-MS in Münster, Germany, following the procedure described in Münker et al. (2001) and Polat and Münker (2004). The 176Hf/¹⁷⁷Hf ratios were normalized to ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325 using the exponential law for mass bias correction. The external reproducibility of 176 Hf/¹⁷⁷Hf was ± 0.5 ε-units (2σ), which was determined by multiple digestions of rock standards. All ¹⁷⁶Hf/¹⁷⁷Hf data are given relative to a value of 0.282160 for the JMC-475 standard. Lu and Hf concentrations were measured using a mixed 180Hf-176Lu tracer.

Using a least square fitting routine (Isoplot 2.49, Ludwig, 2001, model 3 fit), we regressed the Lu-Hf data for the Zunhua peridotites, and obtained a whole-rock isochron age of 2528 \pm 130 Ma (2 σ , mean square of weighted deviates [MSWD] = 3.5) using the decay constant of Scherer et al. (2001) (Fig. 5A). The chondritic values of Blichert-Toft and Albarède (1997) were used for calculation of the initial ε_{Hf} at 2547 Ma. This age, within uncertainties, is in a good agreement with the Re-Os isochron age of 2547 ± 10 Ma obtained from the spatially associated podiform chromites (see Kusky et al., 2004b). Because of its smaller error, the latter age $(2547 \pm 10 \text{ Ma})$ is used to calculate the initial ε _{Hf} values of the Zunhua peridotites (Table DR5, see footnote 1). They are characterized by tightly clustered, large positive initial ε_{ur} (+7.9 to +10.4) values, plotting well above the depleted mantle evolution curve (Fig. 5B).

DISCUSSION

Mantle Composition and Secondary Enrichment

Similar isochron ages yielded by podiform chromites (2547 ± 10 Ma) and whole-rock samples $(2528 \pm 130 \text{ Ma})$ suggest that the amphibolite facies metamorphism that recrystallized the Zunhua peridotites took place shortly after their formation, probably within 10–30 m.y. Despite the recrystallization, the coherent REE and HFSE patterns in the Zunhua peridotites (Fig. 4C) indicate that these elements remained relatively immobile on the whole-rock scale during metamorphism. In addition, similar initial ε_{Hf} values in clinopyroxene separates (+7.4 to +9.5; Münker, 2005, personal commun.) and wholerock samples $(+7.9 \text{ to } +10.4)$ indicate that the amphibolite metamorphism did not significantly disturb the Lu-Hf isotope system. Accordingly, we suggest that the initial $\varepsilon_{\rm HF}$ values, and HFSE and REE systematics in the Zunhua peridotites represent the near-primary composition of the 2.55 Ga upper mantle beneath the Zunhua belt (broadly speaking).

The strongly positive initial ε_{Hf} values of the Zunhua peridotites are consistent with a strongly elevated Lu/Hf ratio relative to the chondritic value and a long-term depleted mantle domain (Table DR5, see footnote 1). According to the best knowledge of the authors, these initial ε_{ref} values represent the most depleted mantle composition that has been reported from Archean magmatic rocks (see Corfu and Stott, 1993, 1996; Blichert-Toft et al., 1999; Vervoort and Blichert-Toft, 1999; Polat and Münker, 2004). They plot above the commonly assumed depleted mantle evolution curve on an ε_{Hf} versus time diagram (Fig. 5). Given the observations that the majority of Archean magmatic rocks have initial ε_{HF} values between +3 and +7 (see

Figure 4. Chondrite-normalized rare earth element (REE) and primitive mantle–normalized trace-element patterns of peridotites, pyroxenites, and amphibolites (picrites) in the Zunhua and Wutaishan belts. Data for Solomon Island picrites are from Schuth et al. (2004). Chondrite normalization values are from Sun and McDonough (1989), and primitive mantle (PM) values are from Hofmann (1988).

Polat and Münker, 2004), the extreme depletion in the Zunhua peridotites is interpreted to represent a regional rather than a global depletion of the Archean mantle. Similarly, extremely low REE and HFSE concentrations and high Mg-numbers in the Wutaishan dunites and harzburgites require a strongly depleted (e.g., midocean-ridge basalt–source-like, residues left after komatiite melt extraction) mantle domain. The initial ε_{Hf} values in the Zunhua peridotites

overlap with, but extend to lower values than, modern arc lavas $(+5 \text{ to } +18)$ (Pearce et al., 1999; Woodhead et al., 2001; Borg et al., 2002; Münker et al., 2004; Schuth et al., 2004; Marini et al., 2005).

Whole-rock X-ray fluorescence (XRF) data indicate enrichment in Fe and Cr in the Zunhua peridotites compared to average upper-mantle peridotites (Herzberg, 1993, 2004). The enrichment of these elements is the effect of either an

inherited property of the Archean mantle in this area, or secondary addition to the source. The Cr and $Fe²⁺$ numbers in spinels provide greater insight into the possibility of secondary enrichment. All Zunhua peridotite host and bulk spinel compositions have much higher Fe^{2+} and Fe^{3+} contents than spinels from peridotites in modern ophiolites, abyssal ocean basins, and subduction zones (Barnes and Roeder, 2001; Parkinson and Pearce, 1998; Kamenetsky et al., 2001). Indeed,

Figure 5. (A) 176Lu/177Hf versus 176Hf/177Hf isochron diagram for Zunhua peridotites, yielding an isochron age of 2528 ± 130 Ma. (B) Hf isotopic evolution of the depleted mantle through time (modified from Bennett, 2004). The initial ε _{Hf} data for Zunhua peridotites plot well **above the depleted mantle curve, which is consistent with an extremely depleted mantle domain beneath the Zunhua belt at 2.55 Ga. Isoplot program of Ludwig (2001) and 176Lu decay constant of Scherer et al. (2001) were used for calculation of isochron age. Wawa represents the Hf isotopes of 2.7 Ga adakites (Data from Polat and Münker, 2004). MORB mid-ocean-ridge basalt; MSWD—mean square of weighted deviates.**

it can be shown that the spinels could not have been in equilibrium with the host peridotites, based on minimum whole-rock Mg-numbers of 83.4–87.4 from Table DR4 (i.e., 100MgO/ $[MgO + FeO_r]$; see footnote 1) and the olivinespinel equilibrium systematics of Kamenetsky et al. (2001). Spinels in the Zunhua peridotites more closely resemble spinels found in continental mafic intrusions (Barnes and Roeder, 2001). However, the whole-rock geochemistry of the Zunhua peridotites is similar to modern arc peridotites, and completely different from any continental mafic intrusion. The spinels are clearly a late-phase addition to the Zunhua peridotites, and this can account for the Fe and Cr enrichment in the Zunhua peridotites.

In order to determine the original composition of the mantle, spinel must be extracted from the whole-rock data. This includes host oxide phase from all seven peridotites, and inclusion oxide phases from samples ZU02-04, ZU02-05, and ZU02-08 (i.e., bulk spinels; Table DR1). We carried out such a mass balance calculation to determine the 2.55 Ga mantle composition beneath the Zunhua belt (Appendix A). For the calculation, it was assumed that the mantle had an average Cr_2O_3 content of 0.43%, the average value for peridotites reported by Herzberg

(1993). This Cr_2O_3 content is similar to those reported in other compilations (Maaloe and Aoki, 1977) and to fertile mantle peridotites (Sun and McDonough, 1995). Using Cr_2O_3 for the mass balance, we calculated that between 1.3 and 12.1% of spinel was added by mass to the original Zunhua peridotites, in good agreement with the very large spinel modes observed petrographically in some samples. The composition of the original mantle was modeled by extraction of this amount of spinel (Appendix A, in the Data Repository), and results are shown in Table DR6 (see footnote 1). The composition of the model Archean mantle contains significantly less FeO, Cr_2O_3 , Al_2O_3 , and higher SiO_2 and MgO compared to XRF whole-rock data (Tables DR1 and DR6, see footnote 1).

The FeO_r content of the 2.55 Ga mantle determined from the Zunhua peridotites corrected for spinel addition ranges from 8.45 to 12.28 wt% (Fig. 6A; Table DR6), which is higher than average spinel lherzolite of 8.31 wt% (Herzberg, 1993), and higher than residues of fractional melting (Herzberg, 2004). Therefore, these peridotites cannot be simple residues for any assumed fertile peridotite. There are two possible explanations for the elevated FeO_r of the Zunhua peridotites: (1) the Archean mantle was intrinsically enriched in FeO_r (Francis et al., 1999), or (2) Fe was metasomatically added to some precursor mantle composition.

The mass balance calculations indicate that the Zunhua peridotites are also enriched in $SiO₂$ compared to simple residues (Figs. 6A and 6C). The results of extraction calculations reveal 45.33–45.98 wt% $SiO₂$ for the Zunhua peridotites (Table DR6, see footnote 1). The Si enrichment may be attributed to a melt/rock reaction (Kelemen et al., 1998; McInnes et al., 2001), and is seen in peridotites from both active subduction zones (Parkinson and Pearce, 1998; Herzberg, 2004) and some kimberlite-hosted cratonic mantle xenoliths of Archean age (Kelemen et al., 1998; Herzberg, 2004). However, there is an important difference between Si-rich cratonic mantle xenoliths and the Zunhua peridotites. Cratonic mantle xenoliths are low in FeO_T , whereas Zunhua peridotites are variably enriched in FeO_T . In this sense, the Zunhua peridotites more closely resemble peridotites from modern arcs and forearcs (Fig. $6B$) and ophiolites (Fig. $6C$). Fe enrichment in modern subduction zones probably arises from addition of Fe3+ from melts or hydrous fluids from the subducting slab (Parkinson and Arculus, 1999; Lécuyer and Ricard, 1999). It has been suggested that this oxidized metasomatic component also adds SiO_2 , which reacts with peridotite in the mantle wedge to produce orthopyroxene (Herzberg, 2004). Accordingly, we attribute the enrichment of Si and Fe

Figure 6. $(A-C)$ FeO $_T$ and SiO $_2$ versus MgO **variation diagrams for the Zunhua peridotites and Wutaishan dunites. Zunhua peridotites are model compositions corrected for spinel addition (Table DR6, see text footnote 1). The Wutaishan dunites are from Polat et al. (2005). Numbered lines in panels B and C indicate initial melting pressures of model residue compositions of fertile peridotite (Herzberg, 2004). Many peridotites from modern arcs and ophiolites are too enriched** in SiO₂ to be residues, as are the Zunhua **peridotites.**

in the Zunhua peridotites to a secondary metasomatic process, one that also elevated LREE, as we discuss in the following.

Mantle Metasomatism

In contrast to large ion lithophile element (LILE) and LREE, Hf (Zr) concentrations in the subarc mantle wedge are not significantly affected by mantle metasomatism (Pearce et al., 1999; Münker et al., 2004). The Hf isotopic compositions of the Zunhua peridotites are consistent with a long-term depleted mantle reservoir that was strongly depleted in incompatible elements (e.g., Th, Nb, Zr, Hf, Ti, and LREE). The incompatible trace-element–enriched primitive mantle–normalized patterns, however, imply that the depleted mantle must have been fertilized by metasomatism. These peridotites appear to have been fluxed with LILE- and LREE-enriched and HFSE-depleted subduction-derived siliceous fluids and/or hydrous melts, similar to a present-day subduction setting (cf. Saunders et al., 1991; Pearce and Peate, 1995; Peate et al., 1997; Hawkins, 2003; Münker et al., 2004). Similarly, the U-shaped REE patterns of the Wutaishan peridotites likely resulted from metasomatism of a depleted mantle by slab-derived hydrous melts or fluids (Polat et al., 2005).

Studies of mantle xenoliths in modern arc lavas suggest that Si-rich hydrous melts or fluids migrating through the subarc mantle wedge are responsible for the metasomatism of the mantle (Kepezhinskas et al., 1996; Takazawa et al., 2000; McInnes, et al., 2001; Kamenetsky et al., 2002). Hornblende, pargasite, and orthopyroxene are found as metasomatic assemblages in subarc mantle xenoliths. These metasomatizing melts and fluids are characterized by LILE- and LREE-enriched and Nb- and Ti-depleted traceelement patterns, and contain high SiO_2 and FeO_r concentrations (Kepezhinskas et al., 1996; Takazawa et al., 2000; McInnes, et al., 2001). For example, metasomatic veins in Kamchatka

xenoliths have high SiO_2 and FeO_T contents, and high FeO_r/MgO ratios (Kepezhinskas et al., 1996). On the basis of these observations, we suggest that subduction zone geochemical signatures in the Zunhua peridotites have been inherited from interaction between slab-derived metasomatic fluids and the Late Archean subarc mantle wedge.

Xenoliths from metasomatized subarc mantle in Papua New Guinea have U-shaped REE patterns (Franz et al., 2002). U-shaped REE patterns have also been reported from modern forearc peridotites (e.g., Izu-Bonin-Mariana, South Sandwich) and peridotites from several Phanerozoic ophiolites (e.g., Oman, New Caledonia, Trinity, Zhangbo, Luobusa; Bay of Islands) (Ishii et al., 1992; Parkinson and Pearce, 1998; Pearce et al., 2000; Suhr and Edwards, 2000; Takazawa et al., 2000; Bodinier and Godard, 2004; Dubois-Côté et al., 2005; Zhou et al., 2005). The U-shaped patterns in these peridotites are explained as products of interaction of mantle with LREE-enriched slabderived melts or fluids (Godard et al., 2000; Pearce et al., 1999). Although no boninitic volcanic rocks have been found in the Wutaishan belt, it is likely that the U-shaped REE patterns and high Mg-numbers in the Wutaishan peridotites were produced by geochemical processes in an Archean suprasubduction zone similar to

Phanerozoic forearc peridotites and ophiolites (see Bodinier and Godard, 2004).

Cr-diopside peridotite xenoliths from continental lithosphere below the Canadian Cordillera display similar subduction-related metasomatic properties in REE and HFSE (Peslier et al., 2002). These authors have ascribed arc metasomatism as a cryptic event unrelated to prior melt extraction, a process that can occur at the base of the lithosphere. We interpret the Zunhua peridotites somewhat differently, in that both the trace and major elements were subduction related. They are more depleted in Al_2O_3 and CaO, similar to arc peridotites, but we acknowledge that additional work might reveal more fertile samples. Additionally, the association of the Zunhua peridotites with podiform chromitites favors a subduction zone setting (see Edwards et al., 2000).

A more complex problem surrounds the origin of the Wutaishan dunites prior to metasomatic enrichment. Whole-rock analyses (Polat et al., 2005) show the dunites have Mg-numbers of 93.5–94.5, similar to some olivines in dunites from the Bay of Islands and Luobusa ophiolites (Suhr et al., 2003; Zhou et al., 2005). These have been interpreted to be the products of incongruent melting of orthopyroxene in peridotite by slab-derived infiltrating hydrous melts (Suhr et al., 2003; Zhou et al., 2005). However, the

Figure 7. Fe number (Fe²⁺/Fe²⁺ + Mg) versus Cr-number (Cr/Cr + Al), comparing Zunhua podiform chromites with those of abyssal peridotites, mantle xenoliths, and ophiolitic chromites. Filled circles are analyses of 100 chromites in four podiform chromitite samples.

Wutaishan dunites differ in detail; they do not have similar spinel compositions, and wholerock Cr_2O_3 is about half. The crosscutting, metasomatic replacement field characteristics seen in the Bay of Islands and Luobusa ophiolites are not seen in the Wutaishan area, but this might be because of limited field exposure. It is notable that the Wutaishan dunites are very similar to olivine cumulates in Archean komatiites and to olivines that are expected in the residues of these komatiites (Herzberg, 2004). However, no komatiites have been reported in our field area, indicating they may be residues rather than cumulates. More work is needed to examine this alternative possibility.

Origin of Podiform Chromites

Individual analyses (a total of 100) of podiform chromites were performed on four samples from the Zunhua belt; these are shown in Figure 7, and averages are given in Table DR3 (see footnote 1). The Cr-numbers of these chromites are remarkably constant at 88.0. They are compositionally similar to the more chromiumrich chromites in ophiolites reported by Barnes and Roeder (2001), but outside the field defined by continental mafic intrusions (Fig. 7). Compared to chromites in the same area reported by Zhang et al., (2003a) and discussed in Zhao et al. (2005), they have higher but overlapping Cr-numbers, and lower but overlapping $Fe²⁺$ numbers (Fig. 7). Zhao et al. (2005) concluded that these chromitites were formed in continental mafic–ultramafic intrusions. However, Barnes and Roeder (2001) also showed that a substantial part of the field defined by continental mafic–ultramafic intrusions cannot be distinguished from the ophiolite field (Fig. 7). In this case, the podiform texture of the chromites in our samples is helpful because they are not characteristic of continental mafic-ultramafic intrusions (Barnes and Roeder, 2001). Indeed, the only place that podiform chromites are found is in ophiolite settings (Barnes, 2005, personal commun.).

On the basis of experimental studies, Matveev and Ballhaus (2002) showed that waterrich fluids percolating through the uppermost mantle play an important role in the generation of podiform chromitites. The upper mantle beneath the mid-ocean ridges is too dry to exsolve a water-rich fluid at a depth where podiform chromitite would form. Current models for the origin of podiform chromitites require a combination of crystal fractionation and melt peridotite reaction as hydrous basaltic melts migrate through the upper mantle (Edwards et al., 2000). In keeping with these constraints, and the common association of podiform chromitites with ophiolites, we suggest that the presence of podiform chromitites in the Zunhua belt indicates a Late Archean subarc mantle wedge origin for these rocks.

Geodynamic Origin for Peridotites in the Zunhua and Wutaishan Belts

There is an ongoing debate about whether the peridotites in the central orogenic belt are ophiolitic fragments or intracontinental intrusions (Li et al., 2002; Kusky, 2004; Kusky and Li, 2003; Zhai et al., 2002; Zhang et al., 2003a, 2003b; Zhao et al., 2005). Given the absence of a complete Penrose-type ophiolitic sequence in the Zunhua and Wutaishan belt, Zhang et al. (2003a, 2003b) and Zhao et al. (2005) argued for a continental intrusion origin for peridotites in these belts in particular, and in the central orogenic belt in general.

Most of the known Precambrian and Phanerozoic intracontinental ultramafic-mafic intrusions are exposed as a single large body with mafic rocks dominating the lithology (Wager and Brown, 1967; Eales and Cawthorn, 1996; Emeleus et al., 1996; Mathison and Ahmat, 1996; McBirney, 1996). These intrusions range from several kilometers to several hundreds of kilometers in size, rather than as hundreds of smaller lenticular bodies, as seen in the central orogenic belt. In contrast, dismembered fragments of ophiolites in various sizes occur as mélange blocks throughout the Phanerozoic Altaid, Tethyan, and circum-Pacific orogenic systems (Gansser, 1974; Şengör and Natal'in, 2004, and references therein).

If peridotites in the Zunhua and Wutaishan belts were intruded as small pocket of melts, similar to their present sizes, into the continental crust, they would have been crustally contaminated given high country rock/melt ratio. The strongly positive initial ε_{Hf} (+7.9 to +10.4) values are inconsistent with contamination of these rocks by continental crust. Large negative Nb anomalies (Nb/Nb $* = 0.10 - 0.25$) in the Zunhua peridotites could have resulted from continental contamination. However, the presence of large negative Zr $(Zr/Zr^* = 0.21-0.68)$ and Hf $(Hf/Hf^* = 0.23-0.81)$ anomalies is inconsistent with crustal contamination, given that the average Archean upper continental crust had small negative Zr and Hf anomalies $(Zr/Zr^* = 0.97;$ $Hf/Hf^* = 0.85$; Taylor and McLennan, 1995).

We prefer an intra-oceanic suprasubduction zone ophiolitic origin over intracontinental intrusion for the following geological and geochemical reasons: (1) more than a thousand fragments of lenticular-shaped peridotites and associated mafic volcanic rocks, ranging from several tens of meters to several kilometers in length, have been recognized in the central orogenic belt (Li et al., 2002); (2) they are discontinuously exposed as mélange blocks for over 600 km (Li et al., 2002; this study); (3) podiform chromitites with high Cr-numbers are present (see Edwards et al., 2000; Barnes and Roeder, 2001; Matveev and Ballhaus, 2002); (4) there is an absence of crustal contamination; and (5) major- and traceelement geochemistry and isotopic compositions of whole rocks are very similar to those for peridotites from modern subduction zones and subduction-influenced ophiolites.

CONCLUSIONS AND IMPLICATIONS FOR GEODYNAMIC SETTING

Northwest and Wutaishan Southeast the central orogenic belt Western Block Zunhua and Wutaishan periodotites Eastern Block

2.60-2.55 Ga Geodynamic evolution of

Late Tertiary–Quaternary island-arc picrites have been documented in the Solomon and New Hebrides (Vanuatu arc) oceanic-island arcs (Ramsay et al. 1984; Eggins, 1993; Schuth

et al., 2004). The generation of these picrites appears to be associated with the subduction of young, hot oceanic crust, resulting in higher geothermal gradients compared to island arcs associated with the subduction of old, cold oceanic crust. The depletion of HFSE (Nb, Ta, Zr, Hf, Y) relative to LREE in these lavas is attributed to the metasomatism of the mantle source by slab-derived hydrous fluids or melts (Schuth et al., 2004). In the Solomon Islands, picrites occur only in New Georgia Island above the subducting Woodlark spreading center. In the New Hebrides subduction system, the overriding plate is currently undergoing extension in the east of the Vanuatu arc, forming the North Fiji Basin as a suprasubduction ophiolite (Pearce, 2003). We suggest that the Zunhua picrites and peridotites formed in a similar tectonic setting (Fig. 8).

At the present time, we cannot accurately restore the original depleted mantle composition prior to metasomatism because we do not have data on a sufficient number of samples. However, modern backarc peridotites removed from the effects of metasomatism are too low in FeO and high in Al_2O_3 to be mid-ocean-ridge basalt (MORB) residues (Herzberg, 2004). Their petrology is more consistent with residues expected from magma extraction in a hotter plume environment below an oceanic plateau (Herzberg, 2004). Niu et al. (2003) examined this possibility, and they concluded that modern subduction might be initiated at locations where there is a change from ridge-type to plateau-type oceanic lithospheric mantle. A similar line of reasoning might apply to the Archean (cf. Polat et al., 1998), although it is noted that the higher ambient mantle potential temperatures might have produced ridge-type Archean residues that are similar to Phanerozoic plume-type residues (Herzberg, 2004).

The U-shaped REE patterns of dunites and harzburgites in the Wutaishan belt are consistent with a suprasubduction zone geodynamic setting, as are the associated mafic to felsic volcanic rocks. Slab-derived hydrous melts that metasomatized the depleted upper mantle resulted in U-shaped REE patterns (Fig. 4). The dunites might have formed through dissolution of orthopyroxene in reactive melt channels, similar to those in Phanerozoic ophiolites. However, they might be residues of Archean komatiites located at the edge of an Archean oceanic plateau where subduction was initiated. More work is needed to evaluate these possibilities.

Whatever model we prefer for the origin of the Zunhua and Wutaishan peridotites, it is clear that their identity has become obscured by at least two metasomatic events. The first was likely to be hydrous fluids of subduction origin, which determined the REE and HFSE contents, and we expect that this occurred when the Zunhua and Wutaishan peridotites were trapped between the subducting slab and magmatic arc, forming the basement of the forearc ophiolite(s). During closure of the ocean between the Eastern and Western blocks, peridotites of the forearc oceanic lithosphere were emplaced onto the Eastern block, and they were further deformed and dismembered during the collision of the two blocks at ca. 2.5 Ga. We expect that a late metasomatic event added Fe- and Cr-rich spinels, possibly by magmatism that postdated closure of the ocean between Eastern and Western blocks.

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