**Forum**

**Dating of zircon from Ti-clinohumite–bearing garnet peridotite: Implication for timing of mantle metasomatism: Comment and Reply**

**COMMENT**

Jian-Jun Yang*

*LTE Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences, P.O. Box 9825, Beijing 100029, China*

Katayama et al. (2003) dated zircon in some ultramafic rocks dominated by garnet and titanian clinohumite (hereafter Ti-clinohumite rocks) from the Kokchetav ultrahigh-pressure (UHP) metamorphic terrane, and interpreted that the zircon cores formed in the mantle in the Proterozoic and the zircon overgrowths formed as a result of UHP metamorphism and mantle metasomatism by slab-induced fluids/melt during the early Paleozoic. However, the data presented in this and their foregoing papers (Muko et al., 2002; Okamoto et al., 2000) cast considerable doubt about their interpretation and conclusions.

Metasomatism of mantle peridotite by crustal materials adds Si (and conceivably Ti, Al, Fe, Ca, Na, K, and large ion lithophile elements), and removes Mg (and conceivably Cr, Ni, and Co). The mantle metasomatism proposed by Katayama et al. (2003) does not explain why the rocks are even more depleted in Si, Na, and K than garnet peridotites (Muko et al., 2002) (Fig. 1), or how the enormous amount of Al, an element known to be relatively immobile in fluid and melt, could be added into a peridotite to produce abundant garnet. Garnet rims in the Kokchetav Ti-clinohumite rocks are significantly higher in Mg relative to the cores (Muko et al., 2002), suggesting that the rocks were enriched in Mg rather than Fe before or during UHP metamorphism.

Katayama et al. (2003) suggested that large amounts of Ti and other high field strength elements (HFSE) were added into a peridotite protolith by metasomatism, based on the experiments by Iizuka and Nakamura (1995) at 80 kbar. The pressure estimates for the Kokchetav UHP rocks are mostly ≤60 kbar, although Okamoto et al. (2000) argued for ≥60 kbar. At these conditions, fluid derived from crustal materials is not enriched in Ti but in Si, causing olivine to transform into pyroxene (Iizuka and Nakamura, 1995). The high HFSE and H2O contents in Ti-clinohumite rocks do require metasomatism, but not necessarily of garnet peridotite in the subduction zone. In contrast, Scambelluri and Rampone (1999) demonstrated that the Ti-clinohumite–bearing rocks from western Liguria (Italy) were derived from Fe-Ti gabbros by Mg metasomatism in an oceanic crust and subsequent high-pressure metamorphism. A Ti-clinohumite rock similar to the Kokchetav ones occurs in the Chinese Su-Lu UHP metamorphic terrane (Yang, 2003). In terms of MgO, CaO, Fe2O3, and Al2O3 compositions, the Ti-clinohumite rocks are intermediate between ultramafites and unaltered Fe-Ti gabbros (Fig. 1). Mg metasomatism of a Fe-Ti gabbroic protolith by fluids from a contacting mantle-derived ultramafic rock in the crust may explain the enriched feature of Ti (and other HFSE), Fe, Al, Mg, Cr, Co, Ni, and volatiles and the depleted feature of Si, Ca, and Na in the Su-Lu Ti-clinohumite rock (Yang, 2003). Subsequent UHP metamorphism at a mantle depth transformed the altered gabbro into assemblages characterized by garnet + Ti-clinohumite + pyroxene + zircon + apatite. It is likely that similar chemical and tectonic processes took place in the Kokchetav Ti-clinohumite rocks, because these also better explain their chemical features.

The Proterozoic zircon cores are interpreted by Katayama et al. (2003) to have formed at depths where plagioclase or spinel was stable. The zircon cores contain high U and some also contain high Th (Table 1 in Katayama et al., 2003), suggesting that they may have formed in crustal materials. The zircon overgrowths contain much lower U and Th, indicating involvement of mantle components. This is consistent with the Mg metasomatism–UHP metamorphism scenario proposed above, but not with the corner convection hypothesis (Katayama et al., 2003). Moreover, pristine mantle peridotites are known to be depleted in Zr and can hardly contain zircon (Bea et al., 2001, and references therein). On the other hand, zircon could be abundant in gabbroic rocks, and it could continue to grow while the rocks transform into Ti-clinohumite rocks during subduction.

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*E-mail: jjyang@mail.igcas.ac.cn.*
REPLY

Ikuo Katayama*
Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520, USA

Atsumi Muko
Department of Earth Sciences, Waseda University, Tokyo 169-8050, Japan

Juhn G. Liou
Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA

We welcome the comments by Yang, who proposed that the Kokchetav ultramafic rocks have an Fe-Ti gabbroic protolith based on whole-rock major element chemistry (Muko et al., 2002), and have been subjected to a Mg metasomatism at crustal depths. The Kokchetav Ti-clinohumite–rich rocks described in our paper contain abundant volatile and high field strength element (HFSE)–bearing minerals. Combined with zircon U/Pb dating and trace element characteristics, we interpreted these features as fluid-infiltrated mantle metasomatism at a subduction zone.

The Kokchetav ultramafic rocks have clearly experienced long and complex metamorphic evolution that consequently buries their original histories as well as compositions. They contain abundant serpentine and amphibole minerals along secondary veins that resulted from later stage overprinting during exhumation. The whole-rock analysis would therefore include an effect of such alteration, and to use major chemistries to correlate the nature of protolith for metamorphic rocks, as shown by Yang, could be greatly misleading. However, examination of mineral inclusion and compositional zonation of refractory minerals, such as garnet and zircon, can reveal evidences prior to such overprintings (e.g., Schertl et al., 1991; Zhang et al., 1997; Katayama et al., 2000).

Compositions of garnet from the Ti-clinohumite–bearing ultramafic rocks compared with those from different rock types are shown in Figure 1. The analyzed garnet has similar composition to that of orogenic peridotites in the Dabie Mountains (Zhang et al., 1995), but is significantly different from those of associated eclogites and diamond-bearing pelitic gneisses from the same locality (Shatsky et al., 1995; Zhang et al., 1997; Okamoto et al., 2000). The garnet displays a pronounced zonation with increasing pyrope content from core (51–56 mol%) to rim (58–63 mol%). The pyrope-rich rim contains abundant inclusions of Ti-clinohumite, ilmenite, zircon, and apatite; in contrast, the garnet core includes green spinel, amphibole, and phlogopite. The absence of Ti-bearing phases in the garnet core suggests that Ti enrichment occurred during high-pressure recrystallization. This fact is not consistent with the suggestion of the Fe-Ti gabbroic protolith enriched in Mg during magnesite metasomatism prior to subduction as proposed by Yang. Trace element abundance of stubby-shaped zircon separated from the ultramafic rocks (see Figure 3 in Katayama et al., 2003) also indicates that they recrystallized at high pressures where garnet is stable. The zircon rare earth element abundances display significantly different patterns from those of associated eclogite and country gneisses, but are similar to the characteristics reported in kimberlite. The calculated pressure (>35 kbar) required for the coexistence of low-F Ti-clinohumite, olivine, and ilmenite is consistent with our proposed model.

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