

## A note on compositional variation of olivine and pyroxene in thermally metamorphosed ultramafic complexes from SW Japan

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This short article presents some diagrams showing the compositional variations of primary and metamorphic olivine, orthopyroxene and clinopyroxene in peridotites and serpentinites from thermally metamorphosed ultramafic complexes in SW Japan. In contrast to olivine, which shows a gradual change of chemical composition corresponding with metamorphic grade, orthopyroxene and clinopyroxene show clear differences in composition between primary and metamorphic phases. Compared with primary pyroxenes, even though their compositions could be variable depending on original rock composition, metamorphic orthopyroxene and metamorphic clinopyroxene is clearly deficient in  $\text{Cr}_2\text{O}_3$  and  $\text{CaO}$ , and in  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , respectively. These characteristics are useful for the discrimination between the pyroxenes of different origin.

**Keywords:** chemical composition, olivine, orthopyroxene, clinopyroxene, metaperidotite

### I. Introduction

Prograde and retrograde metamorphism of mantle peridotites is important for understanding several aspects of global mass balance, and geological and geophysical processes at variable tectonic settings.

The most effective retrogression process of peridotites is serpentinization, which commonly forms serpentine, brucite, chlorite, secondary clinopyroxene, magnetite, and minor amounts of Fe- or Fe-Ni sulfides/metals. Relict grains of primary minerals originated in mantle peridotites, such as olivine, orthopyroxene, clinopyroxene and chromian spinel or chromite, locally occurs where serpentinization is incompleteness. On the other hand, prograde metamorphism after serpentinization commonly takes place as well in most of peridotites exposed on land, and forms variable mineral association of olivine, orthopyroxene, Mg-Fe-amphibole, Ca-amphibole, talc and Al-spinel, depending on pressure-temperature conditions and whole-rock compositions. As a consequence, the simultaneous occurrence of primary and metamorphic olivine and pyroxene is commonly observed in ultramafic complexes that were metamorphosed after partial serpentinization. The distinction between these minerals of different origin is necessary for understanding the metamorphic processes and tectonic history of the lithospheric mantle.

Many of ultramafic complexes exposed in SW Japan were originated from the upper mantle and were thermally metamorphosed after serpentinization. This short article presents some compositional diagrams showing characteristics of primary and metamorphic olivine, orthopyroxene and clinopyroxene in these ultramafic complexes for coming comparative studies.

### II. Outline of regional geology and thermal metamorphism

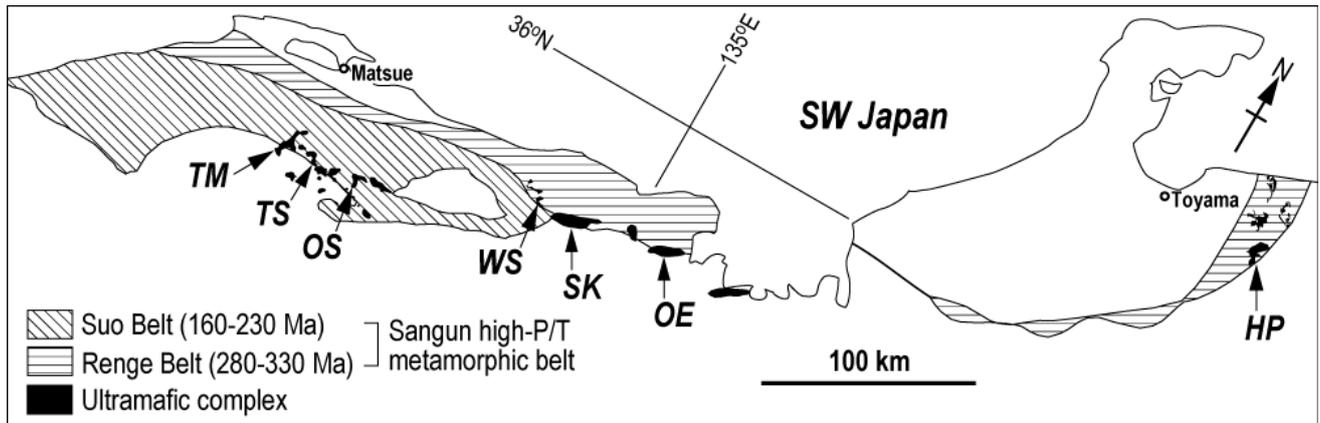
Ultramafic complexes are sporadically exposed in so-called "Sangun high-P/T metamorphic belt" in SW Japan (Fig.1; Igi and Sakamoto, 1977; Hattori, 1978; Mitsuno and Uchida, 1980; Ishiwatari, 1989, 1990; Nishimura, 1998; Takeuchi, 2002; Teraoka et al., 1996). The ultramafic complexes consist mainly of serpentinized harzburgite and dunite that contain small amounts of relict primary minerals. Arai (1980) interpreted the peridotites as refractory residues left after partial melting of primitive peridotites and as dismembered ophiolites embedded in Paleozoic accretionary complexes. The ultramafic complexes and surrounding regional metamorphic or Paleozoic sedimentary rocks were thermally metamorphosed by Cretaceous intrusions of granitic, dioritic or, locally, more basic rocks.

Each of the thermally metamorphosed ultramafic complexes in SW Japan can be divided into four or five metamorphic zones (Fig. 2; Arai, 1975; Matsumoto *et al.* 1995; Nozaka and Shibata, 1995; Nozaka, 2003). Zone I is almost unaffected by thermal metamorphism, whereas Zones II, III, IV and V are characterized by the first appearance of metamorphic olivine, talc, anthophyllite and orthopyroxene, respectively, indicating increasing temperatures of metamorphism from Zone II to V. In Zone V, cordierite, aluminous spinel and clinopyroxene rarely occurs in aluminous rocks (Arai, 1975; Nozaka and Shibata, 1995). The cordierite-bearing rocks look to be derived from chromitite (Arai, 1975).

The existence of relict grains of primary olivine, orthopyroxene, clinopyroxene, and chromian spinel or chromite is obvious in less serpentinized peridotites in Zone I and more sparsely in Zone II. The primary silicate

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**Figure 1.** Distribution of ultramafic complexes and the Sangun high-P/T metamorphic belt in SW Japan (Igi and Sakamoto, 1977; Hattori, 1978; Mitsuno and Uchida, 1980; Ishiwatari, 1989, 1990; Nishimura, 1998; Takeuchi, 2002; Teraoka et al., 1996). Abbreviations for ultramafic complexes: TM, Tari-Misaka; TS, Takase; OS, Ohsayama; WS, Wakasa; SK, Sekinomiya; OE, Oeyama; HP, Happo.

minerals are relatively coarse-grained and free from opaque inclusions. Primary orthopyroxene and clinopyroxene are prismatic in shape, and each of them has exsolution lamella of the other (e.g., Nozaka and Shibata, 1995).

Metamorphic minerals produced by thermal metamorphism can be distinguished from primary minerals by means of spatial distribution and mode of occurrence (e.g., Nozaka and Shibata, 1995). Metamorphic olivine is commonly fine-grained and contains many inclusions of opaque minerals (mostly magnetite). Metamorphic orthopyroxene, which occurs exclusively in Zone V, is free from the exsolution lamella of clinopyroxene, contains abundant opaque inclusions, and frequently forms radial or fan-shaped aggregates. Clinopyroxene looks to be absent in thermally metamorphosed rocks with normal peridotitic composition. Instead, secondary (retrograde) clinopyroxene, which looks to coexist with serpentine, occurs as fine-grained acicular or rhomboid crystals, selvages replacing primary clinopyroxene, or aggregates forming veinlets set in a serpentine matrix in Zone I and low-grade parts of Zone II. The secondary clinopyroxene lacks exsolution lamella of orthopyroxene.

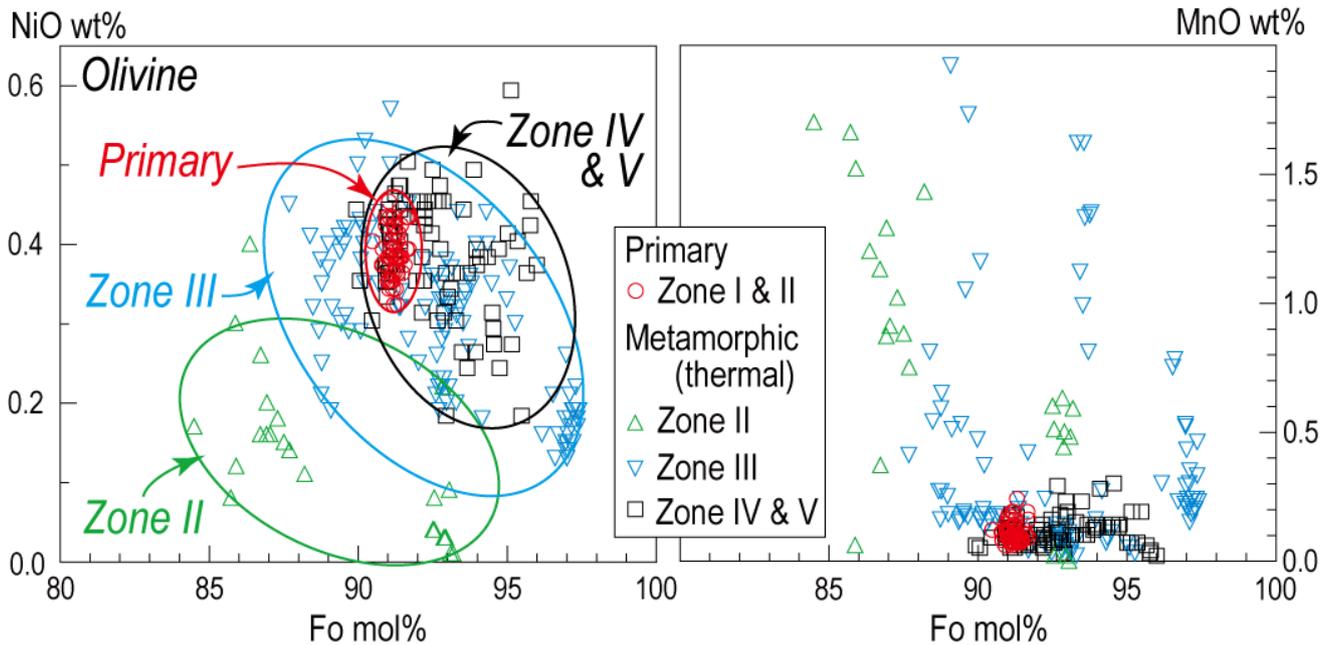
### III. Compositional variations of olivine and pyroxenes

Chemical compositions of minerals were analyzed using a JEOL JXA-733 electron microprobe at Okayama University (for procedures, see Nozaka, 2005). Chemical compositions of primary minerals derived from residual mantle peridotites are almost homogeneous, whereas those of metamorphic minerals are significantly

Zone	I	II	III	IV	V
Srp	■	■			
Cpx	■	■			
Cam			■	■	■
Ol		■	■	■	■
Tlc			■		
Ath				■	
Opx					■

**Figure 2.** Distribution of metamorphic silicate minerals in peridotites/serpentinities from each zone of thermally metamorphosed ultramafic complexes in SW Japan (compiled after Arai, 1975; Matsumoto et al. 1995; Nozaka and Shibata, 1995; Nozaka, 2003). Abbreviations for minerals: Ath, anthophyllite; Cam, calcic amphibole (tremolite up to lower-grade Zone V; hornblende in upper-grade Zone V); Cpx, clinopyroxene; Ol, olivine; Opx, orthopyroxene; Srp, serpentine; Tlc, talc. Primary minerals are omitted from this figure.

heterogeneous even within individual grains. Some chemical variables were selected for the illustration of the compositional variations of minerals (Figs. 3-5). Among the ultramafic complexes investigated, the Oeyama, Wakasa and Happo complexes (Fig. 1) show evidence for crystallization from differentiated basaltic melts and/or re-equilibration during high-temperature retrogression



**Figure 3.** NiO and MnO vs. Fo contents of olivine in serpentinized mantle peridotites and thermally metamorphosed serpentinites/peridotites from SW Japan. Composition range of metamorphic olivine from each zone is drawn excluding a point with the highest NiO content, which was obtained in the proximity to an opaque inclusion, in order to show a general tendency of the shift of compositional range with increasing metamorphic grade.

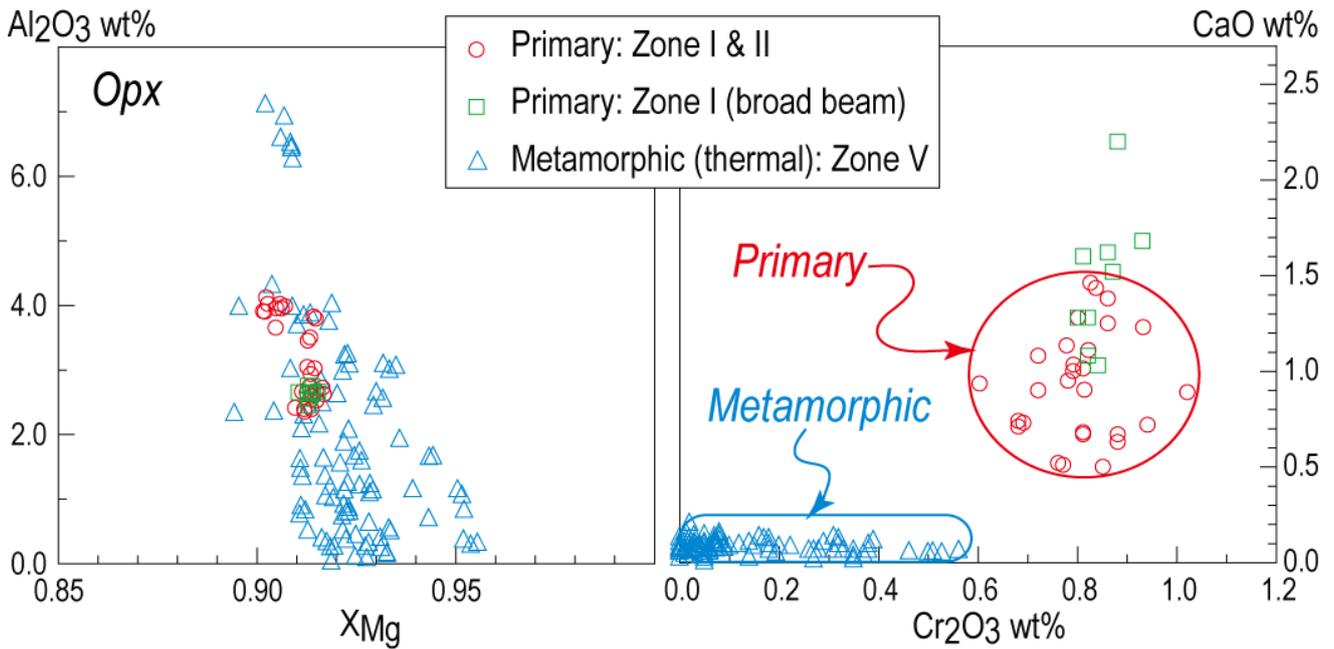
(Nozaka, 2005; Nozaka and Ito, in press). Minerals from these complexes are omitted from Figs. 3-5, except for primary orthopyroxene from an Oeyama harzburgite that is similar to mantle peridotites in mineral assemblage, texture and mineral composition, and for secondary clinopyroxene coexisting clearly with serpentine in the Diopside Zone of the Happo complex.

Olivine in Zones II-V shows variations in NiO, MnO and Fo contents (Fig. 3). Corresponding with increasing metamorphic grade, the compositions of metamorphic olivine become less variable and approach those of primary olivine, suggesting the progress of intracrystalline cation diffusion and homogenization of olivine (see also, Nozaka, in press). The simultaneous occurrence of primary and metamorphic olivine is evident in Zone II (Nozaka, 2003). The frequency of the occurrence of primary olivine in Zones I and II suggests that relict grains of primary olivine are not uncommon in higher grade zones as well. However, the existence of primary olivine in these zones has been obscured, probably because of the progress of cation diffusion between primary and metamorphic grains of olivine.

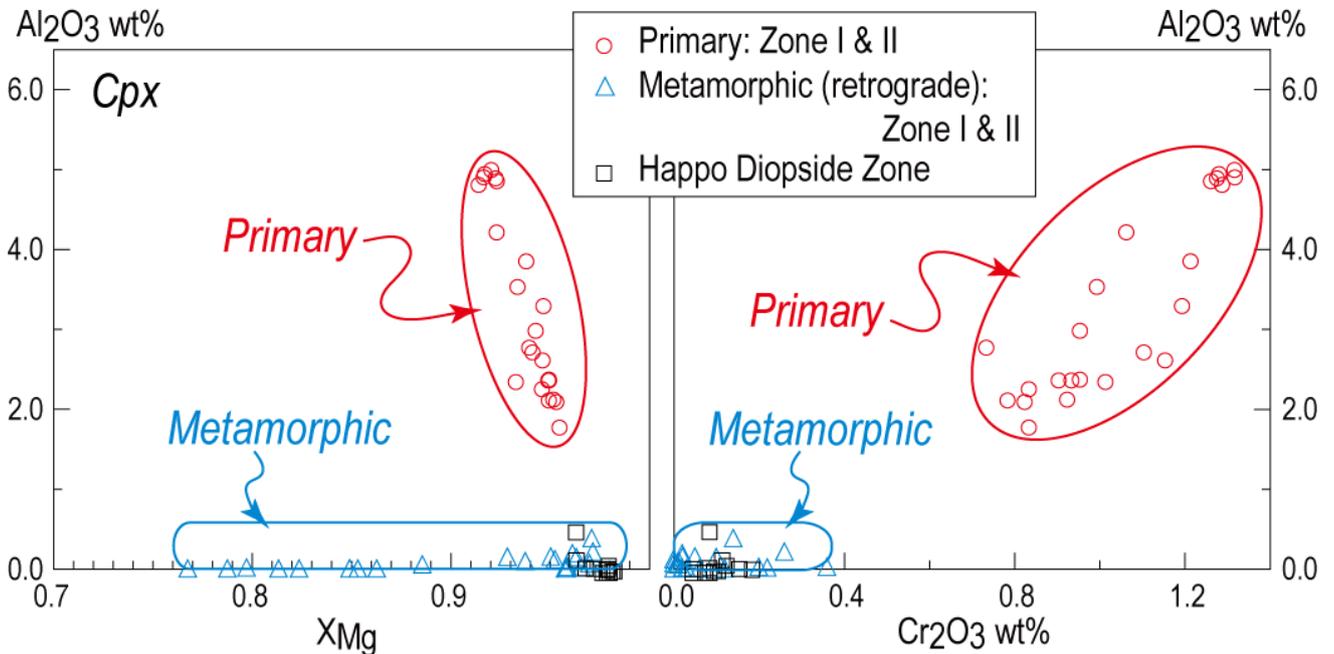
Orthopyroxene in Zone V shows significant variation in  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  contents, and  $\text{XMg}$  [=Mg/(Mg+Fe)], compared with primary orthopyroxene (Fig. 4). However, in the  $\text{Al}_2\text{O}_3$ - $\text{XMg}$  diagram, there is an overlapping range of composition between primary and metamorphic

orthopyroxene, and it is impossible to distinguish the two groups of orthopyroxene by means of these variables. In contrast, the  $\text{CaO}$ - $\text{Cr}_2\text{O}_3$  diagram shows no overlap of the ranges of two types of orthopyroxene (Fig. 4). Although the electron-probe analyses of primary orthopyroxene may be affected by adjacent clinopyroxene lamella, analyses using a defocused, broad beam (30  $\mu\text{m}$  in diameter) indicate that the involvement of lamellar clinopyroxene yields an enrichment of Ca without significant changes in other elements, and the composition of orthopyroxene itself can be known by careful examination of data. It is clear that deficiency in CaO is a prominent feature of metamorphic orthopyroxene, and the  $\text{CaO}$ - $\text{Cr}_2\text{O}_3$  diagram is useful for the discrimination of orthopyroxene (Fig. 4). The existence of relict primary orthopyroxene in contact aureoles is expected as the case of olivine. However, relict grains of primary orthopyroxene have never found in Zones III-V. The primary orthopyroxene was probably decomposed by the formation of talc in Zone III and anthophyllite (though sluggish; see Nozaka, in press) in Zone IV, and by the recrystallization of orthopyroxene in Zone V.

Clinopyroxene formed during retrograde alteration or serpentinization occurs in a minor amount in low-grade, Zones I and II. Where original peridotites are relatively rich in Ca like the Happo complex, the occurrence of secondary clinopyroxene is frequent. The  $\text{XMg}$  of



**Figure 4.**  $\text{Al}_2\text{O}_3$  vs.  $\text{XMg}$  [=Mg/(Mg+Fe)] and  $\text{CaO}$  vs.  $\text{Cr}_2\text{O}_3$  contents of orthopyroxene in serpentinized mantle peridotites and thermally metamorphosed serpentinites/peridotites from SW Japan. Broad-beam (30  $\mu\text{m}$  in diameter) probe analyses of primary orthopyroxene are shown in order to know the effect of thin exsolution lamella of clinopyroxene.



**Figure 5.**  $\text{Al}_2\text{O}_3$  vs.  $\text{XMg}$  and  $\text{Al}_2\text{O}_3$  vs.  $\text{Cr}_2\text{O}_3$  contents of clinopyroxene in serpentinized mantle peridotites from SW Japan. Metamorphic clinopyroxene with low  $\text{XMg}$  (< 0.9) forms veinlet aggregates in a serpentine matrix. The compositions of retrograde clinopyroxene from the Happo ultramafic complex, in which primary clinopyroxene has not been found, are also shown for comparison.

clinopyroxene that coexists with serpentine is commonly high ( $> 0.95$ ), but some grains of secondary clinopyroxene, particularly those of veinlet aggregates have  $X_{Mg}$  lower than primary clinopyroxene (Fig. 5). Although the compositions of primary clinopyroxene are variable, secondary clinopyroxene is distinguishable by means of the deficiencies in  $Al_2O_3$  and  $Cr_2O_3$  (Fig. 5). Because of the presence of the overlap of  $X_{Mg}$ , the more useful for the discrimination between primary and secondary (i.e., retrograde) clinopyroxene is the  $Al_2O_3$ - $Cr_2O_3$  diagram (Fig.5).

#### IV. Summary

The range of compositional variation of olivine in thermally metamorphosed serpentinites, as described in previous studies, gradually changes corresponding with metamorphic grade, and in high-grade zones, metamorphic olivine is indistinguishable in composition from primary olivine. In contrast, orthopyroxene and clinopyroxene show clear differences in composition between primary and metamorphic phases. Compared with primary pyroxenes, even though their compositions could be variable depending on original rock composition (i.e., degree of depletion), metamorphic orthopyroxene and metamorphic (retrograde) clinopyroxene is clearly deficient in  $Cr_2O_3$  and  $CaO$ , and in  $Cr_2O_3$  and  $Al_2O_3$ , respectively. These characteristics are useful for the discrimination between the pyroxenes of different origin.

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