Interactive comment on “Possibility of titanium transportation within a mantle wedge: formation process of titanoclinohumite in Fujiwara dunite in Sanbagawa belt, Japan” by S. Ishimaru and S. Arai

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We greatly appreciate these comments, which are very helpful to carefully reconsider our results. We revised manuscript as you suggested and followings are the replies to specific comments

Major comments #1. Based on geochemical and petrological features, we judged the Fujiwara dunite is a cumulate from intraplate high-Ti magma within the oceanic lithosphere. At first the Fujiwara dunite was serpentinized at the ocean floor, and followed by deserpentination process during prograde metamorphism (Sanbagawa metamorphism) along subducting slab. Second serpentinization occurred during exhumation
process of the Sanbagawa metamorphic belt including the Fujiwara complex (cf. Fig. 9). But unfortunately our previous manuscript failed to convey the history properly. We modified introduction and discussion parts to convey the whole story.

1. Introduction We rewrote the statement of mobility of Ti via aqueous fluid, and at the last part we refer to what are the points for discussion in this paper as you suggested.

p.206, line 18-19: We used the words “serpentinites” and “serpentinitized ultramafic rocks” to refer to the difference in degree of serpentinization, but we did not show exact discrimination. Then, we deleted “serpentinites” in this sentence to mean the metagabbro-serpentinitized ultramafic rock complexes.

p.207, line 5-7: We deleted Scanbelluri et al. (2001) and Khedr and Arai (2010) as references in this section as you suggested. There are some papers discussing about the metamorphic processes (e.g., Onuki et al., 1978; Enami, 1980) and their cumulus origin of the Fujiwara complex (Enami, 1980; Kunugiza, 1984) (see introduction part).

p.207, line 20-22: In current situation, it is totally impossible to make new field observations to check relationships between dunite and other members of the Fujiwara complex (metagabbro and wehrlite), but Onuki et al. (1978) and Ishibashi et al. (1978) described their relationships in detail as we referred to in the manuscript.

p.208, line 3-4: See #1. These samples clearly show “breccia-like” textures in their protoliths. It is now just showing the difference in degree of serpentinization between the clasts and matrix, and is not a breccia formed after metamorphism.

p. 208: line 5: Carbonates are not the main phase and are not observed in all 5 thin sections we examined. If present, carbonates are in contact with magnetite, chlorite, olivine and titanoclinohumite irrespective of the carbonate species (dolomite or Ca carbonate). We judged carbonates are prograde phase based on textural equilibrium with other prograde metamorphic phases, especially that one Ca carbonate grain is rimmed by the magnetite that was formed during the first serpentinization stage.
p. 208, line 9-10 and other lines: The reason why you cannot see titanoclinohumite in some plate is their small size. We changed some panels for better understanding of readers as you suggested.

p. 208, line 13: We added a new panel (f) for showing methane fluid inclusion.

p.209, line 8-11: As we stated in text, the mode of occurrence of titanoclinohumite is unfortunately unclear on the outcrop. We safely can say, however, that the titanoclinohumite veinlet is not continuous over a few meters.

4.1. Major-element compositions We prefer this way of presentation. The way we took in Table 1 does have a great merit to know coexisting phases in individual samples. As you commented, we added cation ratios of each mineral, and we replaced some data with better ones in quality.

About Ti-Chu 1. Fluorine was not detectable in our qualitative analysis even though F content occasionally shows positive correlations with the TiO2 content in titanoclinohumite (e.g. Gaspar, 1992). This does mean that F is absent in our titanoclinohumite. 2. We could not see any compositional differences depending on their textural types. We added one sentence about this situation in the text. 3. Then, we added one section referring to the Ti substitution in 5.1. 4. We could not see any definition of titanoclinohumite in “Rock forming minerals 1A”, and also many examples call “titanoclinohumite” even for low-TiO2 clinohumite (e.g., Okay, 1994; Zhang et al., 2007).

About ludwigite But the analyzed oxide total for ludwigite (1-ldw-2) in Table 1 actually included B2O3, (15.46 wt%), so the total of 101.19 % was not so bad. In addition, recalculated Mg# of this ludwigite is quite low (≈ 0.5) due to the low MgO content (21.8 wt%). That is, the data quality is not so bad. We modified the way of data showing in Table 1 to avoid misunderstandings.

4.2. Trace-element compositions

As we stated in the sample description section, all the samples we examined are
dunite. We analyzed 4 dunite samples to determine trace-element compositions of minerals.

We analyzed all the elements shown in Fig. 6 but the elements not shown are below their detection limits. We added lines showing detection limits in each panel.

4.3. Raman spectroscopy We determined fluid phase in relatively coarse olivine and titanoclinohumite. First, the fluid inclusion in lamellar titanoclinohumites is very low in abundance. We think all types of titanoclinohumite have been formed simultaneously during prograde metamorphism, and then the fluid phases are not so different each other, if any.

There are no H2O inclusions but the presence of brucite and serpentine without talc implies the initial presence of H2O as a component.

5.2. Ti source for the formation of titanoclinohumite As we modified the sentence about modal amounts of clinopyroxenes, it is quite a minor phase. The TiO2 content of clinopyroxene is not so high in dunite from oceanic hot spots; most of them are less than 1 wt% (e.g., Klügel, 1998; Neumann et al., 2002), as compared with chromian spinel (up to 3.5 wt%) in the Fujiwara dunite. Contribution from clinopyroxene as a Ti source was so low due to its composition and volume in the Fujiwara dunite.

1. Yes, we think ferritchromite and magnetite were formed during serpentinization prior to deserpentinization. 2. Magnetite with chromian spinel core is occasionally associated with chlorite but no obvious relation with tremolite. 3. Relatively coarse grains (>100 \( \mu \)m) have spinel or ferritchromite core survived from further alteration, and the degree of their survival basically depends on the size and the species of coexisting minerals. As we described, the degree of modification to magnetite is high even for coarse spinel grain (≈500 \( \mu \)m) when in contact with titanoclinohumite. In summary, the small magnetite grain was formed by breakdown of olivine, and the coarse one was possibly formed by modification of the primary chromian spinel during serpentinization. 4. We cannot understand why this contradicts with p. 209, l. 5-7, but tried to change
this sentence to avoid misleading. We found perovskite only in the titanoclinohumite vein, but we discussed its possibility for the Ti source of titanoclinohumite. 5. We found only one grain of ilmenite in sample T4-1. Based on petrography, ilmenite was formed simultaneously with titanoclinohumite.

We discussed here that Ti from chromian spinel was not sufficient in thin section scale, and stated as “This indicates that, although chromian spinel is possibly the source of Ti, the Ti addition is indispensible for formation of titanoclinohumite within a limited volume of the sample”. We think that Ti was locally concentrated via fluid from other part of Fujiwara dunite.

p. 215, line 14-22: Yes, but we have no good standard for LA-ICP-MS analysis, especially for calculations of HFSE in chromian spinel. Here we just pointed out the possibility and we should check this in the future.

5.3. Titanoclinohumite formation process and HFSE mobility p.216, line 1.: Relatively low-Mg# olivines without magnetite inclusions may be primary, but it is very hard to identify which is of primary or recrystallization (deserpetinization) origin under the microscope.

p. 216, line 9: We added the explanation.

p. 216, line 5-7: See reply to the comment to 5.2.

p.216, line 9-24: We added some sentences about the relation between the Sanbagawa metamorphism and the deserpentinization process of the Fujiwara dunite.

Reactions1 and 2: Methane was not involved in the reaction, indicating that the methane was not a reaction product from H2O-CO2 fluid and minerals.

p.216, line25-26: Water is very reactive with silicates to form hydrous minerals. There are a few reports of water inclusions even from peridotite xenoliths from arc settings. We assume that there were water inclusions but changed to antigorite and brucite through reaction with their host (e.g., Arai & Hirai, 1985; Mizukami et al., 2004).
p.217, line 2-6: See the reply to the comment for p. 208: line 5.

p. 217, line 7-9: We slightly modified this part.

p. 217, line 9-14: We added some sentences explaining these things in section 5.2.

Fig. 9: We added some explanations about this figure. The reason why we draw retrogressive path is that the Fujiwara complex is a part of the Sanbagawa metamorphic complex, of which P-T trajectory is well known (Enami, 2004; Mizukami and Wallis, 2005). P-T trajectory of Bessi unit shows the Sanbagawa metamorphism. Higashiakaishi unit is composed of ultramafic rocks originated from mantle wedge.

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