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Solid Earth Discussions

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

Anonymous Referee #1

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Referee Comment

This manuscript displays some interesting data about metane fluid inclusions in Ti-Chu from serpentinized dunites. The work is, nevertheless, hampered by an incomplete field and petrographic description, by low quality and disordered mineral chemistry data, and by some a priori hypothesis (about the origin of Ti and the significance of the studied processes for mantle wedge environments) not sufficiently supported by data or discussed arguments. Accordingly, I am afraid the paper should be rejected and rewritten. Detailed suggestions and comments below could eventually be helpful for this latter task.

Specific comments

0. Abstract

It should be rewritten after questions below are addressed.

1. Introduction

First paragraph should be rewritten and connected with the main challenge of this paper: explaining the influence of the fluid composition on the formation of Ti-Chu. The possibility that the studied rocks come from the mantle wedge should be discussed in the discussion.

First sentence of introduction (page 204, lines 23-24) is based on a reference applying to low temperature processes. See López Sánchez-Vizcaíno et al. (2009; Lithos) and references therein for evidences indicating that Ti is a rather mobile element in certain metamorphic environments and specifically during metamorphism of ultramafic rocks.

Page 204, Lines 25-26. This is a too categorical statement and deserves, at least, a reference supporting it.

page 205,lines 3-5. It is not evident why the mentioned experimental results imply the presence of HFSE in the mantle wedge.

page 205,lines 8-10. It is not correct to write a simplified chemical formula of Ti-Chu as there are several substitutions controlling it. See Trommsdorff and Evans, 1980.

Other references concerning experimental works on Ti-Chu stability should be also included (Weiss, 1997)

page 206,lines 10-11. There is, again, no support for deducing that these results are relevant for the mantle wedge processes.

2. Geological background

page 206,lines 18-19. Explain the difference between serpentinites and serpentinized ultramafic rocks. Explain what you mean with "their complexes".

page 207,lines 5-7. None of the two cited works refers to the Fujiwara complex. The Khedr and Arai paper deals with a relatively nearby complex, but this (unless you give arguments supporting this) does not necessarily mean that they have the same origin and evolution. In fact, you have already said that some serpentinites have been interpreted as fragments of mantle wedge and some others as being original from the oceanic lithosphere. Are there specific papers on the origin of the Fujiwara Complex? In case they exist they should be cited here. If not, own data must be supplied by the authors, elsewhere in the manuscript, supporting their starting hypothesis: the studied rocks have a mantle wedge origin. Nevertheless, when reaching section 5.3 you say they were possibly cumulates from and intra-plate basalt.

page 207,lines 20-22. This is not a minor problem. Owing to the dam lake the rocks can not be observed any more. On the one hand, however, and attending to the authors own words, field relationships between the different rock types of the complex are "unclear". On the other hand, a more complete study of the rocks should be necessary in order to determine their possible wedge origin (see previous comment).

3. Sample descriptions

page 208,lines 3-4. What kind of serpentinization are we talking about? Do you have a late retrograde serpertinite or a serpentinite previous to metamorphism and affected by it? The second possibility might be suggested attending to the presence of antigorite (the higher temperature serpentine mineral) and brucite in the rocks and to what shown in figures 2a-d and especially g, but this should be clearly explained in the paper as it seems to be relevant in order to understand the evolution of the rocks and their mineral assemblages (see also comments for section 5.3). When did the breccias-texture formed? What is the relationship with serpentinization? Which arguments support that they are breccias? Attending to what shown by Fig 2b there is an incomplete replacement of olivine grains by serpentine? How do these rocks look like in the field? Do they

really look like breccias?

page 208,lines 5. How abundant are carbonates? Describe their textural relationships. What is their origin? Are they retrograde? This is an important point when considering the composition of the fluid during metamorphism.

Petrography description needs to follow a more precise order. I would propose describing first what you consider the original rock (dunite) and then the serpentinite. In each case, different textural positions of one mineral should be compared with each other, and should not appear scattered through the text. This is especially important for the case of Ti-Chu

page 208,lines 9-10 and other lines in this section. Ti-Chum grains are not to be seen in the figures you cite.

At least a rough estimation of the minerals modal amounts, and not only of spinel (line 17), should be supplied.

page 208,lines 13. Fluid inclusions can not be seen in the figure you cite.

Why don't you describe clinopyroxene any more (line 6)? It could be important to explain the occurrence of chlorite and Ti-Chu.

page 209,lines 3. Are you sure about the occurrence of titanite? This is a typical mineral of Ca-rich rocks. Is titanite related with carbonates here?

page 209,lines 8-11. I am afraid you don't pay enough attention to what seems to be one of the most outstanding features of these rocks. How do the veins look like in the field?

There are too many photographs in Figure 2 and not all of them are necessary (i.e. at least d, e, f, h, j, m). On the contrary, some representative photographs (may be two) are missed which illustrate the occurrence of the B and Ti minerals of the veins.

4.1. Major-element compositions

There are several main concerns about the way the mineral chemistry data are shown in this manuscript. 1. I would propose grouping the analyses by minerals and not by samples. This would allow comparison of compositional variations between different rock types, samples or textural types. In case they were grouped by samples, it should be stated which rock type (dunite or serpentinite or veins) they belong to. 2. Structural formulae of all the minerals must be calculated and shown in the tables! 3. There are several errors in the tables: T4-19 (totals in 3-ol1 and 5-ol1 are too high); SP01 (2-ant1 is not antigorite, but probably chlorite; T4-8 (5CH2 is olivine).

Concerning the composition of Ti-Chu: 1. In spite of what said in 24-25, F should be analyzed. Attending to the temperatures undergone by the rocks it is highly improbable that they were F-rich Ti-Chu, but the presence of carbonates in the rocks (unless precise explanations are given about their late origin) could attend for the presence of F. Low Ti contents would also be consistent with high F-contents. 2. All the Ti-Chu textural types (including veins) should be analysed and represented with different symbols in the figures. Explanations about this are completely lacking in the text. 3. Analyses above 6 wt. % TiO2 should be revised for they are above the maximum possible contents in this mineral. You already say this in page 205. 4. Analyses below 4 wt% TiO2 can not be considered as titanian clinohumite, but as clinohumite (see Deer et al., Rock Forming Minerals, vol 1A). 5. Thus, all the discussion of page 210 about the chemical variation Ti-Chu should be revised once all the above points (including structural formulae) have been checked.

The ludwigite analysis of Table 1 seems to be of quite bad quality: the total analysis sums 101.19 without having analyzed B203 (which ideally sums around 17 wt%) and without having made the transformation from FeO to Fe2O3 (around 40 wt%). New ludwigite analyses (more than one) must be done.

4.2. Trace-element compositions

A table with the laser-ablation analyses and analytical errors is essential.

How many samples were analyzed? Which rock types they belong to? Which Ti-Chu textural types were analyzed?

Attending to figure 6, it seems that all elements were not analyzed in all the samples. What is the reason for this? The complete trend of each sample can not be seen for not all the points are joined by lines. This should be done.

4.3 Raman spectroscopy

page 212,lines 17-26. Again, which are the Ti-Chu textural types in which fluid inclusions were analyzed? All of them? Is methane the only fluid filling the inclusions? Is there no water at all?

5.1 Chemical characteristics of the Fujiwara titanoclinohumite

As said in 4.1., I would carefully check the quality of Ti-Chu analyses and their formulae before writing this part of the discussion.

5.2 Ti source for the formation of titanoclinohumite

page 214,line 1. Attending to Sample descriptions, clinopyroxene is not absent from these rocks, but you simply ignore it both in the description and the subsequent discussion.

Description of opaque ores (here and in section 3) and discussion of their origin and implications are confusing: 1. Do you propose that both ferritchromite and magnetite rims grew during serpentinization? Again, when did the serpentinization process took place? Before metamorphism? 2. p 214, l 12-13. Which are the other hydrous minerals you mention? This is important. Contradiction: on the one hand you say chlorite grows and, on the other hand, you say this mineral is not common. In fact, in section 3 you say chlorite is not always associated with altered chromian spinel. 3. p 214, l 14-15. In fig. 2l you don't show Ti-Chu in contact with sp, but in contact with mt. In other photographs (i.e. 2i) you label sp and mt as different minerals. Do all mt grains have a sp core? Are there homogeneous mt grains? What's their origin? 4. p 214, l 15-

16. But this contradicts p 209, l 5-7:"Ti-Chu was also observed as discrete grains and veinlets in the serpentinized dunite clasts"; and also the following paragraph in this same page 214, were you discuss the occurrence of coexisting perovskite and Ti-Chu, which according to page 209 only occurs in the serpentinized dunites. 5. Which origin do you propose for ilmenite in the serpentinites? It is only present here or also in the dunites?

Concerning the Ti budget estimation of page 215, I would rather clarify all the previous questions before making such calculations. Anyway, the conclusion you reach (chromian spinel can not be the source of Ti) contradicts the conclusion you want to reach ("chromian spinel is possibly the source of Ti"). I propose you explore and discuss other possibilities.

p 215, l 14-22. If your hypothesis is true, you should obviously analyze HFSE contents in chromian spinel, but in the previous paragraph you have already concluded that this mineral is not so important for the formation of Ti-Chu.

5.3 Titanoclinohumite formation process and HFSE mobility

page 216,line 1. I agree the rocks may have olivines of various origins, but this should be reflected in the petrography and mineral chemistry description and also in Fig. 3, with a different symbol for each olivine type. Nevertheless, as in the case of Ti-Chu, I would check the quality of the analyses after calculating the structural formulae.

page 216,line 9 (and other lines in pages 215 and 216). A clear explanation should be given about what the authors call serpentinization-deserpentinization, when these took place, what is their relative time with metamorphism and which mineral assemblages correspond to each event. I would assume it isn't meant that the dunites formed after deserpentinization of a previous rock (p.215, l.27), but that during metamorphism prograde antigorite breakdown reactions (but not the final breakdown one) took place giving place to the formation of Ti-Chu, brucite, olivine, the veins, etc.

page 216,lines 5-7. If it was not clear that Ti-Chu (with maximum 6% wt TiO_2) could have formed from Ti released from primary spinels, this is even more difficult for much Ti-richer minerals like ilmenite or perovskite. It must be decided, nevertheless, if the same Ti mobilization process can be invoked for both dunites (what you call somewhere the matrix) and serpentinites.

page 216,lines 9-24. Discussion about the origin and behavior of B is again hindered by the confusion about the deserpentinization process and again it must be asked if the authors consider that the present serpentinites are the ones which underwent deserpentinization.

To this point, nothing has been said about the metamorphic evolution of the Sanbagawa pelitic schists and their dehydration reactions. If both schists and serpentinites underwent a common metamorphic evolution, are there field evidences (veins) suggesting fluid flow between both rock types?

Reactions R1 and R2 must be explained (write the name of the minerals below them). Despite what said in lines 20-22, metane appears in none of the reactions.

Lines 25-26. What's the reason for the lack of water in the fluid inclusions if all the important reactions taking place during progressive metamorphism are dehydration reactions? Did you look for water-rich fluid inclusions? Could the occurrence of metane-rich fluid inclusions refer to a (late) event different from the main dehydration reactions mentioned? See also next question.

page 217,lines 2-6. What's the name of Ca carbonate? Is it not calcite? As stated, a more detailed description of carbonates is missed: how abundant are they, which are their textural relationships with other minerals. It would be very important to determine if they seem to be prograde metamorphic or late minerals.

Concerning their origin, again: which evidences do you have supporting the gabbros provenance of Ca? Would the following hypothesis be more realistic? Carbonates have a sedimentary origin (marine precipitation during serpentinization) and the subsequent metamorphism releases C, that together with H2O from the serpentinites, gives place to the methane inclusions. This hypothesis would preclude the requisite of explaining the origin of the large quantities of methane necessary for producing carbonates precipitation in the rocks.

page 217,lines 7-9. As already stated for the introduction, you can have a look at López Sánchez-Vizcaíno et al. (2009; Lithos) and references therein for evidences indicating that Ti is a rather mobile element in certain metamorphic environments and specifically during metamorphism of ultramafic rocks.

page 217,lines 9-14. This is finally the explanation we were missing about the serpentinization and deserpentinization processes. I would move it to the beginning of the discussion or even to the description of the rocks, as this is one of the keys to understand all the paper.

Fig. 9. It is not clearly explained why you draw both a prograde and a retrograde path for the Fujiwara rocks. Do you consider brucite as a retrograde mineral? In that case, which are the arguments supporting your proposal? If not, I consider you simply have an assemblage which did not reach the Ti-Chu breakdown conditions. Do perowskite and ludwigite supply additional thermobarometric information? Nothing is said about their formation conditions.

page 217,lines 22-24. Comparison of the estimated metamorphic conditions with the very different ones of the nearby Higashi-akaishi ultramafic complex or that of the Bessi unit (also a ultramafic complex? where is it located?) would need further explanations: are the rocks similar? Why are the conditions so different or similar, respectively?

6 Conclusions and implications I would carefully revise this section of the paper after all the previous questions have been addressed and would explore what seems to be the novelty of this work: the role played by hydrocarbon-rich fluids in he transport of HFSE (in case it can be demostrated that they were really abundant; see above).

Technical corrections

There are several technical corrections all through the manuscript, but it is not worth highlighting them all as the whole paper must be rewritten.

page 207,lines 7. Which Khedr and Arai paper do you refer to? The one from 2010 in the references list (in this case you have to correct year 2009) or the one from 2009 of these same authors not appearing in the references? Khedr, M.Z., Arai, S., 2009. Geochemistry of metasomatized peridotites above subducting slab: a case study of hydrous metaperidotites from the Happo-O'ne complex, central Japan. Journal of Mineralogical and Petrological Sciences 104,313–318.

page 208,lines 3. Check publication year. 1978 in the references list.

Interactive comment on Solid Earth Discuss., 4, 203, 2012.