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Solid Earth
Discussions

Interactive comment on “First report of ultra-high pressure metamorphism in the Paleozoic Dunhuang orogenic belt (NW China): Constrains from P-T paths of garnet clinopyroxenite and SIMS U-Pb dating of titanite” *by* Zhen M. G. Li et al.

Anonymous Referee #1

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Review of ’First report of ultra-high pressure metamorphism in the Paleozoic Dunhuang orogenic belt (NW China): Constraints from P-T paths of garnet clinopyroxenite and SIMS U[Pb dating of titanite" //

Summary This manuscript presents results from garnet clinopyroxenite enclaves in the Dnhuang Orogenic Belt, southwest China. The authors produce a comprehensive and thorough microstructural characterization of successive mineral assemblages, upon which geochemical analyses are built to construct a quantitative thermobarometric history of the P–T conditions prograde, peak, and retrograde metamorphism. Application of conventional thermobarometry. crystallographically controlled exsolution of rutile, and the high Al content of titanite is used to suggest that these enclaves were subducted as part of a tectonic melange to high pressures of 28–41 kbar, well within the UHP metamorphic regime. SIMS U-Pb titanite dates of c. 390–370 Ma are interpreted as post-peak cooling ages associated with exhumation. Below, I present several general comments and my recommendations for the manuscript, in addition to some more detailed line-by-line comments encompassing those suggestions.

General comment

Overall, this is an interesting paper that presents nice microstructural observations, a wealth of geochemical data, and some well-constrained ages. I enjoyed reading it. The manuscript is succinct, if a little lacking in detail and discussion in places. Below, I have pointed out places that I feel rephrasing is necessary to ensure clarity, and a few technical corrections, but an additional careful language edit would be valuable to ensure total clarity of the scientific content and ideas. The presentation of a new UHP setting is very exciting and certainly appropriate for publication in Solid Earth, and the authors do a good job of using the relatively scarce literature pertaining to UHP metamorphism preserved in lithologies other than eclogites. However, as the submission proposes to identify a new UHP locality—certainly a significant and important contribution to a wide range of geoscientists—I have a couple main issues that I believe need to first be addressed that would ensure that the authors' interpretation is robust and watertight.

Much of the interpretation of UHP conditions of peak metamorphism comes from the presence of exsolved rutile needles in clinopyroxene. As the authors discuss, this may indeed be a consequence of decompression from UHP, but it is not ubiquitous or uniquely diagnostic of this setting. The same process can happen during cooling from high-T granulite facies metamorphism (e.g., in garnet clinopyroxenites in the Jijal Complex of the Kohistan Arc). Given that the compositions of clinopyroxene (neither the analyzed nor the recalculated) is jadeitic, the possibility of this having formed during cooling from the granulite facies to the amphibolite facies should be discussed in more detail. The authors did not much discuss the host granitic body, or the nature of the contacts between this host and the enclaves, which might also have a bearing on the genesis of such clinopyroxenite bodies (HP and UHP enclaves interpreted as mélange units are often hosted in softer metasediments, rather than granite).

As clinopyroxene are not jadeitic and the compositions used for conventional thermobarometery are recalculated (the methodology of which should also be detailed), I recommend the use of additional thermobarometers to provide additional confirmation of UHP metamorphism. Trace element thermobarometers (several of which are detailed below), may be a little more reliable in that trace element diffusivities are slower than Fe-Mg at high-T, and are thus less sensitive to diffusional homogenization and modification.

Specific comments

L53: Consider rephrasing “in the subduction process” to “during subduction”

L57: Other potential indicators could include acicular inclusions of rutile and pyroxene in metapelitic garnet (Ague and Eckert, 2012), quartz rods and needles in omphacite indicate an exsolution from a supersilicic clinopyroxene that contained a CaâĂŘEskola component (JAnák et al, 2004), or the phengite content of white mica?

L58–59: Please consider rephrasing this sentence.

L61: Is the host lacking in any kind of metamorphic fabric? Woah! If this is the case, how do you explain this?

L63–64: References for the evolution of our understanding of the Dunhuang area would be valuable here.

L83: What evidence is there (or who suggests) that dissection of the block by faults was “possibly in the Tertiary”?

L88: “features”

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L90: It’s not completely obvious to someone unfamiliar with the setting why the slices were metamorphosed at different depths. How different are these depths? Some references here would be valuable.

L92: Suggest removing “unfortunately,” as it implies that your pre-determined conclusion was to identify UHP metamorphism. Instead, better to frame your discussion in terms of the global scarcity of UHP indicator minerals, and whether this reflects the geologically rare set of circumstances required for UHP metamorphism, or if their scarcity reflects a preservation bias.

L92: Recommend replacing “inter-granular” with “matrix” and “inclusions”

L95: As in Franz & Spear (1985), I recommend you reference the alternative nomenclature: sphene

Petrography Section: Perhaps you could describe the field relationships a little more extensively? I would be interested in knowing the nature of the contacts between the enclaves and the granite (conformable, sharp etc). From your Figure 4, it looks as if the enclaves are broadly coherent, meters wide, and aligned parallel to some internal granitic foliation?

L112: In text you refer to Ttn1, but in Figure 6a and 6b it’s potentially labelled Ttn2 (I can’t find a Ttn1 in these figures). Is the Titanite part of the peak or prograde assemblage?

L114–115: Can these accessory phases be seen in Figure 5 at all?

L116: “worm-like”

L118: “rimming”

L119–121: Yes, this texture has been documented to reflect exhumation from high-pressure conditions to the amphibolite facies if the clinopyroxene is jadeitic. However, if the clinopyroxene is more augitic in composition it may reflect cooling from the granulite

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to amphibolite facies.

L120–128: A really interesting set of observations!

L133: The Hwang et al. (2019) paper only discusses rutile exsolution in garnet; is there precedent for spinel, tremolite and rutile exsolving from garnet? I'm not sure – might be worth doing a mass balance to find out if it's geochemically possible in a closed system! Alternatively, could these be some kind of late recrystallized inclusion or something associated with fluid infiltration along a crack?

L135: Consider rephrasing "midcourt." In Figure 6f, this inclusion looks like it's connected to a fracture. Could it be fluid related?

L147: Please consider replacing "tiny" with smallest

L149: Do you have a record of where the analyses were taken, e.g., cores vs rims of grains?

L155: Please define how you calculate garnet end-members. Is this variation quoted between samples? Is within sample variation in garnet composition negligible?

L156–157: What chemistry would you expect in mantle xenoliths or eclogite? Please be a little more explicit, as it's not necessarily common knowledge amongst all Solid Earth readers.

L159–161: There looks to be a slight Mn peak in the rim of 17D90 and 17D80 also consistent with a little bit of resorption. Be explicit in terms of the petrographic evidence for resorption.

S1 and S2: Please include recalculated cations in data tables. S1 would be useful as a standard table in the main text, rather than as supplementary information.

L164–165: "the chemical composition" Also here, please clarify what you mean by "altered to a different extent." Different to what?

L167–168 and L175: Your calculations are highly dependent on these ‘reintegrated’ compositions, so please provide some information about the approach taken to calculate these? Did you estimate the proportion of exsolution lamellae and reincorporate their chemistry according to this mode?

L168–170: Additional references here could include Carswell et al, Min. Mag (1996) and Castelli, JMG (1991). It should also be noted that these references and those in your current manuscript only document high-Al and F titanite in marbles and calc-silicates, if your measured Al2O3 reflects high P metamorphism (your concentrations are significantly less than those in Franz & Spear, 1985, I believe), your manuscript would (though I’m admittedly not that familiar with the literature so there may be those I’m not aware of) be the first documentation of such compositions in garnet pyroxenites. Frost et al., Chemical Geology (2001) have a good discussion of the expected metamorphic stability of sphere/titanite in metabasites, and because your results extend their general observations, I recommend expanding your discussion to include this paper.

Section: Geothermobarometry: You make some good observations, but it would be useful if there was more evidence for the peak conditions you appeal to, as I think they could be interpreted as having formed during decompression from high-T. I recommend you include the Zr-in-sphene/titanite (Hayden et al, CMP, 2008) thermobarometer which has been shown to sensitive to pressure variations and is calibrated up to 1000 ËŽC with ±20 ËŽC, If coupled with the Zr-in-rutile thermometer and potentially the Ti-in-rutile thermometer (e.g., see Ewing et al., CPM, 2012 and Liu et al., Gondwana Research, 2015) you could provide additional independent constraints on peak P-T. You also have quite a lot of geochemical data, did you consider applying pseudosection thermobarometry (e.g, in Theriak-Domino, Thermocalc or Perplex) or the AveragePT approach in Thermocalc (especially now that there are recently updated models for your chemical system)? For the former, you might get quite large, low variance fields, but it might be a useful exercise to see compare with your more

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conventional barometers.

L174: I don't think it's appropriate to simply use the average chemical composition of garnet with matrix clinopyroxene for conventional thermobarometry to obtain conditions of peak metamorphism unless garnet chemistries are completely homogenous, and you think this homogenization occurred at peak. If you make the assumption that this is the case, it is worth being explicit with this. Your garnets in 17D80 and 17D95 are approximately homogeneous, but rim chemistries might have been incorporated during cooling. You should not use these rim chemistries at all, and only use plateau cores. There is some Mn zoning preserved in the core of 17D78! I would suggest being a little more targeted with the use of these chemistries when using them with conventional thermobarometers.

L179: I recommend you include the error estimates (±4 kbar) in your Figure 9.

L179–180: "…assemblages mainly consist of plagioclase…"

L182: Please include errors with hornblende thermobarometers!

L192: I don't think you've necessarily "certified UHP metamorphism." Generally, this is only really truly the case if coesite pseudomorphs or marjoritic garnet is documented. While your data might well suggest this as it currently stands, your results are highly dependent on results of a single barometer which uses chemistries that are highly modified to their present state. I also find it strange that your jadeite component in clinopyroxene is so low in the chemistry you infer as having equilibrated at UHP conditions; why might this be?

L193–194: Exsolution of rutile lamellae in garnet is not exclusive to decompression from UHP metamorphism (as far as I am aware). It can also be documented as having formed during the retrogression of mafic garnet granulites from high-T conditions so is not necessarily diagnostic.

L203: Remove "scenario"

Dating metamorphism and L226: Please include geochronological data tables in the main text, rather than as supplementary tables! Are the ages you quote weighted averages? Also, in Supplementary Table 4 you quote uncertainties as “±s” which is a good convention to follow; are the ± intervals quoted in the text also s, rather than sigma?

L221: Please correct to “Terra-Wasserburg” Nice ages!!

L221–224: That’s ok, but if titanite formed at the expense of a high-μ phase (e.g., rutile) then it will most likely incorporate more radiogenic Pb than the bulk rock, potentially causing problems with your common Pb projection. Any thoughts on what reactions may have formed titanite?

L227Âň–232: The titanites in 17D90 and 17D95 are altered? Do you mean by diffusion, or something else like fluid fluxing? The zoning in the BSE looks to me to be primary, perhaps? In places, it’s concentric, and the sharp boundaries are consistent with negligible diffusional homogenization. Did you consider trying to put more multiple spots down on individual grains? In a grain in 17D95 you’ve done this, and the core age gives a nearly 20 Myr younger age than the rim, which is interesting/strange and potentially worth investigating! Patchy zoning such as this has been related to interface coupled dissolution and precipitation reactions (Bonamici et al, 2015; Garber et al, 2015; Walters Kohn, 2017), so your observations might provide a nice framework. See next comment for more on this.

L234–236: While you’re correct that titanite U-Pb ages are traditionally thought to record cooling through 600Âň–750 ËŽC (additional references to those you’ve provided include Cherniak (1993) and Spear and Parrish, (1996)), recent studies (including experimental studies) have indicated that Pb diffusion seems to be negligible in titanite at T < 850 ËŽC. Some relevant examples include Castelli and Rubatto, CMP, 2002; Garber et al, J Pet, 2017; Walters and Kohn, JMG, 2017; Holder and Hacker, Chemical Geology, 2019. Rather than cooling, these authors document U–Pb titanite

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dates that record the timing of neo-crystallization, fluid-driven alteration/resetting, or deformation that might facilitate resetting of U-Pb dates and compositions. It is worth considering potential alternative scenarios given increasing evidence that dates such as those you've obtained in this study may not reflect cooling, but some other process.

L242–243: Maybe replace the end of this sentence with "assess the likelihood of UHP metamorphism"?

L255–258: I'm still not entirely sure why "the prograde assemblage (M1) clearly indicates the subduction process". Please expand on this. "Very deep but different depths" is not clear, either. Please clarify.

L245–250: This paragraph should be placed in a little more context to account for its inclusion.

L274–278: I recommend you rephrase this paragraph, but yes, I think the sample could alternatively reflect decompression from high-T conditions (as mentioned in a previous comment), based at least on the microstructures. If there are other barometers that you could apply to this dataset to evidence your UHP conclusion, great! I think the possibility that your pyroxene compositions are not reflective of UHP conditions and instead reflect HT metamorphism should be explored a little more. Would this interpretation potentially fit with the garnet clinopyroxenite field setting (in the undeformed granitic bodies) a little better, too?

L280–282: What about the potentially important role of intracrystalline diffusional exchange (e.g., Pattison Begin, 19094) that results in Fe-Mg exchange at the relatively high temperatures you suggest? Geothermobarometers that use net transfer reactions and Ca, Al and Si tend to be a little more reliable at these conditions.

L293: By "wide representative," do you mean its applicable to a wide range of bulk rock compositions?

L315: Here and in a previous paragraph, you justify use of the geothermobaromers

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as your chosen calibrations are “most accurate.” I would recommend modifying this discussion, because results are only accurate if you know the true result, how do you know the calibration is accurate for your bulk composition? Has it been calibrated for such (in which case, great!!).

L335–338: A subduction mélange? Also recommend changing “. . .large gaps of the peak. . .” to “. . .large differences in the peak. . .”

L345: consider rephrasing “which is neglected to different extent in the past”

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