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Solid Earth Discussions

Interactive comment on "Fluid–rock interactions in the shallow Mariana forearc: carbon cycling and redox conditions" *by* Elmar Albers et al.

Elmar Albers et al.

e.albers@uni-bremen.de

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Dear Melanie, We thank you for your extensive and constructive feedback on our manuscript. Please see the replies to your main concerns below. We will handle your more detailed comments in the manuscript during the main revision of the manuscript within the next weeks. Kind regards, Elmar Albers

MS: 1. The authors claim textural and chemical equilibrium, which I do not find to be sufficient supported by the observations. Please discuss the concept of equilibrium or adjust the text.

EA: From our point of view, microtextures suggest equilibrium conditions during the formation of the vein minerals. For instance, carbonates and barite in sample U1497A-

7X-CC (Fig. 3d) show well-developed crystal faces that can only develop if (1) both phases grew from a fluid in chemical equilibrium with it and (2) the carbonates grew at the same time as barite. If the vein minerals reflected non-equilibrium processes, we would not expect to see straight grain boundaries and instead see some evidence for overgrowth and/or replacement (e.g., different generations of carbonates such as those in Fig. 3c).

MS: 2. The tables are generally well presented. However, I suggest providing more petrographical information in Table 1. This would make it much easier for the reader to follow the paper and to always know what samples and localities you are talking about. For instance, which sample is the fully serpentinized dunite? Can you please indicate samples with 'shallow' and 'deep' carbonates. That information is provided in the text, just adding it to the Table 1 will make it easier to follow the results and discussion.

EA: We added two columns to the table, one stating the carbonates to be 'deep' or 'shallow' and one giving additional information used in the text.

MS: 3. The discussion would become more substantial by estimating the extent of carbonation. This would be particularly interesting in context of the long-term C-cycle. Did you establish the abundances of newly formed carbonates?

EA: We have in great detail thought about estimating the effect of our findings on the global carbon cycle. But we came to the conclusion that it is very difficult to quantify these processes since such quantification would lack one of the most crucial points: how large are the regions from which the individual mud volcanoes are sourcing? Not knowing this, the uncertainties of such estimates would be enormous. Based on these thoughts we have decided not to budget the carbon fluxes.

MS: 4. Figure 4 only displays the upper limit for the shallow carbonates. It would be of advantage to compare the REE pattern, Ce and Eu anomalies between those populations since this is one of the main aspects in the paper.

EA: In earlier versions of the manuscript we had included the entire REE+Y data of shallow carbonates. But during discussion with the co-authors we decided to only show the upper limit since their REE concentrations are in many cases close to (or below) the detection limit (i.e., the precision of these concentrations is low). However, we assume conditions during the formation of the shallow carbonates to be less reducing in comparison to the (serpentinization-dominated) conditions in the mud volcano conduits as they are influenced by seawater. But this is not crucial for the main outcome of our study since the shallow carbonates formed in a completely different environment than the deep carbonates. Hence, we mostly used the REE concentrations to differentiate between deep and shallow carbonates, but the shallow carbonates do not provide additional information on conditions at the slab–wedge interface.

MS: 5. Figure 8: (1) Why is the shaded field, representing the log a H2(aq) and T of your deep carbonates, shaped with a maximum at 160°C? Is the Eu-anomaly more pronounced in the high T-carbonates? Or did I misunderstand? In which case please explain. I think, the scatter in REE pattern is too large to argue for an Eu-anomaly. Thus, I think, you can't say much to the Eu2+/Eu3+ ratio. (2) Based on O-isotopes you calculated T between 130-175°C and between 220-310°C (see Figure 7). If so, the shaded field in Figure 8 should have a gab between 175-220°C.

EA: (1) We do observe slight negative Eu anomalies for some of the samples, indicating that Eu2+ is slightly more abundant than Eu3+ in these cases. These samples should hence plot within the predominance field of Eu2+, i.e., above the Eu2+/Eu3+ line in Fig. 8. At the corresponding T–aH2 conditions, CeO2 represents the predominant oxidation state of Ce in Fig. 8. Following the two reaction lines (staying in the CeO2 field and slightly crossing into the Eu2+ field) creates what you call 'maximum' at 160°C; this merely indicates that if the carbonates formed at 160°C, the conditions had to be less reducing to create the observed REE patterns as compared to the same system at 250°C. (2) Our T estimates indeed are 130-175°C and 220-310°C. These likely reflect the conditions at the slab–wedge interface in the Mariana forearc system,

which are sampled by the mud volcanoes. In other words, just because there is no mud volcano sampling the T range from 175-220°C does not mean that the here described carbonation process does not take place within this range. We hence decided to not indicate this gap in the figure. A respective node has been added to the figure caption.

MS: 6. Figure 9: Its great to have a cartoon illustrating the discussed process. However, I was surprised by the indicated overgrown textures of carbonates around other minerals. I cannot find a description of such overgrown or zoning in the text. Please elaborate on this.

EA: Right, we have not observed overgrowth in our samples. But the interaction between metavolcanic/metasedimentary clasts and slab-derived fluids is probably not restricted to veins/cavities within the clasts. Why should it? We rather think that wherever these lithologies are exposed to the reactive fluids, similar precipitation processes should take place. But you are right, this is an interpretation. We have made a respective comment in the figure caption.

MS: 7. The English need work and the paper would be improved by a careful going over with style as a primary consideration. Some mistakes are highlighted in the pdf, but this is by far not comprehensive.

EA: All authors, including two native speakers, will once again go through the manuscript during its revision.

MS: Additionally, I have a couple of minor suggestions and remarks: Abstract - I suggest to include in the abstract (see your last sentence), that not all the carbon will be released into fluids under the forearc, some carbon will also be subducted deeper.

EA: We have revised the sentence to '[. . .] it highlights that some C is lost from the subducting lithosphere [. . .]'

MS: Introduction Line âĹij31: "These observations are in line with experiments that demonstrated the increase in solubility of calcite in aqueous fluids with increasing

pressure and temperature (Caciagli and Manning, 2003), suggesting that an efficient release of C from downgoing slab should occur even at relatively shallow levels." An 'efficient' release of CO2 into fluids is not only related to the solubility of carbonates. Please include that the 'efficiency' of CO2 release also depends, for instance, (1) the amount of fluid e.g. release of pore water and dehydration and (2) on the proportion of calcite and other carbonates in the slab.

EA: Right, as you point out the efficiency definitely depends on several aspects. We have revised this statement to 'These observations are in line with experiments that demonstrated the increase in solubility of calcite in aqueous fluids with increasing pressure and temperature (Caciagli and Manning, 2003). This suggests that an efficient release of C from the downgoing slab could occur even at relatively shallow levels, given that the conditions such as the flux of slab-derived fluids and the proportion of calcite in the slab are favorable.'

MS: Methodoly: Line 20: Please mention that you used Raman spectroscopy for phase identification. Electron microscopy: Please include which elements you measured by EPMA. Why did you not include Sr in the EPMA analyses? Sr is likely above detection limit at least for the aragonites. Isotope Analyses: How representative is your sampling? How much material did you crashed for picking carbonates?

EA: We have revised the Methodology section to account for these suggestions. Strontium was indeed part of the microprobe analyses, but we later used LA-ICP-MS concentrations to be able to compare concentrations between aragonite and calcite (Sr concentrations of which were below the EPMA detection limit).

MS: Results 4.2.1 Petrography - Are mineral phases ordered with decreasing abundance? Did you establish phase abundances? The proportion of newly formed carbonates would be a first indicator on the extent of carbonation of serpentinites. Knowing the proportion of deep formed carbonates would also add much to your discussion on the C cycle.

EA: Unfortunately, the proportions of these samples are highly variable over the different samples, so that we are not able to make a reliable statement on their abundances. We added a note on this: 'The proportions of these phases are highly variable throughout the individual samples.'

MS: - "Several generations of carbonates are observed" → you mention only two generations of carbonates calcite and aragonite; are their more?

EA: Actually, there are only these two generations that we are certain about. We revised the text accordingly.

MS: - There seems to be some confusion on equilibrium: For example, you mention that "intergrown or ... straight crystal contacts (is) indicative of chemical equilibrium". I assume you mean textural equilibrium. Further, you state in Line 25, that an intergrowth of aragonite and calcite evidences equilibrium to a fluid. I do not agree to this. Please explain or adjust.

EA: Please see our above comment for this concern.

MS: - It is often not clear to me, what sample you are referring to which makes the petro- graphic description confusing; e.g. Line 22 23 ". . . in two samples". Which samples?; "Two other metavolcanic clasts. . ." In which sample are they?; "One of those. . ." ???

EA: Where no individual sample name is given, our statements generally refer to the respective sample group (serpentinite clasts, metavolcanic clasts, metasedimentary clasts, authigenic carbonates); each group has its own paragraph. In lines 22-23, we added the sample names to the text.

MS: 4.2.2 Mineral chemistry - "Major and trace elemental compositions in the carbonates are highly variable. Magnesium and Fe concentrations vary from <10 μg g-1 to up to âĹij14000 μg g-1 and âĹij1600 μg g-1, respectively." I am not surprised, you sampled very different rock types and you are dealing with different carbonates (calcite, arago-

nite) so it can be expected that the Mg and Fe content are variable. Did you establish the Mg# of the host rock? It would be interesting to set those into context with Mg# of carbonates.

EA: Right, the different host rocks and/or environments from which the carbonates formed can easily explain these heterogeneities. Based on the presented data we think that the conditions during the formation of most veins was fluid-dominated instead of rock-dominated. We hence did not compare the carbonate XMg to those of phases of the host rock or to the Mg# of the bulk rock (which, at this stage, do not exist anyways).

MS: - The section is better written compared to the petrographic description, but some clarifications are needed: Can you think of a way to report your results more systematic and in context to the lithology? When are you considering the entire data-set and when do you refer to a particular sample?

EA: We have once again gone through the Mineral chemistry section and still tend to retain the structure of this part of the manuscript. The structures is as follows: description of major elements within the carbonates, followed by trace elements including REEs. Whenever we consider a particular sample group, i.e., serpentinite clasts, serpentinite mud, metavolcanic- or metasedimentary clasts, this is described in the text. We do not describe individual samples within this section at all.

MS: - Figure 4: I would like to see the variability of REE in “shallow carbonates”. Are chondrite normalized REE patterns of shallow carbonates also spreading by an order of 2-3? Further, I would like to compare the Ce-and Eu-anomaly between shallow and deep carbonates.

EA: Please see our above reply to your main comment on Fig. 4.

MS: 4.2.3 - Figure 5: You mentioned in 4.2.2 that some aragonites have Sr concentrations of up to 1.5wt%: did you analyse the Sr-isotopy of those aragonites or does Figure 5 only includes data for calcites?

EA: Since some clasts contain both aragonite and calcite, we have not differentiated between the two with regard to Sr isotopes. Fig. 5 does hence include aragonite as well as calcite data. Also see Tab. 1 for the carbonate types within the individual samples.

MS: Discussion 5.1 - “Quartzite breccias have not been previously described from the serpentinite mud volcanoes. We suggest that this sample represents lithified sedimentary siliceous ooze from the subducted Pacific plate”. Please include the indicated alternative explanations for the occurrence of quartzite.

EA: We are unsure how (and if) we indicate an alternative explanation with this statement!? Also, is there a (plausible) different explanation? We think of the lithification of sedimentary oozes as the most likely way.

MS: 5.2 - “We suggest that the deep carbonates formed from dehydration fluids in the subduction channel soon after they were released from the downgoing slab”. I agree that the fluids released from the subducting slab formed carbonates in the subduction channel. However, your observations do not support time estimation.

EA: Right, we revised this statement to ‘We suggest that the deep carbonates formed from dehydration fluids in the subduction channel close to where they were released from the downgoing slab.’

MS: - see main comment to Figure 8. - “Our data suggest that simple devolatilization reactions (e.g., Kerrick and Connolly, 2001) do not account for the mobilization of C within these shallow portions of the subduction system. Instead, we suggest that fluid-induced dissolution of carbonate (e.g., Poli et al., 2009) is the more likely process that leads to the release of C under shallow forearc conditions.” I agree that your data shows that carbonic fluids are released from the subducting slab and react with serpentinites. However, I don’t see from your data that you can rule out that devolatilization reactions are an additional source of C released from the slab. Please explain or modify.

EA: We have revised this to ‘Our data are in line with the suggestion that simple de-

volatilization reactions do not account for the mobilization of C within these shallow portions of the subduction system (Kerrick and Connolly, 2001). Instead, we suggest that fluids induced dissolution of carbonate (e.g., Poli et al., 2009) is the more likely process that leads to the release of C under shallow forearc conditions.

MS: - If I understand correctly, you argue that serpentinization may not occur simultaneous to carbonation in the subducting channel. So the composition of the released fluid may have become more carbonic over time. What do you think may have caused this? We do not imply that we can determine relative age sequences between deep carbonate vein formation and serpentinization of the ultramafic clasts. We also don't see why the fluid should become more carbonic over time.

EA: We do argue that there must be a gradient within the subduction channel from more oxidizing at the slab to more reducing conditions at the mantle wedge (see Fig. 9). Such a gradient is easily explained by: fluids released from the slab are likely oxidizing but turn more and more reducing during the reaction with olivine from the wedge peridotite (likely occurring more towards the mantle wedge where peridotite dominates volumetrically over metasediments/-crust). We could not find evidence for peridotite/serpentinite carbonation at depth. But metavolcanics and -sediments react with slab-derived carbonic fluids in that they form carbonates. So there is a sink for carbon in the subduction channel. Why the mafic clasts are more prone to have $CaCO_3$ veins form than the ultramafic clasts is not clear. We excluded a detailed discussion of possible reasons for this apparent bias, as it would be beyond the scope of the manuscript. But we did expand Fig. 9 slightly to indicate that DIC is high in the slab-dominated part of the channel (CO_2 flux coming off the slab plus oxidizing conditions well within the CO_2 predominance field), whereas in the wedge-dominated part of the channel, DIC is likely lower due to (1) prior removal in $CaCO_3$ veins and (2) partial reduction to CH_4 by H_2 produced during serpentinization. We also added this short discussion to Section 5.2 of the manuscript.

MS: - rest of the discussion is very interesting. My only request is to correct the typos

and to explain the overgrown of carbonates indicated in Figure 9 (see main comments above).

EA: All authors have once again gone through the manuscript. Please see our above reply for your comments on Fig. 9.

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