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Interactive comment on "Sedimentary mechanisms of a modern banded iron formation on Milos Island, Greece" *by* Ernest Chi Fru et al.

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Anonymous Referee #2 Received and published: 24 January 2018 Review of: Modern Banded Iron Sedimentary Rocks on Milos Island, Greece.

Comments The manuscript is well written, though it does suffer from a smattering of grammatical mistakes.

Responses: We extend thankfulness to this reviewer for taking time off to read and comment on our manuscript. His comments have condensed the sedimentology, tightening up loose parts suffering from lack of clarity. To satisfy the comment about a smattering of grammatical errors, we have taken care to minimize errors that might previously have escaped careful editing. Attached to this document is a PDF file named,

supplement, containing the manuscript with changes, including those requested by the reviews, in red.

The layers under study do seem somewhat similar to Precambrian BIFs and are thus worth investigation, though it must always be emphasized that Precambrian ocean chemistry was very different than today's seas. I have not directed many comments at the iron deposits themselves as their description and interpretation is reasonable. This review concentrates mostly on the sedimentological aspects of the manuscript, which are problematic. Basically not enough substantiating data is provided for the interpretations given. Many of the interpretations are very specific and the limited exposures available do not provide the types of data necessary to validate the interpretations. The author's interpretations, in general, could be correct, but there are other equally as valid interpretations of the depositional systems possible. This situation is not helped by the inclusion of references after an interpretation is put forward that describe a depositional process or rock unit that was formed in a similar environment to that proposed but appear to bear little in common with the rocks present in this study. This reduces down to the problem that the characteristics of the rocks described in this study are not detailed enough to support specific interpretations. For example: a conglomeratic unit is interpreted as a channelized mass flow deposit in a submarine fan. If it was deposited by a high-density turbidity current it will have certain internal characteristics that are well defined in the literature (see some of Walker and Lowe's older papers). If it was a debris flow it will have other characteristics, such as disorganized clast orientations, matrix support, poor sorting etc. that these conglomerates do not appear to have. However, there is an even bigger problem with this interpretation. Submarine fan channel successions form thick fining upwards successions, commonly over tens of meters vertically. Finally submarine fans are one category of submarine base of slope deposit, a group that also includes ramps and aprons, and no evidence is given why this would not be a ramp or an apron, or simply, and much more likely, a conglomerate bed. I put in the latter as a few conglomerate beds do not make a fan, ramp or apron, which are very much larger features. These are just the problems that exist with one interpretation of depositional environments. Similar problems exist with the others. It would have been beneficial if the authors delegated more discussion to the deposition of the silica-rich layers as the Fe-rich layers forming from hydrothermal fluids are easy to understand but the deposition of the silica layers in BIF is much more difficult to explain. The use of references is perplexing. Most of them do not have direct bearing on what they are referencing in the text. They are on the same general subject, but many do not reinforce the correctness of the preceding statement. I recommend that the interpretations of the depositional environments of the siliciclastics be eliminated. They are very problematic and greatly distract from the manuscript.

Response: For the sake of clarity, we should indicate that we are not proposing the Milos BIF-type rocks as the exact equivalent of Precambrian BIFs or insinuating that the seawater in which they formed had the exact composition of the Precambrian oceans. But we have found several components of the deposit that have the potential of providing and aiding mechanistic models aimed at understanding how BIFs formed. They may give new insights into the deep past from the present-day seawater biogeochemical perspective. These are some of the challenges we wish to resolve by detailed description of the geological and geochemical processes behind the perplexing deposition of the Milos IF. To enable comparison, we use the simple definition of BIFs as marine sedimentary rocks with alternating layers of Fe-rich and Si-rich bands, containing at least 15% Fe. This definition does not restrict the potential for BIFs to form only in Precambrian oceans, although they are a major feature of this unique period, a time when seawater had extraordinarily high levels of dissolved Fe and Si.

What our data are showing is that these local conditions of elevated and cyclic supply of dissolved Fe and Si and accompanied by strict bottom water anoxic conditions in a localised reservoir cut off from the open ocean, can in principle allow the rare deposition of BIF-type rocks in the modern ocean. The rarity of these types of deposits in the present-day ocean hints that such conditions seldom develop under the existing atmosphere, but that they can indeed occur. Therefore we present these as a rare modern

BIF-type facies, different from the Precambrian BIFs, in the same way the rare Neoproterozoic BIFs are different from the widespread Paleoproterozoic Superior BIFs, which are in turn distinct from the mainly Algoma-type Archean BIF deposits that are limited in scale. This paragraph has been edited and included in our conclusions to highlight the importance of distinguishing this deposit from the Precambrian formations.

We strongly agree that sedimentary features can be difficult to interpret with certainty. We have therefore reduced the degree to which these interpretations have been made for the above reasons laid down by this reviewer. We however believe that it is important to keep solid parts of the interpretations that help explain how anoxic conditions could have apparently developed in the CVSB to enable dissolved Fe enrichment and its oxidation to Fe(III). Further, sedimentology must not be interpreted independently from the geochemistry and redox. This has become even more crucial with the new Figure 13C-D that unambiguously supports the contentious anoxic depositional conditions previously illustrated by REEs. This new information has been acquired using the widely accepted iron extraction redox proxy (See Poulton, S.W. and Canfield, D.E. 2011. Ferruginous conditions: A dominant feature of the ocean through Earth's history. Elements 7, 107–112, for a review).

This reviewer indicates that it would have been more helpful to dedicate more time discussing the Si bands. Our data show that band formation was mainly controlled by the activity of Fe, while Si precipitation was a passive process that cannot be explored beyond the fact. As we have shown and discussed, it is the cyclic release and oxidation of ferrous Fe that in fact controls the enrichment of Fe in the Fe-rich bands and Si in the Si bands. This particular observation provides the first independent modern verification for similar processes suggested to have formed the ancient BIFs (See Bekker et al. 2010 for details and references therein, cited in the main text).

The description and discussion of the IF can stand alone. Its lack of current formed structures implies a low energy environment and that is about all that can be inferred about physical processes from the IF. Thus, the manuscript would need major revisions.

A more detailed line by line review follows:

Response: We agree with this reviewer about the low-energy environment in which the IF formed, which is in agreement with our initial conclusions. However, it would appear that the switch from one redox state to the other was often accompanied by tectonic activity that caused deepening and shallowing.

Line 73: Rare Earth Elements should not be capitalized.

Response: Corrected

Line 115: Rhyolite is not intrusive.

Response: Corrected to extrusive

Line 226: It is much more common in work on iron formations to us PAAS to normalize the data.

Response: The rationale for using the NASC is as follows:

1. The NASC normalization maintains data consistency with the REE data published in our previous papers on the Milos IF ((1) Chi Fru, E., Ivarsson, M., Kilias, S.P., Bengtson, S., Belivanova, V., Marone, F., Fortin, D., Broman, C., and Stampanoni, M.: Fossilized iron bacteria reveal a pathway to the origin banded iron formations. Nat. Comm., 4, 2050 DOI: 10.1038/ncomms3050, 2013. (2) Chi Fru, E., Ivarsson, M., Kilias, S.P., Frings, P.J., Hemmingsson, C., Broman, C., Bengtson, S. and Chatzitheodoridis, E.: Biogenicity of an Early Quaternary iron formation, Milos Island, Greece. Geobiology, 13, 225–44, 2015.

2. There are no scientifically demonstrated discrepancies between the PAAS and NASC.

3. Following the above suggestion, data was normalized to PAAS for comparison with the NASC normalized trends. The results produced the same trend as observed when data are normalized to NASC. See new Figure 14 in the manuscript text, accessible

in the attached supplement PDF file. Further explanations are also provided under sections 2.6-2.6.1 in the manuscript supplement text. Line 327: Below storm wave base does not necessarily mean below 100 to 200 meters. At present storm wave penetration is deepest in locations such as southeastern Australia and Atlantic Canada where it reaches 120m. But these are very storm prone open ocean facing areas. It is difficult to give an estimate for paleo-storm wave base in the study area, but I doubt that it could be even close to 100m as more would mean waves with greater than 200 meter wavelengths in a sheltered area compared to the open Atlantic.

Response: We have omitted our attempt at specifying a value in the text for the depth. The new wording has been rephrased to:

The MFIF rests directly on the submarine dacites-andesites that were deposited in a relatively shallow submarine environment (Stewart and McPhie, 2006).

Line 340: Not enough evidence is given to justify the turbidite interpretation. Graded beds just mean they were deposited by powering-down events, which can occur in many different environments. Even if they are turbidites, which I have no idea whether they are or not from the evidence, the setting cannot be termed a fan, ie, why not a ramp or apron or a number of other environments that can have turbidites.

Response: Removed from text.

Line 344: Slump deposits infers an intact or partially intact block that slid. The conglomerates are not slump deposits. They could be debris flows, but again there is not enough evidence given to say this.

Response: Lines 337-361 have been deleted and replaced with this short paragraph:

In the overlying sandstone-conglomerate facies, the presence of sedimentary structures indicative of wave action and currents (e.g. cross-stratification), that signify rapid deposition during a high energy event, are consistent with a switch to a shallow-submarine high energy environment (Stewart and McPhie, 2006; Chi Fru et al., 2015).

This shift in depositional environments may have been controlled by a combination of submarine volcano-constructional processes, synvolcanic rifting and volcano-tectonic uplift known to have formed the CVSB (Papanikolaou et al., 1990; Stewart and McPhie, 2006).

Line 347: If a flow is carrying pebbles it is not a low density turbidity current.

Response: Deleted and replaced with the paragraph above.

372: gravel to pebble is not proper terminology. Pebbles are gravel if unconsolidated.

Response: Lines 370-373 have been deleted and replaced with:

The lower sandstone facies represents the host of the main economic grade Mn oxide ores in the CVSB. This constitutes part of a separate study devoted to the Mn ores and will not be dealt with further here.

Line 395: mm-scale layers are not beds, they are laminae.

Response: Deleted and replaced with laminations.

Line 418: Why not below storm wave-base?

Response: Corrected.

Line 422: The only evidence for the interpretation that the conglomerates are " a series of channel deposits in an inner turbidite fan-like setting" appears to be that they are conglomerates. A great deal more evidence is necessary to be so specific about the depositional environment.

Response: Lines 420-434 have been deleted.

Line 424: No evidence has been given for a tidal environment and little evidence for a shoreface.

Response: Lines 420-434 have been deleted.

Line 427: There are also many papers that describe iron formations in other settings.

Response: Lines 420-434 have been deleted.

Line 434: This is an example of a reference that has little bearing on the preceding statement. The Mesoarchean Barberton is not a good analog for the sedimentary environment of the basin described here.

Response: Lines 420-434 have been deleted.

Line 439: The sedimentary structures described could have been formed in the environments proposed, but they are not limited to the environments given the lack of evidence.

Response: Lines 335-340 deleted.

Line 458: The description of these deposits has little in common with GIF. It is also better to reference the originator of the term GIF (Simonson), rather than Bekker, which is just a review article.

Response: References to GIF have been deleted from the text.

Line 481: This is circular reasoning.

Response: We agree and further demonstrate this in the new Figure 13D. These emphases must be highlighted to show some of the similarities these rare deposit shares with true BIFs.

Line 482: Precambrian BIF can be sulfide facies.

Response: We agree. We are trying to make the statement that these are those type of BIF facies that are sulfide rich. We have therefore peplaced with the text:

Lack of association of the framboidal-iron-rich particles with S, following SEM-EDS analysis, rules out a pyrite affiliation and is consistent with the non-sulfidic depositional model suggested by the sequential iron extraction redox proxy (Fig. 13D).

Line 522: This statement is not correct. Planavsky and others (see authors' references to this statement) put forward that the anomaly for Ce must be less than .95 and greater than 1.05 to be significant, not less than or greater than 1.

Response: This has been corrected.

Line 528: They do not have similar enrichment levels; they are light depleted. Response: Enrichment changed to depleted.

Line 574: The positive Eu anomalies are quite small compared to those associated with oceanic hydrothermal vent sediments. Also, volcanic detritus can carry positive Eu anomalies. A plot of Ti vrs Eu* would be useful to distinguish if the anomaly is related to volcanic detritus in the IF.

Response: We agree, but this effort will not tell us anything more than what we have already shown, since multiple evidence shows that we are dealing with materials being released into the basin intermittently by hydrothermal/volcanic activity as demonstrated by the ash particles in the bands. As we have shown in Figure 13 and from using multiple lines of evidence, the supply of materials from the continent to the basin was not an important source of sediments during the formation of the alternating Fe and Si layers. Our main interpretation is a hydrothermal source, backed by data in our cited publication in Nature Communications and Geobiology, in addition to the present submission.

Line 614: What is described as an upward fining trend appears to me to be simply one single graded bed. The fining upwards in the bed is better explained by the depositional mechanism losing energy through time. Also, conglomeratic beds usually represent rapid deposition during a high energy event, ie. storm or mass flow, rather than the slow pebble on pebble accumulation over years.

Response: This text has been revised as suggested. The new text reads like this:

Geomorphological/chemical reconfiguration orchestrated the deposition of the NFIF in

a deeper, small-restricted basin (Fig. 2). The deepening of Basin 3 is reflected in the underlying graded conglomerate bed that exhibits an upward fining trend, followed by transition into the fine-grained NFIF. The conglomerate bed may represent rapid deposition during a high-energy event, i.e. storm or mass flow, whereas the upwards fining in the bed is better explained by the depositional mechanism losing energy through time. These high-energy conditions apparently must have ceased during the deposition of the overlying NFIF, where we interpret that increased abundance of finely laminated IF and decreased evidence of storm and/or mass flow reworking reflects deepening conditions. The hypothesized deepening of Basin 3 is consistent with the interpretation that active rifting was an important mechanism in the formation of the CVSB (Papanikolaou et al., 1990).

Line 682: Comparing the small Eu anomalies present in this study with the larger Precambrian anomalies should include giving the values for the average Precambrian anomalies. Simply stating the values of Eu anomalies of samples in this study are more similar to Archean anomalies is somewhat misleading.

Response: The paragraph has been deleted.

Line 757: If even small amounts of seawater are mixing with the hydrothermal fluid, as previously stated, anoxia could not exist.

Response: See new Figure 13C-D that firmly establishes the anoxic/ferruginous depositional conditions. Moreover the statement made by this reviewer that even if small amounts of seawater are mixing with hydrothermal fluid, anoxia cannot exist, is misleading and a bit perplexing because this argument means that redox gradients should not exist in nature. Following the rules of stoichiometry in chemical reactions, large volumes of highly reduced solutions such as hydrothermal fluids require equally large concentrations of oxidants (especially oxygen) to make the fluid oxidizing. From this reasoning, considerable amounts of oxygen are required to react with the large volumes of the highly reduced chemicals and compounds present in hydrothermal fluids.

This argument is given as an explanation for why it took so long for oxygen to rise in the atmosphere (See Lyons et al., 2014. The rise of oxygen in Earth's early ocean and atmosphere. Nature 506:307–315: and the review by Bekker et al. 2010, cited in the manuscript). The reasoning is that reduced hydrothermal fluids that made up a bulk of the early oceans were eventually overwhelmed stoichiometrically by oxygen (meaning more oxygen was being produced than consumed by the reduced fluids), leading to the rise of oxygen in the atmosphere, c. 2.4 billion years. Even after that, although the Paleoproterozoic surface ocean was oxidized for close to two billion years, complete ocean oxygenation only came at the end of the Precambrian despite the fact that reduced deep ocean hydrothermal fluids continuously mixed with the oxygen-rich ocean surface seawater. If we were to follow the argument given by this reviewer, then the whole ocean would have been oxidized following the mixing of the reducing fluids with the thin layer of oxygen-rich seawater on the ocean surface. This indicates that the sedimentology, geochemistry and redox must be jointly interpreted to understand what occurred at Milos.

Line 842: The presence of a conglomeratic bed does not commonly mean deepening of a marine succession. There are literally thousands of papers where the upward transition of sandstones to conglomerates is interpreted as shallowing as energy levels increase with shallowing in a marine setting.

Response: We strongly agree that the paragraph was not well-phrased, leading to the difficulty in understanding the meaning of the sentence. It has now been revised to:

All of this is feasible with the three-basin-fault-bounded hypothesis as a requirement for movement along fault lines in response to temporal tectonic activation. The upward sequence transition from the Mn-rich sandstone facies, through the pebbly conglomerate and the final termination in the overlying mud-grained NFIF (Fig. 8B), reflect sedimentary features formed during multiple changes in seawater levels (Cattaneo & Steel, 2000). This study proposes that the NFIF that overlies the transgressive-type conglomeratic lag along an erosional contact surface was likely deposited during max-

imum flooding, when the basin became stagnant and stratified, and subsequently was uplifted to emergence.

Line 848: The presence of a transgressive conglomeratic lag implies that the area was emergent prior to this and the conglomerate formed by wave reworking in a shore proximal environment. Evidence has not been given to support this, and if I am not mistaken the conglomerate has previously in this manuscript been interpreted as a mass flow.

Response: Deleted.

Line 853: In these references the maximum regressive surface is overlain by a transgressive lag and then very shallow shoreline deposits affected by wave activity. A very different scenario to what these authors are proposing.

Response: Paragraph and references removed.

Line 855: The referenced BIFs are not deposited in sandstone/grainstone environments, the IFs are grainstone with very low siliciclastic contents and they are interlayered with chemical muds, but the IFs are not banded.

Response: Because this interpretation is not of immediate relevance to the strength of the paper, the paragraph has been deleted.

Line 1004: This process would be expected to produce a sharp bottom contact to the Fe-rich layer, which would then mineralogical grade upwards into the silica-rich layer. Is this the way the layers are organized?

Response: Yes. We show this in supplementary Figures 8 and 9.

Please also note the supplement to this comment:
https://www.solid-earth-discuss.net/se-2017-113/se-2017-113-AC1-supplement.pdf

Interactive comment on Solid Earth Discuss., https://doi.org/10.5194/se-2017-113, 2017.