

## ***Interactive comment on “Iron isotope fractionation in marine invertebrates in near shore environments” by S. Emmanuel et al.***

**Anonymous Referee #2**

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I have now reviewed the manuscript (bg-2014-110) titled ‘Iron isotope fractionation in marine invertebrates in near shore environments’ by Emmanuel et al. The submitted study presents for the first time the natural variability in the stable isotope composition of iron ( $\delta^{56}\text{Fe}$ ) measured in biomineralized magnetites extracted from several species of modern chitons. These were acquired from the museum collections, and sampled some 100 years ago in areas of the south and north Pacific, as well as the sub-tropical and the north Atlantic ocean. The main objectives of this study were (i) to explore  $\delta^{56}\text{Fe}$  variability in modern marine chitons and its possible species-dependence, and (ii) to constrain the isotope offsets (i.e. fractionation factors) between the magnetite-hosted Fe and the published  $\delta^{56}\text{Fe}$  signatures of modern seawater. The ultimate goal was then to investigate whether the  $\delta^{56}\text{Fe}$  of chiton’s magnetite could be possibly used as a natural proxy, or a recording phase, for the  $\delta^{56}\text{Fe}$  signature of the ambient ocean

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water with the implications for paleo-studies and the investigation of redox changes in seawater over geological time. This is highly original and novel approach, and the submitted manuscript (MS) presents some very interesting and high-quality Fe isotope data measured by MC-ICP-MS, and therefore I would like to see this work eventually published. However, in the current version of the MS there are some ‘weaker points’ that undermine the validity of the proposed interpretations for  $\delta^{56}\text{Fe}$  data (for details see Specific Comments, below), and thus these aspects should be addressed and hopefully improved before this work is ready for the final publication in the journal of Biogeosciences. Therefore, I do recommend a minor to moderate revision of the MS under the editor’s supervision.

Specific Comments Page 5535 (Lines 13 to 24): In this introductory part of the MS the authors should mention that although the fossil record of chitons, and thus possibly also of their biomineralized magnetite components (i.e. the radular teeth), could be dated back to Late Cambrian times, it is basically only since about Eocene (last ca. 56 Ma) when the occurrences of chitons remnants are more abundant in the fossil record (cf. Puchalski et al. 2008, The effect of sampling bias on the fossil record of chitons; Amer. Malac. Bull. Vol. 25, p. 87-95). This significantly lower occurrences of chitons in the Paleozoic and Mesozoic sections could thus severely limit the applicability of their magnetite-based  $\delta^{56}\text{Fe}$  record to studies focusing primarily on the post-Mesozoic periods.

Page 5535 (Line 28), and Page 5536 (Lines: 1 to 4): When discussing the spatial variability of  $\delta^{56}\text{Fe}$  in modern oceans, it would be reasonable to also mention somewhere in the MS what is the estimated residence time of Fe in the modern ocean. Based on the published data it should be close to 100 to 200 years (Boyd and Ellwood, 2010, Nature Geoscience, Vol. 3, p. 675-681), which is about one order of magnitude shorter compared to the average mixing time of the global ocean (about 1000 years). Such a short residence time of Fe in modern seawater has implications for the paleo-studies as it limits the applicability of marine  $\delta^{56}\text{Fe}$  proxy (e.g. chiton-based) to investigate

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basically only the local scale (i.e. basin scale) phenomena. In addition, this extremely short residence time of Fe might also have some implications, or cause possible complications, for the presented comparisons of modern seawater  $\delta^{56}\text{Fe}$  values relative to  $\delta^{56}\text{Fe}$  data measured in 'modern' chitons, as these were collected way back in the early 1900's (See Page 5537, Lines 1 to 2) when the local seawater might have had distinct  $\delta^{56}\text{Fe}$  signatures compared to those published in recent papers from the early 2000's (see data in Fig. 2; Page 5553, and References herein, e.g. Lacan et al. 2008, 2010; John and Adkins, 2010).

Page 5543 (Lines 27 to 29), and Page 5544 (Lines 1 to 12): Here you mention that "In addition to magnetite ( $\text{Fe}_3\text{O}_4$ ), chiton radula contain other Fe minerals, including goethite, lepidocrocite, ferrihydrite", and also that during the ontogenesis of chitons "the ferrihydrite precursor is transformed to magnetite". This is an important information and a factor that, in my view, might be quite relevant for the interpretation of the observed  $\delta^{56}\text{Fe}$  variability in your 'bulk magnetite' samples. As from the theoretical calculations, as well as experimental data, it is now well known that there is different 'equilibrium Fe-isotope fractionation' for different Fe-bearing minerals, relative to the aqueous Fe species, i.e.  $\text{Fe}(\text{II})_{\text{aq}}$ . Specifically, published data indicate that at temperatures of 20°C the representative Fe isotope fractionation factor ( $\Delta^{56}\text{Fe}$ ), between dissolved  $\text{Fe}(\text{II})$  and mineral-hosted Fe is as follows: about -1.5 per mil for magnetite; -1 per mil for goethite; and up to -2.5 per mil for ferrihydrite (see data in Wu et al. 2011; ES&T, Vol. 45, p. 1847-1852; and Frierdich et al. 2014, GCA, Vol. 139, p. 383-398). Thus, in theory, it is also possible that the observed large variability in your 'bulk magnetite' samples could be partly controlled by different mineralogy of your samples. For example, the extremely light  $\delta^{56}\text{Fe}$  signatures (up to -2 per mil) measured in your 'Mopalia muscosa' samples could be due to higher contribution of the isotopically lighter 'ferrihydrite precursor' phase in your bulk 'magnetite' sample. This possible effect of mineralogy on your bulk 'magnetite'  $\delta^{56}\text{Fe}$  data could be tested by X-ray diffraction (XRD) analysis of your samples, if enough material is left for such analysis. Hence, if realistic, I strongly recommend that the authors would provide and discuss

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also 'mineralogical data' in the revised version of the MS to further evaluate the role of such mineralogy-controlled effects on their  $\delta^{56}\text{Fe}$  values. Alternatively, if the limited sample size will render such additional XRD analysis impossible, the authors should at least mention and discuss in their revised MS also the 'mineralogy-controlled' scenario, outlined above, as possible explanation for their  $\delta^{56}\text{Fe}$  variations observed in chitons.

Technical Corrections Page 5535 (Line 9): The reference of Brantley et al. 2004, mentioned here, is not included in the Reference list (see Page 5546), so please correct this.

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