

## Response to Reviewer #2:

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 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).

1. 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 also ‘mineralogical data’ in the revised version of the MS to further evaluate the role of such mineralogy-controlled effects on their  $d^{56}\text{Fe}$  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  $d^{56}\text{Fe}$  variations observed in chitons.

*The reviewer makes an import point: mineralogy could well play a role in controlling the isotopic composition. Unfortunately, all the material was used for the Fe isotope analyses and mineralogical analyses were not carried out on our samples. However, this is certainly worth exploring in future studies, and in the revised manuscript we will include a discussion of the potential influence of mineralogy on isotopic composition, including the references cited by the reviewer.*

2. 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.

*This will be corrected in the revised manuscript.*