



Selenium isotopes trace anoxic and ferruginous seawater conditions in the Early Cambrian



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ABSTRACT

Selenium (Se) isotopes can yield substantial isotopic fractionation (up to 20‰) confirmed by experiments and field investigations, depending on various biotic or abiotic redox transformations. Therefore, it is expected that redox changes in the ancient oceans would induce significant isotopic fractionation, and the Se isotopic signatures recorded in old sedimentary rocks might provide new insight into how the redox state of the ancient ocean has evolved. However, previous studies have shown that Se is slightly enriched in the lighter isotope relative to the bulk earth values in most deposited conditions (oxic, anoxic, and even sulfidic). Here, our results reveal that ferruginous conditions can result in excessive accumulation of Se in sediments with an elevated Se/S ratio and significant isotope fractionation (about 6‰), which leads us to propose that Se isotopes are an appropriate geochemical proxy to trace unique oceanic conditions over time. Accordingly, Se isotopic variations measured in three Early Cambrian formations in southern China suggest that anoxic waters with ferruginous conditions must have been present in early Cambrian ocean along the eastern margin of the Yangtze platform, and oceanic circulation was stepwise reorganized. This may have triggered biological diversification from the Ediacaran to the Early Cambrian.

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1. Introduction

Redox-sensitive metals (e.g., Fe, Mo) and their isotopes have been increasingly used as proxies for changing redox conditions in the oceans (Anbar and Rouxel, 2007). Selenium is also redox-sensitive, potentially existing in four redox states (VI, IV, 0 and -II), and its chemical behaviour depends strongly on redox reactions (Johnson, 2004). Under oxidizing conditions, Se(VI) is favored thermodynamically and forms the selenate (SeO_4^{2-}) anion, is highly soluble and not strongly adsorbing (Neal and Sposito, 1989); under mild reducing conditions, Se(VI) is reduced to Se(IV) (selenite, SeO_3^{2-} and biselenite, HSeO_3^-), is highly soluble and strongly adsorbing onto Fe and Al oxides. Under moderate reducing conditions, Se(IV) reduces to Se(0). Under strong reducing conditions, Se(-II) as HSe- is the thermodynamically stable form, with behavior similar to that of sulfide (Johnson, 2004).

Selenium has six stable isotopes: ^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , ^{80}Se and ^{82}Se with relative molar proportions varying from 0.8% (^{74}Se) to 49.6% (^{80}Se) (Coplen et al., 2002). Experimental work has shown that Se isotope

fractionation occurs during reduction of Se(VI) or Se(IV) to Se(0) and/or Se(-II), through various biotic or abiotic reactions (Krouse and Thode, 1962; Rees and Thode, 1966; Rashid and Krouse, 1985; Johnson et al., 1999; Herbel et al., 2000; Ellis et al., 2003). Fractionation may vary from 7‰ to 11‰ in the $\delta^{82}\text{Se}$ value, depending on environmental conditions (e.g. reducing agents, Se concentration), with the reduced product being depleted in heavier isotopes. Reduction experiments in the presence of natural sediment slurries have also yielded similar fractionation factors for Se(VI) reduction (2.6–3.1‰) and for Se(IV) reduction (5.5–5.7‰) to those performed on pure cultures (Herbel et al., 2002). Thus, substantial isotopic fractionation suggests that Se isotopes may be a powerful paleo-environmental proxy, as has been established for Mo and Fe isotopes (Anbar and Rouxel, 2007).

Based on above Se isotopic framework, greater isotope fractionation should presumably occur under anoxic and euxinic conditions when dissolved Se in the water column is reduced by microbial or abiotic processes. However, an important implication for Se is the lack of strong enrichment in light isotopes evident in most marine sediments deposited under anoxic and even euxinic conditions (Hagiwara, 2000; Mitchell et al., 2012). For example, Mitchell et al. (2012) analysed ~120 samples

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of fine-grained marine sedimentary rocks and sediments spanning the entire Phanerozoic, and they found that $\delta^{82}\text{Se}$ values fall within a narrow range, from -1 to $+1\%$. This phenomenon was also observed by Hagiwara (2000) in a survey of marine sediments and algae. For unweathered (fresh) black shale samples, the mean $\delta^{82}\text{Se}$ value is $-0.30 \pm 1.01\%$ with a mean Se concentration of 77 ± 3.49 ppm; however, weathered samples yield a $\delta^{82}\text{Se}$ value of $3.98 \pm 3.90\%$ and mean Se concentration of 716 ± 1670 ppm. The largest range of Se isotopic composition for a single sedimentary formation is reported in the Yutangba Se deposit, where supergene alteration has produced a fractionation of $\sim 23\%$ (Wen and Carignan, 2011; Zhu et al., 2014). It appears that in most cases only secondary alteration (weathering, diagenesis) can lead to a greater isotopic fractionation and Se enrichment. Overall, results from analyzed shales and sediments have not yet shown that marine sedimentary Se isotope ratios provide an indication of past redox conditions. For this reason, we report on systematic measurements of Se isotopes in some Cambrian strata. Results from Fe speciation measurements indicate that isotopically lighter Se is associated with ferruginous waters, and therefore we propose that strongly

negative $\delta^{82}\text{Se}$ values may be indicative of ferruginous conditions in the sedimentary record.

2. Geological setting and stratigraphy

The Ediacaran to early Cambrian successions were well preserved over the Yangtze platform in South China with different stratigraphical settings, including platform facies, transition belt and protected basin as illustrated in Fig. 1-a (Steiner et al., 2001; Guo et al., 2007). In several areas, they are exposed across a transection from platform to basin, offering an opportunity to investigate the stratigraphic features during this critical interval in Earth history, which can provide clues of sea-level fluctuations, ocean anoxia, metal accumulation and corresponding ocean-atmosphere-biology evolution. Three sections were selected for this study, the Huangjiawan (HJW), Chuanyanping (CYP) and Silikou (SLK) sections, which are separated from each other by approximately 400 km (Fig. 1-a), and located at sites from the carbonate platform (HJW section and CYP section) and protected basin (SLK section)

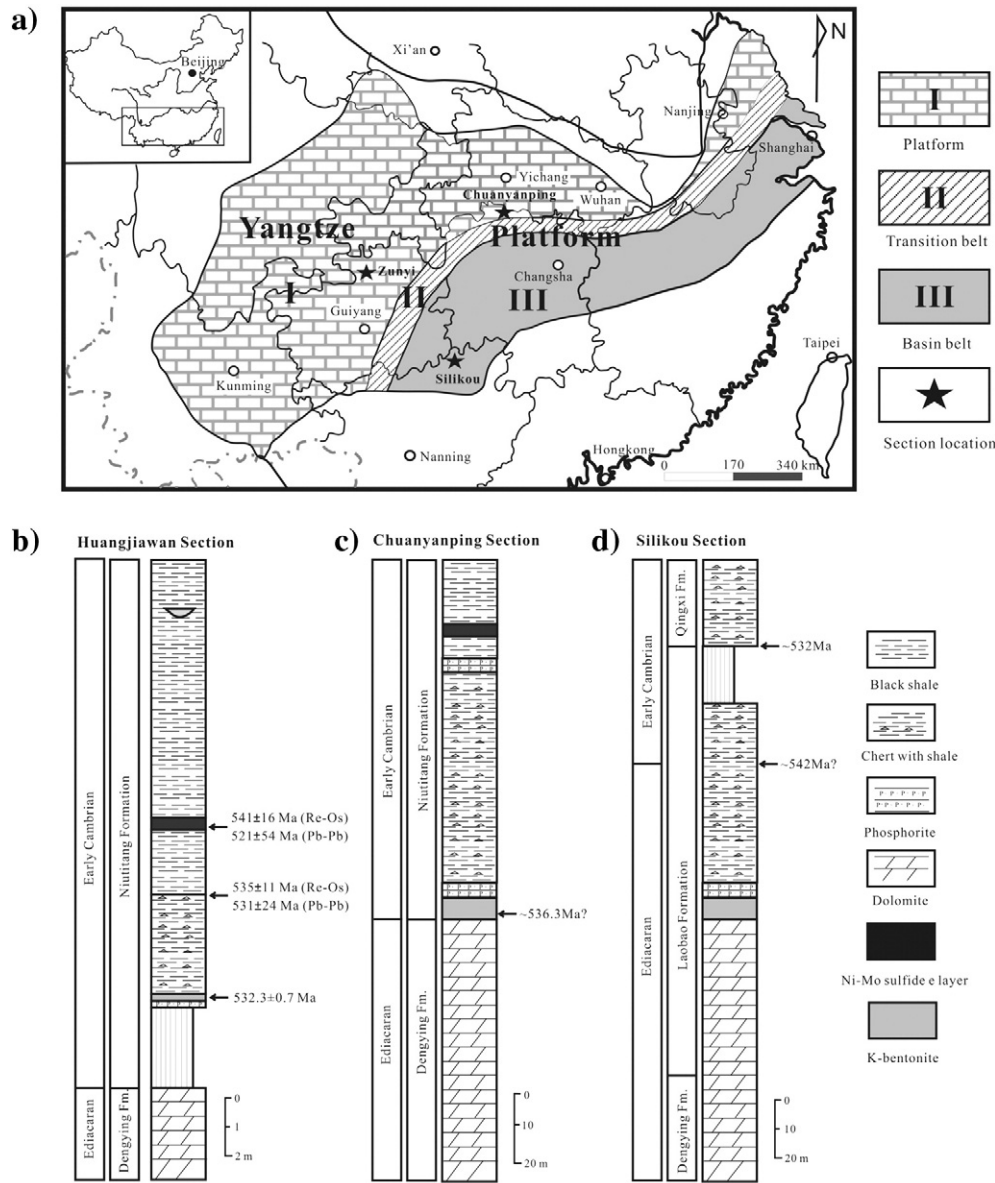


Fig. 1. (a) Simplified palaeogeographic map of the Yangtze Platform during Ediacaran–Cambrian transition modified from Steiner et al. (2001); (b) Lithological profile of the Huangjiawan section; (c) Lithological profile of the Chuanyanping section from Fan et al. (2013); (d) Lithological profile of the Silikou section from Chang et al. (2012).

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