

Growth of a Se^0 /calcite composite using hydrothermal carbonation of $\text{Ca}(\text{OH})_2$ coupled to a complex selenocystine fragmentation

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In this study, the hydrothermal method was carried out in order to produce an elemental selenium (Se^0)/calcite composite. Under O_2 -poor conditions (i.e. with a purge step using Argon), the composite was mainly characterized by spherical selenium nanoparticles (<500nm) deposited on the calcite matrix. The carbonate matrix was constituted by nano- and micro-rhombohedral crystals (<2 μm) and micrometric agglomerates and/or aggregates (<5 μm). For this case, the spherical Se nanoparticles give a stable red coloration to the composite. In contrast, under O_2 -rich conditions (i.e. without a purge step), the composite was characterized by hexagonal selenium microparticles (<25 μm) dispersed in the calcite matrix. For this case, a gray coloration of composite was observed [1].

In conclusion, the complex selenocystine fragmentation mechanism led the precipitation/growth of elemental selenium with different morphologies and particles sizes. Furthermore, it was noticed that the selenocystine fragmentation also participates to the precipitation/growth of calcite particles with star-like morphologies. Finally, the results presented here demonstrate that Se^0 /calcite composite, with spherical or hexagonal morphologies for elemental selenium can be produced, this composite could possibly have a high potential for medical (ex. dietary supplement) or industrial (ex. pigments) applications. In addition, this study may have implications in the field of biomineralization.

[1] Montes-Hernandez *et al.* (2008) *Crystal Growth & Design* (in press)

Fractionation of $^{238}\text{U}/^{235}\text{U}$ in modern and ancient anoxic marine environments: A paleoredox tracer?

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Uranium is a redox sensitive trace element that is strongly enriched in anoxic sediments. It has been shown that burial of U from seawater into such sediments is coupled with U-isotope fractionation [1]. While seawater has a constant $\delta^{238}\text{U} = -0.41\text{‰}$ (relative to SRM 950a), modern sapropels (e.g. Black sea) display heavier U isotope composition ranging from $\approx -0.2\text{‰}$ to $+0.44\text{‰}$ [1]. Black shales are also isotopically heavier than the crust ($\delta^{238}\text{U} \approx -0.3\text{‰}$), the major source of U to the oceans. There is a crude positive correlation of U-isotope compositions with U concentrations and TOC for euxinic sediments. In contrast, oxic sediments display U-isotope compositions, which are slightly lighter than that of seawater. The U-isotope fractionation between oxic and anoxic environments is similar to that observed for Mo [2, 3], although contrary in directions and extents. Thus, a shift in the abundance of oxic versus anoxic sinks through geological timescales should affect the oceanic mass balance of U-isotopes, similarly as previously observed for Mo [4].

We are focusing our investigations on ancient black shales from periods, which are believed to represent anoxic events of global extent, such as the mid-Cretaceous OAE-2 [5] and the Toarcian OAE [6]. We will present a comparison of U- and Mo-isotope systematics and abundances of redox sensitive trace metals. Preliminary U-isotope data of black shales from OAE-2 and the Torcian OAE also display heavier U-isotope compositions ($\approx -0.3\text{‰}$ to $\pm 0\text{‰}$) than that of modern seawater. However, they may be shifted by 0.1-0.3 ‰ towards lighter compositions compared to modern black shales. OAE-2 samples from Leg 207, core 1261 (an open ocean setting), which provides a continuous record through the entire OAE, are also isotopically lighter than black shales from the time before the onset of the OAE. These findings may indicate a larger extent of anoxic environments during both OAEs compared to modern times.

[1] Weyer *et al.* (2008) *GCA* **72**, 345-359. [2] Barling *et al.* (2001) *EPSL* **193**, 447-457. [3] Siebert *et al.* (2003) *EPSL* **211**, 159-171. [4] Arnold *et al.* (2004) *Science* **304**, 87-90. [5] Erbacher *et al.* (2005) *G3* **6**, 2004 GC000850. [6] Suan *et al.* (2008, in press) *EPSL*.