Formation mechanisms of carbonate concretions of the Monterey Formation: Analyses of clumped isotopes, iron, sulfur and carbon

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Carbonate concretions can form as a result of organic matter degradation within sediments. However, the ability to determine specific processes and formation temperatures of particular concretions has remained elusive. Here, we employ concentrations of carbonate-associated sulfate (CAS), $\delta^{34}S_{CAS}$ and clumped isotopes (along with more traditional approaches) to characterize the nature of concretion authigenesis within the Miocene Monterey Formation.

Integrated analyses reveal that at least three specific diagenetic reaction pathways can be tied to concretion formation. One calcitic concretion from the Phosphatic Shale Member at Naples Beach yields $\delta^{34}S_{CAS}$ values near Miocene seawater sulfate (~ +22‰ VCDT), abundant CAS (ca. 1000 ppm), depleted $\delta^{13}C_{carb}$ (~ –11‰ VPDB), very low concentrations of Fe (ca. 700 ppm) and Mn (ca. 15 ppm) and clumped isotope temperatures of ~18°C—characteristics most consistent with shallow formation in association with microbially mediated, organic matter degradation by nitrate, iron-oxides and/or minor sulfate reduction. Cemented concretionary layers of the Phosphatic Shale Member at Shell Beach display elevated $\delta^{34}S_{CAS}$ (up to ~ +37‰), CAS concentrations of ~600 ppm, mildly depleted $\delta^{13}C_{carb}$ (~ –6‰), moderate amounts of Mn (ca. 250 ppm), relatively low Fe (ca. 1,700 ppm) and clumped isotope temperatures of ~27-35°C, indicative of somewhat deeper formation in sediments dominated by sulfate reduction. Finally, concretions within a siliceous host at Montaña de Oro and Naples Beach show minimal CAS concentrations, positive $\delta^{13}C$ values (up to +16‰), the highest concentrations of Fe (ca. 11,300 ppm) and Mn (ca. 440 ppm) and clumped isotope temperatures of ~28-35°C, consistent with formation in sediments experiencing methanogenesis in a highly reducing environment. This study highlights the promise in combining CAS and clumped isotope analyses with more traditional techniques to more precisely characterize subsurface biospheric processes and particularly how they relate to Fe-S-C cycling in ancient sediments.

Two contrasting Sn- and W-bearing granites in the Nanling Range, South China: evidence from Hf isotopes

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The Nanling Range where many granite-related lager-superlarge rare-element deposits occur, is the most important area in terms of W-Sn deposits in the world. The Middle-Late Jurassic period (170-140Ma) is the most important metallogenic time for W and Sn in this area. The most granites associated with W-Sn deposits formed during this time can be divided into two groups: the W- and Sn-bearing granites. These two kinds of granites have different petrochemical and trace element geochemical features [1]. The W-bearing granites comprising biotite granites, two-mica granites and muscovite granites are peraluminous and belong to S-type, whereas the Sn-bearing granites consisting of hornblende-bearing biotite granites and biotite granites and containing little muscovite are metaluminous and belong to A-type [2].

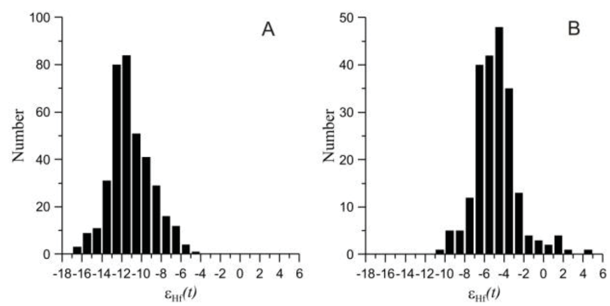

Figure 1: Histograms of zircon Hf isotopic compositions for the W-bearing (A) and Sn-bearing (B) granites

We have investigated the Hf isotope compositions of zircons in both the W- and Sn-bearing granites. The εHf(t) values of the zircons in the W-bearing granites vary from -8 to -14, with a peak value of -12; whereas the εHf(t) values of the zircons in the Sn-bearing granites range from -2 to -8, with a peak value of -5. The hafnium isotope compositions for these two kinds of ore-bearing granites in the Nanling Range indicate that the W-bearing granites were dominantly derived from the continental crustal materials; whereas the Sn-bearing granites were mainly generated by the crust-mantle mixed sources.

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[1] Chen, Lu, Chen, et al. (2008) *Geological Journal of China Universities,* **14**, 459-473. [2] Lu, Zhang & Wang (2011) *Mineralogical Magazine* **75**, 1359.