Geochemical expressions of early marine diagenesis in corals – implications for paleoceanographic reconstructions

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Geochemical expressions of diagenesis in corals

Detecting the potential geochemical consequences of early marine diagenesis is essential for establishing the validity of past climate reconstructions from coral. Long-term trends in reconstructed sea surface temperatures (SSTs) for a well preserved coral correlate strongly with instrumental SST records spanning the 20th century. In contrast, the δ^{18} O and Sr/Ca for a diagenetically altered coral give identical cool SST anomalies of 4-5°C, as a consequence of the addition of secondary aragonite enriched in O and Sr.

Fig.1: (A) δ^{18} 0 and Sr/Ca values for diagenetically altered coral (Muiron Island). (B) Comparison of SST unit data for pristine (Tantabiddi Bay) and altered coral from Ningaloo Reef, Western Australia.



Conclusions

Cross-checking of paleoclimate reconstructions with two supposedly independent paleothermometers ($\delta^{18}O$, Sr/Ca) may not be valid, and coral records showing cooler SSTs in the past need to be interpreted with caution. Furthermore, modern coral records with long-term trends in $\delta^{18}O$ indicating recent warming and freshening of the ocean can be potentially explained by early marine diagenesis.

Sulfur Isotope Imaging of Interplanetary Dust Particles

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Introduction: Interplanetary Dust Particles (IDPs) are amongst the most primitive material available for laboratory studies of astrophysical processes. Iron nickel sulfides are ubiquitous in IDPs and at least some of these sulfides may be presolar in origin [e.g., 1, 2]. In addition, recent studies [e.g., 1] suggest that Fe-sulfides in IDPs may have formed in a different solar system environment than meteoritic sulfides. However, there have been no published S isotopic measurements in IDPs. Therefore, we have started a systematic investigation of S-isotopic composition in IDPs to look for nucleosynthetic effects and better constrain the formation of the FeNi-sulfides. In the first stage of this investigation we have focussed on IDPs that are almost exclusively comprised of large (10-15 μ m) pyrrhotite grains.

Analytical Technique: Analyses were done in a scanning ion imaging mode with a Cs⁺ beam focused to ~1 μ m on an IMS-6f ionprobe. Images of ³²S⁻, ³³S⁻, ³⁴S⁻, ^{16,18}O⁻, CN⁻ and Si⁻ were acquired for five pyrrhotite rich IDPs. Analyses were carried out at a mass resolution of 4100, sufficient to resolve isobaric interferences on all three S isotopes. Instrumental mass fractionation was corrected using Anderson Lake pyrrhotite as a standard [4] and image processing software was used to extract S isotopic ratios on spatial scales of ~1 μ m or larger.

Results and discussion: No large variations in Sisotopic composition (>50‰) were observed within a single grain. Four of the IDPs have bulk S isotopic compositions that are either statistically indistinguishable from that of Canyon Diablo troilite ($\delta^{33}S = 0$ ‰; $\delta^{34}S = 0$ ‰) or barely distinct at the 2σ level. One of the IDPs, however, shows modest enrichments in ³³S and ³⁴S and the anomaly might be mass independent (δ^{33} S= 16.7±6.2°/_{.00}(2 σ); δ^{34} S = 19.4±9.8°/_{.00}(2 σ)). We are currently verifying the magnitude of this anomaly. The positive δ^{33} S and δ^{34} S may result from enhancement of 33 S 34 S in the gas phase through chemical reactions [e.g., 5] and subsequent transfer of this signature by sulfidation of Fe metal. Alternatively, the enrichments may reflect presolar nucleosynthetic effects. In the future, we will measure ³⁶S in these IDPs and look at S-isotopic composition in smaller (~1µm) sulfides.

References: [1] Bradley J. P., (1994), Science 231, 1542-1544. [2] Keller L. P. et al., (2000), LPS XXXI, #1860. [3] Dai Z. R. and Bradley J. P., (2001), Geochim. Cosmoshim. Acta 65, 3601-3612. [4] Crowe D. E. and Vaughn R. G., (1996), Am. Min. 81, 187-193. [5] Cooper G.W. et al., (1997), Science 277, 1072-1074.