

## Effect of rapid diagenetic calcite deposition on carbonate associated Sulfate and Calcium isotopes

ALEXANDRA V. TURCHYN<sup>1</sup> DONALD J. DEPAOLO<sup>1</sup>,  
CARL I. STEEFEL<sup>2</sup> AND DANIEL P. SCHRAG<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Science, U.C. Berkeley

<sup>2</sup>Lawrence Berkeley National Laboratory, Berkeley, CA

<sup>3</sup>Department of Earth and Planetary Sciences, Harvard University

Carbonate minerals remain the primary mineral proxy used for reconstructing paleoclimate and paleoceanographic changes throughout Earth History. Recent work has expanded the use of these minerals to include the sulfur and oxygen isotopic composition of structurally bound carbonate-associated-sulfate ( $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  of CAS) and calcium isotopes ( $\delta^{44}\text{Ca}$ ). While carbonate minerals are available nearly continuously over the past billion years of the rock record, they are susceptible to diagenetic alteration. Understanding and quantifying the effect that diagenesis may have on both CAS and  $\delta^{44}\text{Ca}$  is critical for proper interpretation of the geochemical record. In addition, the high rates of calcite precipitation in sediment where there is rapid sulfate reduction may produce effects on pore fluid calcium that shed light on calcium isotope fractionation in natural systems.

We measured both the  $\delta^{18}\text{O}_{\text{SO}_4}$  the  $\delta^{34}\text{S}$  of pore fluid sulfate and coexisting CAS from ODP sites 1123 (New Zealand) and 1063 (Bahamas). At both sites the  $\delta^{18}\text{O}_{\text{SO}_4}$  and the  $\delta^{34}\text{S}$  of CAS track the increase in the  $\delta^{18}\text{O}_{\text{SO}_4}$  and the  $\delta^{34}\text{S}$  of sulfate in the pore fluid. These results have implications for the fidelity of the CAS proxy. We also measured the  $\delta^{44}\text{Ca}$  at ODP site 1082 (West Africa). Calcium concentrations at this site decrease at the top of the core from 10mM to ~3mM reflecting rapid calcite deposition. The  $\delta^{44}\text{Ca}$ , which remains at seawater values through the zone of rapid precipitation, gives a view of calcium isotope fractionation due to calcite precipitation at natural rates. We have added formulations for O, S, and Ca isotope fractionation to CRUNCH, the multicomponent reactive transport code, for the purpose of further exploring the effects of diagenesis on these proxies. We will quantify calcite recrystallization from incorporation of isotopically altered sulfate into CAS, to explore natural calcium isotope variation and fractionation, and to assess how both these proxies are affected by carbonate diagenesis.

## Widespread Os isotope evidence for a magmatic pulse at the onset of Oceanic Anoxic Event 2

S.C. TURGEON AND R.A. CREASER

Dept. Earth & Atmos. Sciences, University of Alberta, Canada  
(st23@ualberta.ca; robert.creaser@ualberta.ca)

The Cenomanian-Turonian Boundary Event (CTBE; ca. 93.5 Ma) is one of the best studied global Oceanic Anoxic Event (also referred to as OAE2) that punctuate the Cretaceous stratigraphic record. The CTBE is the most extensive of the Cretaceous OAEs, with global temperatures apparently the highest of the last 115 Ma (Clarke and Jenkyns, 1999; Huber *et al.*, 2002; Wilson *et al.*, 2002). This OAE is characterised by a positive global carbon-isotope excursion in both carbonates and organic matter. The similarity of  $\delta^{13}\text{C}$  curves at distant locations hint at the global nature of this event.

During this time, high amounts of organic carbon were buried in ocean basins due to an increase in primary productivity and/or enhanced preservation of organic matter owing to anoxic bottom waters. Debate, however, still surrounds the identification of the actual "trigger" mechanism of these periods of carbon sequestration.

Rhenium-osmium isotopic analyses were performed on two sample sets located in different basins during the CTBE: the Livello Bonarelli from the Furlo section in central Italy located in the western reaches of the Tethys Seaway, as well as Site 1260B of ODP Leg 207, located on Demerara Rise just off the ENE coast of South America, in the southern proto-North Atlantic. At Furlo, several minor  $\text{C}_{\text{org}}$ -rich intervals ("black levels"), generally thought to be precursor events, are interbedded with siliceous limestones beneath the Bonarelli.

Initial results from the black levels show upward increasing Os contents, peaking abruptly at the base of the Bonarelli (~10 ppb), then decreasing to 0.1-0.2 ppb: the CTBE at Site 1260B shows a similar trend, with Os contents of 25 ppb at the base of the CTBE decreasing to <0.1 ppb upwards. The initial  $^{187}\text{Os}/^{188}\text{Os}$ , calculated for individual samples and reflecting contemporaneous seawater Os isotopic values, are fairly high (0.7-1.2) in the black levels, indicating a continental weathering dominated Os system. The initial Os ratios at the base of the CTBE are, however, very low (~0.14-0.15) in both sections, and gradually increase upward to ~0.5-0.6. Such low values at the onset of the CTBE suggest a strong magmatic/hydrothermal influence (no evidence of bolide impact has been reported near this stage boundary), while the upward increase probably documents a return to a weathering-dominated source of Os in the oceans.

### References

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