Sulfur Isotopic Composition as a Tool for Understanding Dolomitization: Application to Ancient Examples

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Project Purpose

This project is designed to investigate the use of the stable isotopes of sulfur (^{32}S and ^{34}S) in carbonate associated sulfate (CAS) as a possible diagenetic tool to understand the paragenesis of certain carbonates in particular dolomites and carbonates formed in high temperature.

Scope of Work

The project initially developed the equipment necessary to process the samples for the stable S isotopic analyses. This work has been largely completed in 2007 and 2008. In 2009, we presented data from a core retrieved in the south Australian Bight during Leg 182 in an extreme environment, which possesses very high concentrations of hydrogen sulfide, regions which have very little sulfate, and others with very high sulfate. In 2010 we will continue to work on the Leg 182 sites (Figure 1) as well as applying the techniques to two older dolomite occurrences, the Mississippian Madison Formation (Katz et al., 2007; Katz et al., 2006; Westphal et al., 2004) and the Pliocene dolomites from San Salvador (Dawans and Swart, 1988) in the Bahamas.

Key Deliverables

The analytical procedure and workflow for the use of δ^{34}S of CAS to ascertain the nature of the diagenetic environment, i.e. open marine, closed marine, sulfate reduction, and thermochemical sulfate reduction. The data from the various sites will help to assess the validity of the technique.

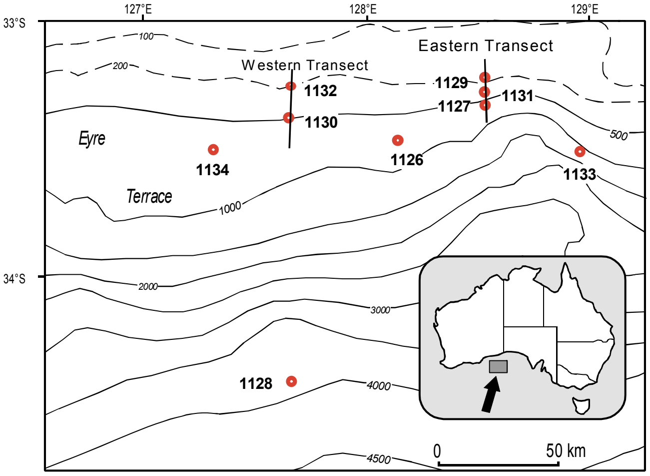

Figure 1. Location map of Site 1129, cored during Leg 182 of the ODP.

Project Description

The issue of carbonate associated sulfate (CAS), or sulfur trapped within the matrix of carbonate minerals, has attracted a significant deal of attention because of the possibility of utilizing this source of sulfur to refine the oceanic sulfur isotopic curve, which at present is based mainly on the analysis of evaporite minerals (Burdett, 1990). In addition to obtaining the δ^{34}S of the

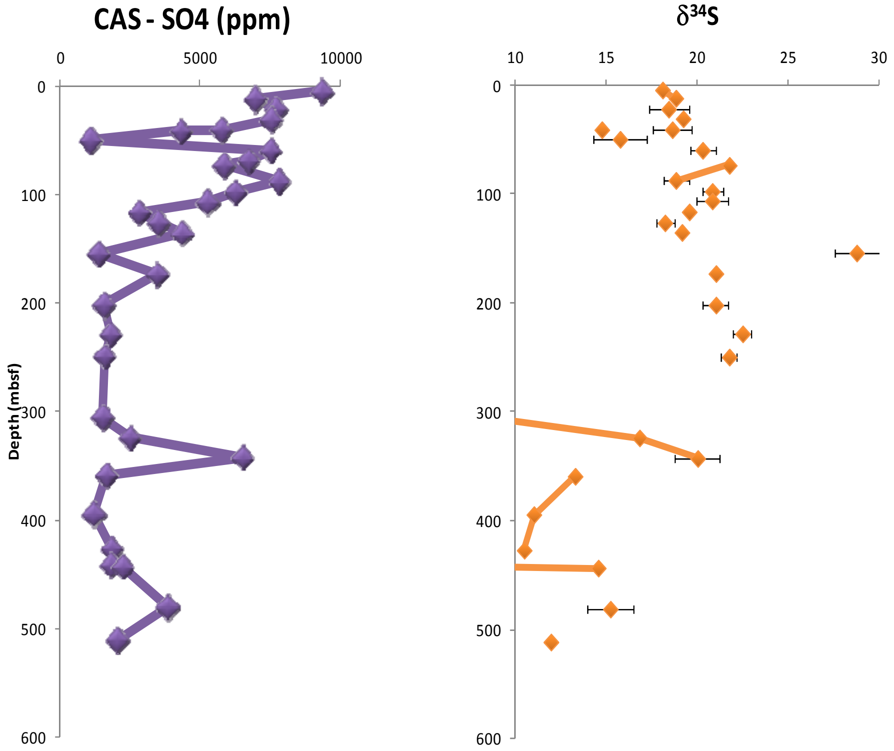

Figure 2. (A) The concentration of CAS as a function of depth. The decrease in the concentration of CAS reflects the loss of aragonite, probably not as a result of recrystallization, but rather as a change in the input of material. (B) Changes in the δ^{34}S of the CAS. Note that in the upper portion of the core there is a slight increase in the δ^{34}S probably reflecting the formation of dolomite in the presence of the current gradient in the δ^{34}S of the sulfate in the interstitial fluids. In the lower portion, the δ^{34}S are quite a bit lower probably indicating recrystallization at a time when the δ^{34}S profile was different than at present. The negative values suggest the oxidation of hydrogen sulfide.

original depositional seawater, the δ^{34}S can provide information in conjunction with the concentration of non-conventional trace elements (S, Na, K, and Cl) regarding the nature of the environment of diagenesis. For example, it is well known that many dolomites are formed within the sulfate reduction zone, where dolomitization is promoted by the degradation of organic material (creating alkalinity) and perhaps by the removal of the inhibitory sulfate ion (Baker and Kastner, 1981). Such dolomite would have lower concentrations of S, normal concentrations of Na, K, and Cl, but slightly elevated δ^{34}S values. In this environment the concentration of sulfate would be expected to be lower than in normal marine sediments and the δ^{34}S would be slightly enriched as the process of sulfate reduction forms H_2S depleted in δ^{34}S thereby enriching the residual sulfate (Goldhaber and Kaplan, 1975). Dolomites associated with evaporite minerals might have low concentrations of SO_4^{2-} (as SO_4^{2-} is removed during the formation of evaporite minerals), normal δ^{34}S values, but elevated values of Na^+, K^+, and Cl^-. Dolomites formed from brines, which have not attained saturation with respect to gypsum or anhydrite, might be expected to show elevated concentrations of all non-conventional trace elements including sulfate and normal $\delta^{34}S$ values.

Preliminary results from the core at Site 1129 in the South Australian Bight show in the upper portion of the profile a slight increase in the $\delta^{34}S$ (Figure 2). This increase is much less than the increase in the $\delta^{34}S$ of the dissolved sulfate (data from Wortmann et al., unpublished), but the increase is consistent with the precipitation of about 5-10% dolomite. In the lower portion of the core, the $\delta^{34}S$ values of the bulk sediment are low (~10‰), suggesting the oxidation of isotopically light H_2S to sulfate and the subsequent incorporation into the carbonate mineral. As the present porewater profile does not display this pattern, this oxidation process must have occurred during an earlier period when the porewater profile was different than today. The data indicate that (i) the dolomite in the lower portion of the core is not forming at the present time, (ii) dolomite in the upper portion of the core is forming under the present geochemical regime, and (iii) at times in the past, oxidation of hydrogen sulfide has contributed to the sulfate pool.

Expected Results

This study will enable us to ascertain whether the $\delta^{34}S$ of CAS can provide important information on the diagenetic environment of carbonate diagenesis including environment in which dolomites are formed.

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