

# Sr heterogeneity and speciation in coral aragonite

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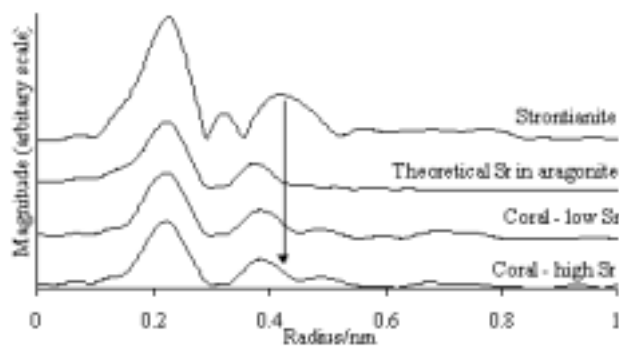
## Introduction

The substitution of Sr for Ca in aragonite is temperature dependent and Sr/Ca ratios in coral aragonite have been used to reconstruct records of past sea surface temperatures [1]. However, microanalytical studies have indicated that Sr in some coral skeletons is more heterogeneously distributed than expected from SST data [2]. The concentration of Sr in coral aragonite is above thermodynamic solubility limits and Sr may exist in two phases: as Sr substituted for Ca in aragonite and as discrete SrCO<sub>3</sub> (strontianite) domains [3]. Variations in the size and/or quantity of these domains may account for small-scale Sr heterogeneity. The present paper describes work to determine variations in Sr concentration and speciation in coral skeletons.

## Methods and Materials

We used synchrotron x-ray fluorescence (SXRF) to map Sr/Ca variations over a 420 x 200 μm area of a *Porites lobata* skeleton at a 5 μm scale. We limited our calculation of Sr/Ca ratios to those points within a narrow range of Ca counts (and sample thickness), and we corrected both Sr and Ca for estimated variation in sample thickness. We standardized the coral Sr/Ca ratios using an ion probe analysis on a high-Sr area of the section. A second ion probe analysis, on a low-Sr area, was in good agreement with these estimates.

To investigate the coordination sphere of Sr in the sample, we collected Sr K-edge extended x-ray absorption fine structure (EXAFS) spectra from one Sr-low and one Sr-high region of the thin section. Fourier transforms of the EXAFS oscillations (weighted by  $k^3$ ) relate to the Sr-next-neighbor distances and therefore give an insight into Sr coordination in the sample (Figure 1).



## Results and Discussion

Sr/Ca variations were large (up to 3 mmol mol<sup>-1</sup>, equivalent to 38°C on the palaeothermometer) and unrelated to changes in local seawater temperature or composition. Fourier transforms of EXAFS oscillations show no discernible difference for Sr-rich and -poor areas of the coral aragonite, indicating that Sr is in the same structural state in both. The data are in good agreement with an *ab initio* calculation (using FEFF8, version 7.0) of the EXAFS spectrum for Sr substituted for a single Ca atom in aragonite with a Sr-Ca distance around 0.38 nm and in poor agreement with measured Sr K-edge EXAFS of strontianite, with a Sr-Sr distance of 0.42 nm. Although Sr heterogeneity exists within the coral skeleton (nominally extending beyond the Sr solubility limit in aragonite), this takes place without the formation of strontianite domains.

The cause of the Sr heterogeneity is still unclear. However, the Sr microdistribution is systematic and appears to correlate with the crystalline fabric of the coral skeleton suggesting Sr heterogeneity may reflect nonequilibrium calcification processes.

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Figure 1: Fourier transforms of the EXAFS oscillations for strontianite, and the Sr-rich and Sr-poor regions of the coral to give the radial distribution of atoms around Sr. The radii are scaled so that the Sr-Sr distance in strontianite corresponds to the 0.42 nm determined from x-ray diffraction studies. A calculation of the coordination sphere of Sr substituted for Ca in aragonite is also shown. The 0.42 nm position for Sr-Sr distances in strontianite is labeled by the vertical arrow. The difference in second shell amplitude between the coral spectra and that of strontianite indicates that the second neighbor of Sr in the coral is Ca, not Sr.

## References

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