

The effects of artificial alteration on sulfur in *Arctica islandica* shells

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Carbonate associated sulfate (CAS) is an important proxy for reconstructing redox conditions in former oceans. Especially for biogenic carbonates it is not fully understood where exactly the CAS is incorporated, how much is incorporated in respect to ambient sulfate concentrations, and how CAS is affected by diagenetic alteration. By combining sulfur K μ -XANES and μ -XRF analyses with geochemical methods (CAS-extraction, sulfur isotope measurements), this study aims at specifying the location of incorporation of CAS. Moreover, the effects of diagenetic alteration on sulfur abundance, speciation and distribution in shells of the marine bivalve *Arctica islandica* will be assessed through alteration experiments. Hereby, shell pieces were hydrothermally altered at two different temperatures (100°C and 175°C) for different times (one to twelve weeks) with sulfate-free artificial seawater.

Our results show that the samples altered at 100°C retain the original/primary sulfur distribution and concentration, similar to a non-altered *Arctica islandica* shell. In contrast, μ -XRF maps of the shells altered at 175°C exhibit a significant change in the sulfur distribution and a decrease in sulfur concentration. The respective incubation solutions, in turn, show an increase in sulfate concentration with longer alteration times at 175°C. Furthermore, μ -XRF maps of sulfur not only record the growth of calcite crystals with longer alteration times at 175°C but also indicate that newly formed crystals are characterized by a near complete absence of sulfur. We propose that the process of recrystallization from aragonite to calcite between 100°C and 175°C causes the loss of sulfur from the bivalve shell. This is consistent with S K XANES analyses which indicate that the majority of sulfur in the *Arctica islandica* shell is present as sulfate integrated into the inorganic, aragonitic part, where the spectra resemble sulfate in aqueous solution.