

Diagenesis and the fate of carbonate associated sulfate

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Carbonate associated sulfate (CAS) is used as a proxy to reconstruct the redox conditions and microbial activity in former seawater. Although a Phanerozoic seawater curve for $\delta^{34}\text{S}_{\text{CAS}}$ exists for more than ten years, possible effects of diagenesis on CAS and its sulfur isotopic composition in natural carbonates are not yet thoroughly constrained. To detect variations in CAS-concentrations and respective $\delta^{34}\text{S}_{\text{CAS}}$ values caused by diagenetic alteration, dolomite samples of the upper Triassic Hauptdolomit-Formation present in the European Alps were investigated. Three sample groups with different thermal histories and burial temperatures from 100°C, 200°C to 300° were studied.

Our results display a broader range of CAS-concentrations (100°C: <10 to 1700 ppm, 200°C: <10 to 950 ppm, 300°C: 0 to 50 ppm) and $\delta^{34}\text{S}_{\text{CAS}}$ -values (+13.9 to +24.9 ‰, V-CDT) than calcites considered to reflect for late Triassic seawater (average values: $\delta^{34}\text{S}_{\text{CAS}}$: +18.4 ‰, V-CDT). Although the CAS concentrations generally vary too much to be correlated with specific burial temperatures, a general decrease and less variability in CAS content with increasing temperature is apparent from our data. However, samples classified as mudstones display decreasing CAS concentrations with increasing burial temperature pointing to even higher CAS concentrations during carbonate formation. With increasing crystallographic order during progressing dolomitization the CAS concentration decreases. Together with the strong positive correlation with the Mol%CaCO₃, iron and strontium content we consider the CAS to be incorporated in the calcite crystal lattice. A comparison of ⁸⁷Sr/⁸⁶Sr with $\delta^{34}\text{S}_{\text{CAS}}$ displays a linear negative correlation within each temperature group and a general shift to higher ⁸⁷Sr/⁸⁶Sr and $\delta^{34}\text{S}_{\text{CAS}}$ values from 100°C to 300°C. We conclude that the different temperature settings of 100°C, 200°C and 300°C within the rock-buffered system of the Hauptdolomit-Fm represent individual semi-closed systems.