

GEOCHEMISTRY AND STRUCTURE OF DOLOMITE AND CALCITE AT OKER (GERMANY)

Stickler, C.P.¹, Deditius, A.P.¹, Baldermann, A.¹, Leis, A.² & Dietzel, M.¹

¹Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, 8010 Graz, Austria

²Institute of Water, Energy and Sustainability, Joanneum Research, Elisabethstrasse 18, 8010 Graz, Austria

e-mail: christian.stickler@student.tugraz.at

Precipitation of dolomite under low-temperature conditions in modern aquatic environments is limited due to the inhibitory effect of Mg^{2+} ions. This effect seems to be less effective in anoxic, organic-rich sediments with abundant bacterial sulfate reduction.

To shed a light on the process of dolomite formation under (Mg, S)-rich environments we investigated a partly dolomitized limestone of Upper Jurassic age (~153 Ma) that was formed at shallow marine, sabkha conditions at Oker (Langenberg, Germany). X-ray diffraction (XRD), electron microprobe (EMP) analysis, and $\delta^{18}O$ and $\delta^{13}C$ isotope measurements were conducted to decipher the geochemical and structural relationship between dolomite, low-Mg calcite (LMC), and high-Mg calcite (HMC) at bulk and micro-scale. The investigated lithological profile starts with layers of massive limestone that gradually transform into fine-grained dolomite followed by a thick limestone horizon at the upper part of the section.

The lower unit consists of micritic limestone of marine origin and is characterized by an isotopic composition of -1.7 to -2.9 ‰ of $\delta^{18}O$, and 1.3 to -0.7 ‰ of $\delta^{13}C$, VPDB. The upper limestone unit has isotopic characteristics of -1.8 to -3.4 ‰ of $\delta^{18}O$ and -1.6 to -4.0 ‰ of $\delta^{13}C$, VPDB, indicative of deposition under marine to sabkha conditions. The lower limestone consists of LMC with the chemical composition: $(Ca_{0.93-0.996}Mg_{0.003-0.03}Mn_{0-0.054}Sr_{0-0.001}Na_{0-0.001}Fe_{0-0.001})_{0.99-1.0}[(C_{0.94-1}S_{0-0.004})O_3]_2$. The transitional contact zone between the lower limestone and the dolomite consists of fine-grained, < 50 μm in size, dolomite, LMC, and HMC (listed from core to rim) deposited in single grains in the alternate mode. EMP analyses of the dolomite cores, ~10-15 μm in diameter, revealed excess of Ca and significant amounts of S (2500 ppm of SO_3); $(Ca_{0.97-1.14}Na_{0-0.01})_{0.97-1.14}(Mg_{0.75-0.97}Fe_{0-0.02}Mn_{0-0.01})_{0.76-0.99}[(C_{0.998-1.0}S_{0-0.002})O_3]_2$. Sulfur was not detected in the subsequently deposited LMC, $(Ca_{0.86-0.99}Mg_{0.006-0.05}Fe_{0-0.004}Na_{0-0.002}Mn_{0-0.001})_{0.96-0.97}CO_3$, and HMC, $(Ca_{0.64-0.78}Mg_{0.19-0.32}Fe_{0-0.004}Na_{0-0.003}Mn_{0-0.002})_{0.91-0.99}CO_3$. The "pure" dolomite (2.2 to 1.7 ‰ of $\delta^{18}O$ and 1.7 to -0.1 ‰ of $\delta^{13}C$, VPDB) has a composition of $(Ca_{1.03-1.24}Na_{0.001-0.006}Sr_{0-0.001})_{1.03-1.25}(Mg_{0.76-0.95}Fe_{0-0.02}Mn_{0-0.002})_{0.76-0.95}[(C_{0.98-0.998}S_{0.001-0.02})O_3]_2$, consists of euhedral crystals with a diameter of 2-50 μm , and shows few microns thick, alternating growth zones of S and Fe. XRD analyses confirmed the dolomite to be non-stoichiometric, with 51-54 mol% of $CaCO_3$. The degree of order in dolomite, with respect to ideal dolomite super structure, decreases from 83 % to 42 % with increasing S content from 0.02 to 0.06 S atoms per formula unit, respectively.

The variation in the isotopic composition ($\delta^{18}O$ and $\delta^{13}C$), distribution, and concentration of Mg, Sr, Fe, and S in calcite and/or dolomite indicates cyclic and abrupt changes of the chemistry of interstitial solution during carbonates formation. The plausible scenario of carbonate evolution involves decrease in sea level coupled with high evaporation degrees which led to increasing Mg/Ca ratios and thus alteration of primary LMC to HMC, subsequently transformed to dolomite.