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Mineralogy and nano-structure of modern dolomite in Lake Neusiedl, Austria

Patrick Meister (1), Mihály Pósfai (2), Peter Pekker (2), Zsombor Molnár (2), Stephanie Neuhuber (3), Attila Demény (4), Susanne Gier (1), and Silvia Frisia (5)

(1) University of Vienna, Department of Geodynamics and Sedimentology, Althanstr. 14, 1090 Vienna, Austria, (2) University of Pannonia, Department of Earth and Environmental Sciences, Egyetem u. 10, 8200 Veszprém, Hungary, (3) University of Natural Resources and Life Sciences, Institute of Applied Geology (IAG), Peter-Jordan-Straße 82, 1190 Vienna, Austria, (4) Hungarian Academy of Science, Institute for Geological and Geochemical Research, Budaörsi u. 45, 1112 Budapest, Hungary, (5) The University of Newcastle, School of Environmental and Life Sciences, Callaghan, New South Wales, 2308, Australia

The formation of dolomite in modern environments is still not completely understood. Despite supersaturation in many aquatic environments, dolomite formation is kinetically inhibited and processes are slow and not directly observable. We studied sediment of Lake Neusiedl (sampled with coring tubes from the Bay of Rust), a seasonally evaporative lake at the Austrian-Hungarian border, consisting to a great part of fine-grained Mg-calcite and Ca-rich dolomite mud. X-ray diffraction (XRD) revealed four different, poorly ordered carbonate phases, ranging from low-Mg calcite all the way to protodolomite, intermixed with clay minerals and detrital quartz. Stepwise centrifugation showed that the mineralogy changes within a grain size range from <0.2 μm to >4 μm (Neuhuber et al., 2015) with detrital grains still present in the <4μm faction and smectite and carbonates dominant in the fine fractions below 2 μm. New analysis of the <2 μm fraction by transmission electron microscopy in scanning mode (STEM) revealed three different morphological types, consisting of 100-nm- to 1-μm-scale rhombohedral crystals, irregular crystals and polycrystalline aggregates, while Mg/Ca ratios as determined using energy-dispersive X-ray spectroscopy in the TEM fall into the same four groups as indicated by XRD but with almost continuous transitions. Comparison of Fourier transform infrared spectra (FTIR) of wet and freeze-dried sediment confirmed that no alteration of the mineralogical composition occurred during sample preparation.
Based on the finding of a rather diverse population of poorly ordered Mg-Ca-carbonate phases we conclude that carbonates are largely authigenic and that they represent metastable phases that formed in alkaline water (pH >8.5) under episodically high supersaturation (>0.5 mmol/l Ca2+ and >4 mmol/l Mg2+), possibly via diverse pathways. Intriguingly, some of the polycrystalline particles have obviously formed via aggregation of smaller crystals in the order of tens of nanometres. But also within crystals with coherent crystallographic orientation, selected area electron diffraction (SAED) and Fourier transform patterns showed dolomite-like ordering in domains of nm 10 to 20 nm. Similar features have been observed in Holocene dolomites in the Abu Dhabi sabkha (e.g. Wenk et al., 1993), but further analysis by HR-TEM is necessary to gain insight into these structures and their nucleation, growth and aggregation pathways. Lake Neusiedl offers an ideal natural laboratory to study pathways of nucleation and growth of authigenic Ca-Mg-carbonates and their transformation to dolomite and, thus, shedding light on the long-standing dolomite problem.

Neuhuber et al. (2015) Geophysical Research Abstracts 17, 15399-15399.
Wenk et al. (1993) American Mineralogist 78, 769-774.