Multilayer fixation of dissolved phosphate on natural calcites derived from sorption experiments

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The predominance of different phosphate fixation mechanisms on natural calcite were studied in short-term batch experiments varying in hydrochemical conditions and physical properties of calcites. The fixation mechanism is crucial for the efficiency of sediment capping with calcite as an active material to reduce phosphate flux from anoxic sediments into the water column of eutrophic lakes.

Depending on the specific surface area of the applied calcite (SSA_{CC}) as well as on the dissolved phosphate concentration different processes are indicated by sorption isotherms. Low P-concentrations (10 - 30 µmol L^{-1}) in the solution together with a small SSA_{CC} (1 - 4.3 m^2 g^{-1}) lead to logarithmic shaped isotherms, indicating that adsorption processes are predominant. The same shape of isotherm can be achieved if both P-concentration (400 µmol L^{-1}) and SSA (67 m^2 g^{-1}) are high. Both cases result in a SSA_{CC}/P-ratio of 0.1 to 0.2. Low P-concentrations (30 µmol L^{-1}) in connection with a large SSA_{CC} (67 m^2 g^{-1}) as well as high P-concentrations (100 - 200 µmol L^{-1}) and low SSA_{CC} (1 - 4.3 m^2 g^{-1}) result in sigmoidal shaped isotherms. The calculated SSA_{CC}/P-ratio for both cases is > 1.8 and < 0.02, respectively. Depending on the residual P-concentration in solution, the sigmoidal shaped isotherms can be divided into three sections indicating different processes responsible for the P-fixation on calcite surfaces. Adsorption prevails in equilibrium with lowest residual P-concentrations. The inflection of the isotherm at moderate residual P-concentrations suggests that precipitation and transformation of Ca-P-compounds becomes dominant. This is supported by characteristic Ca/P-ratios for different Ca-P-compounds, e.g. β-Tri-Calcium-Phosphate, Octa-Calcium-Phosphate. The last section, with highest residual dissolved P-concentration, shows a logarithmic form, which can be attributed to adsorption onto the newly formed Ca-P-surface. Our results indicate that the P-fixation onto calcite is as multilayer process.

In addition, calcite saturation of the solution has an implication on the precipitation process. Subsaturation leads to partial dissolution of calcite followed by heterogeneous nucleation of Ca-P-compounds whereas supersaturation is followed by precipitation via solid solution formation.

Petrography, geochemistry and isotope characteristics of authigenic carbonates from the Mid-Atlantic Ridge

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Although much work focused on sulphide mineralogy of active hydrothermal systems hosted in ultramafic rocks, little is known about the genesis of authigenic carbonates found in these settings. Serpentinization of peridotites at mid-ocean ridges leads to the formation of carbonates. The hydrolysis of peridotite minerals results in an increase in pH. The high alkalinity favours the precipitation of calcium carbonate. Almost 20% of the ocean crust consists of ultramafic rocks. The formation of carbonates in ultramafic rocks may consequently represent a major CO_2 sink in the global carbon cycle. Yet, the geochemical parameters of carbonate formation in ultramafic systems are poorly understood.

We analyzed serpentinite-hosted carbonates, sulphide-hosted carbonates, and dolomite hosted in red jasper from the Logatchev hydrothermal field. The unusal dumbbell-shaped crystal aggregates of dolomite represent the first observation of dolomite in a hydrothermal environment. From the Gakkel Ridge serpentinite-hosted carbonates have been studied. Most serpentinite-hosted carbonates are isopachous and botryoidal aragonite. Occasionally, microcrystalline aragonite is predating these cements. The paragenetic sequence of the sulphide-hosted carbonates is represented by (1) micrite, (2) botryoidal and isopachous aragonite and (3) clotted micrite. Our observations reveal that carbonate formation is not a single event during late-stage seafloor alteration. $\delta^{18}O$ values of the serpentinite-hosted carbonates range from –20.0 to +5.3‰, those of the sulphide-hosted carbonates range from +1.3 to +4.2‰. Dolomite in the red jasper exhibits $\delta^{18}O$ values from –9.2 to –7.0‰. $\delta^{13}C$ values of sulphide-hosted carbonates vary from +2.5 to +3.6‰, those of dolomite dumbbells range from +2.6 to +3.0‰. $\delta^{13}C$ values of the serpentinite-hosted calcite that formed at high temperatures range from –5.8 to –5.5‰, reflecting a signal of mantle CO_2. The $\delta^{13}C$ values of the serpentinite-hosted aragonite range from –1.6 to +2.7‰, which are typical for marine carbonates. We suggest that $\delta^{13}C$ values of +3.0‰ and higher found for carbonates in serpentinites may reflect a partial contribution from methanogenesis. This hypothesis is supported by high Fe contents in these carbonates. Chondrite-normalized REE+Y patterns of the dolomite dumbbells are characterized by (1) a negative Ce anomaly, (2) a positive Eu anomaly, and (3) a slight enrichment of HREE. The negative Ce anomaly of the dolomite dumbbells indicates formation from oxic waters.