

Investigation of microbial calcification in Laduk spring, Yellow Stone National Park by TEM

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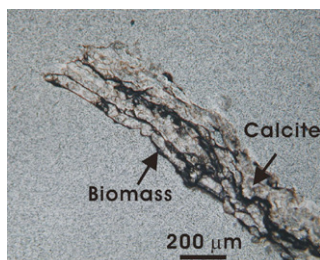
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To understand the mechanism of calcification associated with microbial activity in hot spring, the evolution of calcite formation in Laduk spring, Yellow Stone National Park was investigated by scanning and transmission electron microscopy (SEM/TEM), as well as preliminary optical microscopy (OM). Focused Ion Beam (FIB) technology was applied to prepare the TEM samples providing homogeneous phase of calcite. The samples with various degree of calcification such as microbial mat dominant phase, mixture phase of microbial mat and calcite minerals, and multi-layered calcite dominant phase were collected from a single hot spring. Each sample may represent the stage of calcification associated with microbial activity. OM and SEM observations indicated that the morphology of calcite evolves from aggregates of round-shaped calcite to long and multi-layered calcite surrounded by biomass (Fig. 1). The nano structure of calcite was analyzed by TEM. The selected area electron diffraction (SAED) patterns showed c-reflections indicating superstructures (Fig. 2). The preliminary results in this study indicated that the calcite precipitates randomly mixed with biomass at the initial stage of calcification may grow forming a layered calcite inside the biomass. The growth of layered calcite may be promoted by the biomass resulted from microbial activity. These results were supported by the spatial relationship between calcite precipitates and biomass and the fraction of C-isotope of calcite precipitates. X-ray micro-analysis on calcite precipitates detected only sulfur as impurity element. Superstructures in calcite induced by the random substitution of cations such as Mg^{2+} , Fe^{2+} , and Mn^{2+} in calcite was reported in Reksten (1990 *Am. Miner.* **75**, 807). More TEM investigation is required to understand the origin of superstructures in calcite.

A.



B.

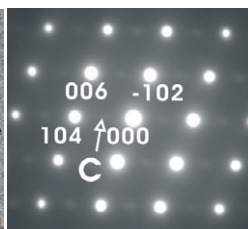


Figure 1: A. OM micrograph of multi-layered calcite inside the biomass. B. SAED pattern of calcite showing c-reflections.

Identification of natural versus anthropogenic contributions to groundwater geochemistry using an integrated hydrochemical, statistical, and mass balance modeling approach

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For hydrochemistry data from 365 samples of surface water and groundwater (alluvial, bedrock, and deep thermal groundwaters) from 150 sites in the Pocheon area, South Korea, a combined hydrochemical, environmental isotopic, statistical, and mass balance modeling approach was used to assess the relative contributions of natural versus anthropogenic sources and processes. The hydrochemistry of groundwaters was highly variable with the concentrations of NO_3^- (mean 27.3 ± 24.0 mg/L), Cl^- (mean 28.4 ± 40.0 mg/L) and SO_4^{2-} (mean 22.4 ± 27.9 mg/L) showing characteristic spatio-temporal changes. The isotopic composition of nitrate ($\delta^{15}N = 10.8 \pm 3.9\text{‰}$ and $\delta^{18}O = 7.4 \pm 3.4\text{‰}$) indicated that elevated nitrate concentrations largely originate from manure and septic effluents from villages and agricultural land use.

Fuzzy clustering yielded two subgroups of groundwater, in addition to surface water (Ca-Na-Cl- SO_4 type) and deep thermal groundwater (Na-Ca- HCO_3 type). These are: 1) a 'natural' group (Ca- HCO_3 type) and 2) an 'anthropogenic' group (Ca-Cl- SO_4 - NO_3 type). Projection of the four groups onto an euclidian space (i.e. principal component space) indicated three major processes controlling the hydrochemical evolution. A mixing and mass balance model (M3) based on the principal component space was finally used for a quantitative estimation of the evolution of groundwater geochemistry. Major evolution paths found were: 1) water-rock interaction involving variable mass transfers through plagioclase dissolution, calcite precipitation and cation exchange, 2) anthropogenic contamination which can be estimated using the mass difference of the sum of chloride, sulfate and nitrate from Ca- HCO_3 type and Ca-Cl- SO_4 - NO_3 type waters, and 3) nitrate loss via denitrification during groundwater discharge into surface water.