Investigation of the Decomposition of Sea Urchin Mg-Calcite

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The skeletal components of sea urchins, teeth, shell and spines, consist of Mg-calcite. This material has a conchoidal fracture and an uniform extinction under polarized light (Schmidt 1930), originating from coherent, slightly tilted building blocks with lengths of about 210 nm (Aizenberg et al. 1997). Mg^{2+} is statistically distributed in the calcite structure, replacing Ca^{2+} cations during the growth of the sea urchin. The space group of calcite, R-3c, is retained. Up to a Mg-content of about 20 mol% Vegard´s rule is valid for the correlation between Mg-content and the unit cell size. The unit cell parameters decrease with increasing Mg-content (Magdans et al. 2004).

We analysed interambulacral segments of the corona of the sea urchin species *Lytechinus variegatus*, to determine the decomposition of Mg-calcite. The samples were annealed two days at different temperatures from 100 °C to 250 °C with intermediate steps of 50 °C, simulating the natural decomposition process, which normally takes a few million years. The structural changes were analysed with chemical analysis and single crystal and powder X-ray diffraction. The chemical analysis showed a constant Mg-content of about 11 mol % in all anealed samples. During the annealing process, the lattice parameters and the Ca/Mg-O bond lengths of the cation octahedra increased continuously, producing an apparent reduction of the Mg-content. With increasing temperature the Mg-calcite splits into domains of several coexisting Mg-calcite-phases with different Mg-contents. In addition to that, a dolomite phase occoured at 250 °C. Our analysis showed, that the negative thermal expansion coefficient of Mg-calcite influences the lattice realignment, so that structural changes in the lattice with tempering cannot be assigned exclusively to Mg-reordering. Also, the effect of the Mg-content on unit cell parameters and bond lengths is larger in the crystallographic c-direction compared to the a-direction.

References

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