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Spectroscopic characterisation of biological vaterite: relations to synthetic and geological vaterites

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The pair aragonite and calcite are some of the most intensively studied polymorphous minerals. These $CaCO_3$ polymorphs are most commonly observed in biological minerals produced by marine molluscs, whereas in freshwater molluscs mostly aragonite and vaterite, the third $CaCO_3$ polymorph is identified (e.g. Wehrmeister et al., 2007). Vaterite is the thermodynamically most unstable $CaCO_3$ polymorph and is often discussed as a precursor phase in the mineralization of aragonite or calcite by organisms. Apart from these biological parageneses, vaterite is also known as rare small polycrystalline aggregates from geological occurrences. In laboratory crystallisation experiments, vaterite can be stabilized either kinetically or with the help of organic macromolecules (e.g. Falini et al., 2005).

Despite considerable research on vaterite, it is less well known that the crystal structure of vaterite is not unobjectionably determined. Due to the overall small crystal sizes, single crystal XRD analysis of vaterite is very difficult and this could be one of the reasons for the lack of a conclusive determination of the crystal structure. At least four different crystal structure proposals have to be considered: One proposed vaterite to be pseudo hexagonal and to crystallise in the orthorhombic space group Pnma (Meyer 1959). In addition, three crystal structures with hexagonal unit cells are proposed: Kamhi (1963) and Meyer (1969) proposed the same crystal space group: $P6_3/mmc$, whereas the site symmetry of the carbonate ion is proposed to be different with 2mm and m, respectively. Lastly, Lippmann (1973) proposed a structure based on the high-temperature modification of $YbBO_3$ with space group 6_322.

Here, we present new and complete Raman spectra for biological, geological and synthetic vaterite. The spectroscopic results are evaluated in light of all published crystal structures for vaterite and are aimed at gaining more detailed information about the crystallographic features of vaterite. Additionally, the influence of magnesium on the widths of the Raman bands (FWHM = full width at half maximum) is studied in order to detect a potential correlation between the magnesium content and the FWHMs in analogy to similar studies on aragonite and calcite.

The results imply that, although a hexagonal symmetry and the space group $P6_3/mmc$ are commonly used in the literature, it is equally possible that there are at least three structurally non-equivalent carbonate groups in the vaterite structure. It could be speculated that the (CO_3) layers are generally similar, whereas the stacking sequence of these layers may lead to a lower symmetry.

Non-beaded freshwater cultured pearls from China and Japan, grown in mussels of the genus *Hyriopsis* were studied for their different $CaCO_3$- polymorphs and chemical composition. Vaterite was identified by Micro-Raman spectroscopy in polished cross-sections. Vaterite forms relatively small areas (1-1.5 mm diameter) which are spherical to irregular and always in close proximity to the centre of the pearl. Trace elements in different $CaCO_3$ polymorphs were measured using LA-ICP-MS (New Wave Research 213 nm Laser/Agilent 7500ce quadrupole ICP-MS).

Geological samples come from the Bellerberg (Eifel Mountains, Germany). The rocks contain a mixture of minerals (e.g. ettringite, calcite, aragonite and tobermorite) including white to dark yellow microcrystalline mineral aggregates of vaterite. Synthetic vaterite samples were produced in collaboration with the Department of Inorganic and Analytical Chemistry at the University of Mainz by precipitation from a solution of $CaCl_2$ and poly(aspartic acid), in the presence of $(NH_4)_2CO_3$ (Loges et al., 2006).

The Raman band position and FWHM of all samples are in relative good agreement, independent of their origin.

The characteristic features of the Raman spectrum of vaterite are: at least eight relative broad bands in the region of the external lattice modes, splitting of the most intense band ν_1 into three distinct bands, activation and splitting of ν_2 and splitting of both, ν_3 and ν_4 into six distinct Raman bands. FWHMs of the lattice modes are large (8 cm^{-1}–44 cm^{-1}) compared to those of aragonite, implying that the structure is not well ordered and possibly affected by stacking faults, layer shifts or syntactic intergrowth; irregularities that further complicate the crystal structure determination.

Correlation of Mg-contents in vaterite areas in freshwater cultured pearls with Raman spectra obtained at the same spots show that the FWHMs are influenced by the magnesium content. Similarly, the spectra for the vaterite samples synthesized with differing Mg contents show successively increasing FWHM with increasing magnesium content both for the lattice modes and the ν_1 – symmetric stretching mode.

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