The Raman spectrum of Ca-Mg-Fe carbonates; Applications in geobiology

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Carbonates form a very important mineral group in geobiological studies. They are a common mineral matrix for putative carbonaceous microfossils in Archean greenstone belts, form an important chemical deposit in seafloor hydrothermal systems, and are a common product in biomineralization processes. In many geobiological studies there is a specific need for simple characterization of carbonate composition while avoiding complex sample preparation or sample destruction. Raman spectroscopy is a highly versatile non-destructive technique enabling in-situ characterization of minerals and carbonaceous materials. It can be combined with confocal microscopy enabling high-resolution Raman mapping of entire rock thin sections, or can be integrated in submersibles and potentially Mars-rovers for direct field-based mineral identification. It is thus important that well-established spectral databases exist which enable unambiguous identification of a wide variety of carbonate minerals. The most common carbonates in the Ca-Mg-Fe system include the $CaCO_3$ polymorphs calcite, aragonite, and vaterite, as well as the solid solutions $CaMg(CO_3)_2$-$CaFe(CO_3)_2$ (dolomite-ankerite) and $MgCO_3$-$FeCO_3$ (magnesite-siderite). Although various carbonate end-members have been studied exhaustively by Raman spectroscopy, a simple protocol for rapid distinction of various carbonate solid solutions is still lacking. Here we present a detailed study of Raman shifts in various carbonate standards of known composition in the Ca-Mg-Fe system. Carbonates with rhombohedral symmetry display a Raman spectrum with six characteristic vibrational modes – four of these represent vibrations within the $(CO_3)^{2-}$ unit and two represent external vibrations of the crystal lattice. We show that Raman band shifts of internal mode $2\nu_2$ (range 1725-1765 cm^{-1}), and external modes T (range 170-215 cm^{-1}) and L (range 285-330 cm^{-1}) for siderite-magnesite and ankerite-dolomite solid solutions display distinct and well defined positive correlations with Mg number (Mg/Mg+Fe+Mn+Ca). Raman shifts calibrated as a function of Mg number were used in turn to evaluate the chemical composition of natural carbonate samples. In particular it is shown that detailed micron-resolution Raman maps can be generated of carbonate crystal-zonation in hydrothermally altered sedimentary deposits from Archean greenstone belts. Large spectral-range analysis (140-2000 cm^{-1}) in static-mode (centered at 1150 cm^{-1}) allows for combined Raman mapping of both carbonate-composition ($2\nu_2$, T, L modes) as well as kerogen structural ordering (D_1-D_4 and G modes in the range 1100-1700 cm^{-1}), and therefore allows for simultaneous characterization of putative organic microfossils and associated carbonate matrix in metamorphosed Archean rock samples. Finally, it will be shown that these carbonate solid solutions can be distinguished from other end-member carbonates such as calcite, vaterite and the orthorhombic polymorph aragonite.