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Raman characterization of synthetic magnesian calcites

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Abstract

Magnesian calcites are important components of sediments and biominerals. Although Raman spectra of calcite, dolomite, and magnesite are well known, those of magnesian calcites deserve further investigation. Nineteen syntheses of magnesian calcites covering the range 0–50 mol% $MgCO_3$ have been carried out at high pressure and temperature (1–1.5 GPa, 1000–1100 °C). The crystalline run products have been characterized by μ-Raman spectroscopy.

For all lattice and internal modes (L, T, ν_1, ν_4, $2\nu_2$) but ν_3, wavenumbers align closer to the calcite–dolomite line than the calcite–magnesite line. The compositional dependence is strong and regression curves with high correlation coefficients have been determined. Full-width at half maximum (FWHM) plot along parabolas that depart from the calcite–dolomite or calcite–magnesite lines. The limited data dispersion of both shifts and FWHM allow using Raman spectral properties of magnesian calcites to determine the Mg content of abiotic calcites.

A comparison with Raman data from the literature obtained on synthetic magnesian amorphous calcium carbonate (Mg ACC) shows that the wavenumber position of the ACC ν_1 mode is systematically shifted toward lower values, and that their FWHM are higher than those of their crystalline counterparts. The FWHM parameters of crystalline and amorphous materials do not overlap, which allows a clear-cut distinction between crystalline and amorphous materials.

In synthetic magnesian calcites, the shift and FWHM of Raman bands as a function of magnesium can be interpreted in terms of changes of metal-O bond lengths resulting from the replacement of calcium by magnesium. The facts that the wavenumber of magnesian calcites are close to the calcite–dolomite line (not calcite-magnesite), that the FWHM of the T, L, and ν_4 modes reach a maximum around 30 ±5 mol% $MgCO_3$, and that a peak specific to dolomite at 880 cm^{-1} is observed in high-magnesian calcites indicate that dolomite-like ordering is present above ~10 mol% $MgCO_3$. Mg atom clustering in cation layers combined with ordering in successive cation basal layers may account for the progressive ordering observed in synthetic magnesian calcites.

Keywords: Magnesian calcite, dolomite, magnesite, amorphous calcium carbonate, Raman spectroscopy, experimental HP/HT syntheses, dolomite ordering