Raman characterization of synthetic magnesian calcites

JONATHAN PERRIN1,*, DANIEL VIELZEUF1, DIDIER LAPORTE2, ANGÈLE RICOLLEAU1, GEORGE R. ROSSMAN3, AND NICOLE FLOQUET1

1Aix-Marseille Université, CNRS, CINaM UMR7325, 13288 Marseille, France
2Laboratoire Magmas et Volcans, Université Blaise Pascal, CNRS-IRD, OPGC, 5 rue Kessler, 63038 Clermont-Ferrand, France
3Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125-2500, U.S.A.

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% MgCO3 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, νL, νT, 2νT) but νS, 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 νt 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 νL modes reach a maximum around 30 ±5 mol% MgCO3, 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% MgCO3. 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

INTRODUCTION

Calcite is the only CaCO3 crystalline polymorph that can accommodate substantial amounts of magnesium (Bischoff et al. 1983; Finch and Allison 2007; Long et al. 2012; Mackenzie et al. 1983; Morse et al. 2007; Wang et al. 2012). Magnesian calcites (Mg calcites) are important components of modern and Pleistocene carbonate sediments (Bischoff et al. 1985; Land 1967). In the sediments, they are mostly found as remnants of skeletons of marine invertebrates and as cement (Bathurst 1975; Bischoff et al. 1985; Chave 1954a, 1954b). Since Raman spectroscopy is sensitive to carbonate ion (CO3⁻) vibrations, micro-Raman spectroscopy is classically used to characterize small volumes of crystalline or amorphous carbonate samples. Raman patterns of the different calcium carbonate polymorphs (calcite, aragonite, vaterite, amorphous calcium carbonate) are well identified; however, the Raman spectral modifications due to variations of chemical composition are less known. The effect of magnesium incorporation in calcite has been thoroughly investigated by Bischoff et al. (1985). These authors characterized the wavenumber shifts and enlargements of the carbonate vibration modes in magnesian calcites as a function of their Mg contents. Carbonate vibration modes of calcite (Cal, CaCO3), dolomite (Dol, Ca0.5Mg0.5CO3), and magnesite (Mgs, MgCO3) show a shift toward higher wavenumber and enlargement as a function of magnesium content. Bischoff et al. (1985) also showed that magnesian calcites display changes of spectral properties aligned along the calcite-magnesite line with slightly positive or negative deviations from linearity for νt and the translational T modes. The full-widths at half maximum (FWHM) of the vibrational Raman bands progressively increase as a function of magnesium contents. However, according to these authors, the shift and FWHM data dispersions are too large to allow the determination...