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Stability of magnesite ($MgCO_3$) at mantle pressure and temperature conditions: A Raman spectroscopic study

PHILIPPE GILLET

Laboratoire des Sciences de la Terre, Ecole Normale Supérieure de Lyon et UCB Lyon I (URA 726), 46, allée d'Italie,
69364 Lyon Cedex, France

ABSTRACT

The stability of magnesite ($MgCO_3$) has been studied by Raman spectroscopy at high pressure and high temperature using a diamond-anvil cell heated by a CO_2 laser. Raman spectra up to 32 GPa at room temperature unambiguously confirm that under quasi-hydrostatic conditions, unlike $CaCO_3$, magnesite does not undergo phase transitions. Raman spectra recorded at simultaneous high pressure (26 GPa) and high temperature (1200 ± 200 K) show that under these conditions magnesite retains its ambient $R\bar{3}c$ structure. Optical observations during heating, as well as Raman spectra recorded at 30 GPa after laser heating up to 2000–2500 K, show that no decarbonation has occurred and that magnesite is stable. All these results are in agreement with other experimental data and show that magnesite can act as a host for C storage down to at least 1000 km and can also be the carrier for C in subducting plates.

INTRODUCTION AND PREVIOUS WORKS

Experimental studies, as well as observations of natural samples, have shown that carbonates could be major hosts for C in the Earth's mantle (McGetchin and Besançon, 1973; Kushiro et al., 1975; Wyllie and Huang, 1976; Berg, 1986; Canil and Scarfe, 1990). Moreover, high-pressure experiments have shown that in the presence of pyroxene and olivine or their high-pressure equivalents $MgCO_3$ is the stable carbonate (Brey et al., 1983; Katsura and Ito, 1990; Biellmann et al., 1993). Redfern et al. (1993) have used their compressibilities in conjunction with low-pressure phase equilibrium data and thermal expansion data, to calculate the stability field of $MgCO_3$ magnesite. They have concluded that under typical lower mantle pressure and temperature conditions, magnesite is stable in the presence of MgO. $MgCO_3$ may thus be the major stable carbonate in the Earth's upper and lower mantle and may thus control mantle f_{O_2} (Blundy et al., 1991). It may also act as a solid carrier of C during recycling by subduction.

Recent in-situ measurements performed at high pressure and room temperature led to controversial results. Fiquet et al. (1994) have established the equation of state of magnesite up to 50 GPa using powder X-ray diffraction. They suggested the existence of a transition at around 25 GPa, which is accompanied by a relative volume change of −8%. This result is discrepant with other in-situ measurements. Katsura et al. (1991) have shown by in-situ X-ray diffraction that at 55 GPa the X-ray pattern of compressed $MgCO_3$ can be indexed in space group $R\bar{3}c$. Williams et al. (1992) have recorded the Raman spectrum of magnesite up to 34 GPa at room temperature. However, at pressures above 25 GPa the spectra were noisy and permitted following only two Raman modes up to 34 GPa. The authors however have concluded that magnesite remains stable with a calcite I structure ($R\bar{3}c$) up to 34 GPa. Gillet et al. (1993a) have recorded the complete Raman spectrum of magnesite up to 24–25 GPa and did not observe spectral changes that could be related to a phase transition similar to those observed in $CaCO_3$.

Katsura and Ito (1990) have observed magnesite in quenched samples recovered from 26 GPa and 1873 K. Katsura et al. (1991) have observed magnesite with its ambient structure in quenched samples recovered from 22 to 54 GPa and from 1300 to 1800 K. Biellmann et al. (1993) have also observed magnesite with $R\bar{3}c$ symmetry in diamond-anvil cell samples recovered from pressures between 20 and 50 GPa and temperatures between 1500 and 2500 K. However, these results do not imply that at simultaneous high pressures and temperatures magnesite remains in the structure with space group $R\bar{3}c$.

Several problems concerning the response of the structure of magnesite to pressure and temperature are thus still unclear and unresolved: (1) does magnesite undergo reversible phase changes at high pressures and room temperature similar to those observed in calcite, as suggested by Fiquet et al. (1994)? (2) Does magnesite still remain in the $R\bar{3}c$ structure at both high pressure and high temperatures, or does it change from an unknown high-pressure polymorph to the $R\bar{3}c$ structure during pressure and temperature quenching?

In order to answer these questions, a new series of experiments on magnesite have been undertaken. We report new Raman spectroscopic data up to 31.5 GPa at 300 K, at 26 GPa and 1200 K, and at 30 GPa after laser heating up to 2000–2500 K. The data are of better quality than those previously published and enable the stability of magnesite in its $R\bar{3}c$ structure to be assessed at pressure

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and temperature conditions down to 1000 km in the Earth's mantle and down to 600–800 km in subducting lithospheric plates.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Magnesite samples were small single-crystal cleavage chips (50–100 μm in diameter and 10–30 μm thick) obtained from a larger single crystal from Brumado (Bahia state, Brazil). This sample has been previously characterized by Raman spectroscopy, X-ray diffraction, and transmission electron microscopy.

A diamond-anvil cell system heated with a CO_2 laser (Boehler and Chopelas, 1992; Gillet et al., 1993b) has been used. Type IIa diamond crystals, selected for low fluorescence, with 600-μm culets, have been used. A sample chamber 200 μm in diameter was drilled in a 301 stainless steel plate preindented to a thickness of about 70–100 μm. Flat chips of $MgCO_3$ were glued with Si grease at the edge of the gasket hole to avoid bridging with the diamond crystals during pressurization. Pressures up to 32 GPa were reached using Ar (cryogenically loaded) as the pressure transmitting medium. Several ruby chips placed at the edge of the gasket hole and on the sample were used to measure pressure. Pressure was quasi-hydrostatic up to 32 GPa, as shown by the well-resolved R_1-R_2 fluorescence doublets of ruby.

The beam of a CO_2 wave guide laser (Melles Griot Model 05 CRF 1200, 120 W) was focused through a ZnSe plano-convex lens (f = 25 mm, diameter 8 mm) on the pressurized sample. Hot spots, 30–50 μm in diameter, were created on the sample.

A specially designed setup allows the recording of the Raman spectra, the ruby fluorescence, and the thermal emission of the sample. A Dilor XY double subtractive spectrograph with premonochromator (1200-g/mm holographic gratings), equipped with confocal optics before the spectrometer entrance, and a N_2-cooled EGG CCD detector are used. A microscope with a long-working distance objective (Leitz UTK 40) is used to focus the excitation laser beam (488-nm exciting line of a Spectra Physics® Ar^+ laser) to a 2-μm spot and to collect the Raman signal in the backscattered direction. The presence of the confocal pinhole before the spectrometer entrance ensures a sampling of the same sized zone (2–3 μm) for both the Raman and thermal emission signals (see details for temperature measurements in Gillet et al., 1993b). It has been shown that the confocal system is in that case essential for discriminating against blackbody radiation emitted by the sample (Daniel et al., unpublished manuscript). Closing the confocal pinhole minimizes the collection of this thermal emission. This experimental setup thus enables the Raman spectra to be recorded at high pressure and room temperature as well as at simultaneous high pressure and high temperature. Also samples synthesized in the DAC at high pressures after temperature quenching can be characterized.

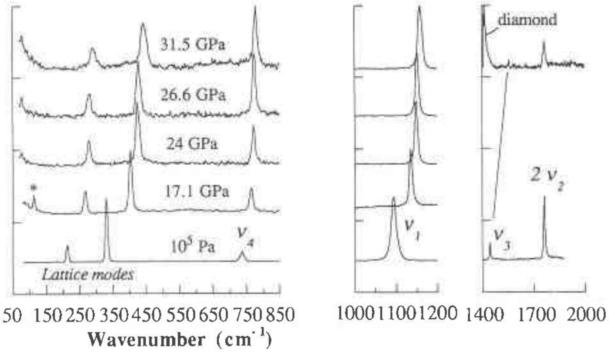

Fig. 1. Raman spectra of magnesite at high pressure and room temperature. No change is observed up to 31.5 GPa. The symbols and letters refer to the mode assignment given in the text. The asterisk shows the laser plasma line.

RAMAN SPECTRA AT HIGH PRESSURE AND ROOM TEMPERATURE

Magnesite has space group $R\bar{3}c$ and has five Raman-active modes (White, 1974) (Fig. 1). Three Raman bands are assigned to internal vibrations of the CO_3 groups: ν_1 (1094 cm^{-1}), ν_3 (1444 cm^{-1}), and ν_4 (738 cm^{-1}). The first overtone of an IR-active internal mode ($2\nu_2$) is also observed, at 1762 cm^{-1}. The lattice modes at 213 and 329 cm^{-1} are not definitively assigned (Fig. 1).

Gillet et al. (1993a) have followed the ν_1, ν_4, and the 329-cm^{-1} lattice mode up to 24–25 GPa. The ν_3, the $2\nu_2$ overtone, and the lattice mode lying at 213 cm^{-1} could only be tracked to 15–20 GPa because of the strong fluorescence of the sample as well as to second-order Raman scattering of KBr used as the pressure transmitting medium in the region at 50–400 cm^{-1}. Williams et al. (1992) encountered similar difficulties, even with ethanol methanol or Ar as pressure transmitting media. They have reported the evolution with pressure of only four of the six previously mentioned modes: ν_1, ν_4 up to 34 GPa, the 329-cm^{-1} mode up to 26 GPa, and the 213-cm^{-1} mode up to 13 GPa.

Because recent X-ray data (Fiquet et al., 1994) suggest a phase change at around 25 ± 2 GPa, we have taken the time to obtain high quality Raman spectra of magnesite between 17 and 32 GPa. Typical spectra are presented in Figure 1. At 31.5 GPa the six Raman modes observed at ambient conditions in the Raman spectrum of magnesite are clearly resolved and indicate that, under the quasi-hydrostatic pressures provided by the Ar medium, magnesite remains a stable phase with increase in pressure at room temperature. The measured pressure-induced shifts are in good agreement with those reported in earlier studies (Williams et al., 1992; Gillet et al., 1993a).

It thus appears that phase transitions similar to those observed in $CaCO_3$, calcite I → calcite II → calcite III, can be ruled out for magnesite, at least up to 31.5 GPa, because these transitions are accompanied by drastic changes in the Raman spectra (Fong and Nicol, 1971; Gillet et al., 1988; Liu and Mernagh, 1990). The phase transition reported by Fiquet et al. (1994) may be due to

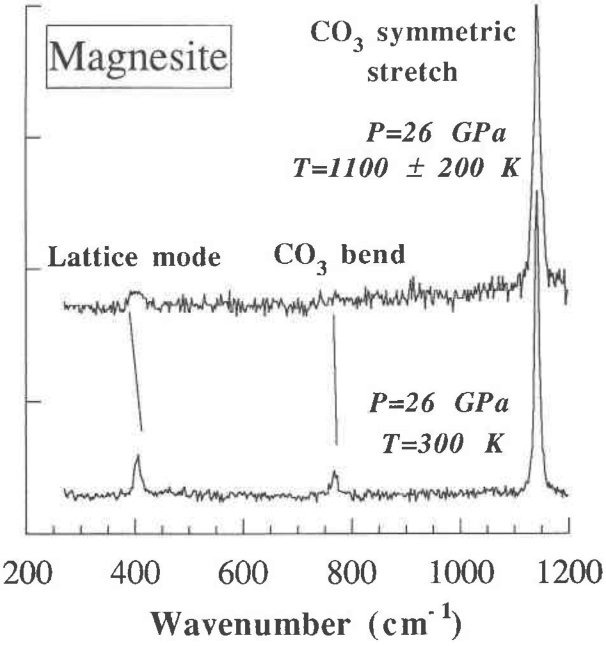

Fig. 2. Raman spectra of magnesite at 26 GPa and 1200 ± 200 K.

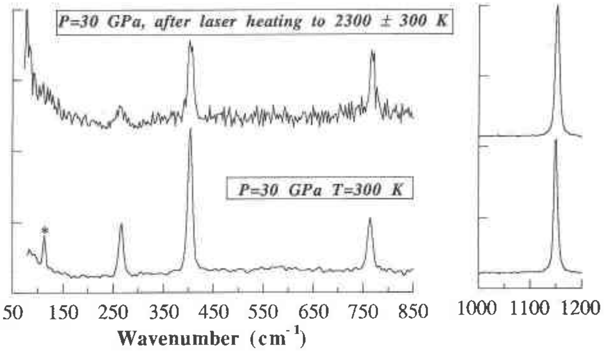

Fig. 3. Raman spectra of magnesite at 30 GPa before and after heating to 2500 ± 300 K. The asterisk shows the laser plasma line.

nonhydrostatic stresses developing in the pressure transmitting medium (Si oil) as pressure is increased.

STABILITY OF MAGNESITE AT SIMULTANEOUS HIGH PRESSURE AND TEMPERATURE

Raman spectra of magnesite were also recorded at 26 GPa during laser heating. Our setup records during the same acquisition a 1000-cm^{-1} spectral range. The spectrometer was thus positioned to record the frequency range 300–1300 cm^{-1}, i.e., to observe three modes characteristic of magnesite: the ν_1, ν_4, and 329 cm^{-1} lattice modes. Figure 2 shows typical spectra before and during laser heating. Spectra could be recorded for orange impact spots of the CO_2 laser. Temperatures were estimated from the thermal emission previously calibrated and also by the temperature-induced shifts of the hard Raman modes (see Gillet et al., 1993b, for more details). In order to avoid the inherent fluctuations of the CO_2 laser power, Raman spectra were recorded with short acquisition times (ca. 10–20 s). Temperatures are estimated to within ±200 K.

During heating up to 1200 ± 200 K at 26 GPa no changes were observed in the Raman spectra of magnesite, with the exception of frequency decrease, intensity decrease (e.g., the ν_4 mode) and band broadening. It can be concluded that magnesite remains in its $R\bar{3}c$ structure at these pressure and temperature conditions, which are likely to exist in subducting plates.

Magnesite has also been pressurized to 30 GPa and heated with the CO_2 laser to 2000–2500 K, i.e., under conditions relevant to depths of 1000 km in the Earth's mantle. Heating duration was on the order of 30–60 s. Optical observation of the sample at high pressure during heating does not reveal features of decarbonation. After heating, no milky aspect of the sample characteristic of decarbonation was observed, and the overall appearance (no recrystallization, no twins) was similar to that observed before heating. Raman spectra of the sample at 30 GPa before and after heating are presented in Figure 3; these spectra are also similar to that recorded on the sample recovered at ambient conditions. These results clearly indicate that neither pressure nor temperature release modifies the magnesite structure.

CONCLUSIONS

The room-temperature rhombohedral structure (space group $R\bar{3}c$) of magnesite is retained up to 32 GPa but also at pressure and temperature conditions of the transition zone and upper region of the Earth's lower mantle. Our results confirm (1) the results of Redfern et al. (1993), which showed that the decarbonation curve $MgCO_3 \rightarrow MgO + CO_2$ is never crossed by the stable mantle geotherm, and (2) that magnesite is the stable carbonate from depths of 100 to at least 1000 km in the Earth's mantle, a conclusion of Katsura and Ito (1990), Katsura et al. (1991), and Biellmann et al. (1993), obtained from quenched samples studied at ambient conditions. The in-situ measurements at high pressure and high temperature show that magnesite is also stable at pressure and temperature conditions that exist in subducting plates down to 600–800 km.

The present study strongly emphasizes the potential role of magnesite for the storage and recycling of C in the deep mantle. As already suggested, carbonates may be fundamental actors in the C cycle in the deep Earth.

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