

Detection of small amounts of H₂O in CO₂-rich fluid inclusions using Raman spectroscopy

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Raman spectroscopic analysis at low (−100 °C) or high (100–200 °C) temperature is shown to be effective for detecting small amounts of H₂O in CO₂-rich fluid inclusions from the deep lithosphere, which have previously been thought to be water-free. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

The presence of water in the Earth's deep lithosphere has been documented by numerous studies,^[1,2] and it is therefore expected that fluid inclusions trapped at deep lithospheric conditions should contain H₂O in addition to the more commonly reported CO₂. However, direct evidence for the presence of water in fluid inclusions from mantle peridotites is only rarely reported.^[3,4] This contradiction might result from (1) the very high CO₂/H₂O ratio of mantle fluids^[5–7] combined with the low solubility of water in dense CO₂ at room temperature, (2) the difference in wetting properties of the immiscible CO₂-rich and H₂O-rich phases^[8] preventing recognition of the H₂O-rich phase that occurs as a thin film on the wall of inclusion at room temperature^[9,10] and (3) the small volume of the submicroscopic H₂O-rich liquid film compared to the size of the excitation laser spot.^[10] Any or all of these factors preclude the detection of small amounts of H₂O by the analytical techniques (microthermometry and room-temperature Raman spectroscopy) that are used routinely in fluid inclusion studies. Here we show that Raman spectroscopic analysis at temperatures below or above ambient temperature permits the detection of previously unresolvable small amounts of H₂O in mantle-derived fluid inclusions.

Method

Inclusions were analyzed in three different laboratories using different instruments and analytical settings. At Budapest University of Technology and Economics (Hungary), inclusions were analyzed using a Jobin Yvon confocal Labram Raman instrument with 532-nm Nd:YAG laser excitation, 20 mW laser energy and 50× objective. At Virginia Polytechnic Institute and State University (USA), a similar instrument with 514-nm argon ion laser, 40 mW laser energy and 40× objective (with adjustable coverslip collar^[11]) was used. At G2R in Nancy (France), a Dilor Labram-type Raman spectrometer with notch filter, 514-nm argon ion laser, 40 mW laser power and 80× objective was used. The analytical settings included a 300–1000 μm confocal hole, 100–200 μm spectral slit, 600–1800 grooves/mm spectrograph gratings, 2–3× accumulations and 2–250 s acquisition time (all depending on the maximum

intensity). Spectra were collected at room temperature, at −100 °C (complete freezing of the inclusion) and in the range of +100 to +200 °C using a Linkam THMS600 heating/cooling stage. Control measurements were conducted on quartz-hosted synthetic CO₂–H₂O fluid inclusions containing 21.4 wt% water.^[12] Note that off the inclusions neither the band of dissolved H₂O nor that of CO₂ clathrate was found, thereby excluding the possibility that it concerns the H₂O of the host mineral or precipitation on the surface, respectively. The studied fluid inclusion set ($n = 53$) is derived from the sub-continental lithospheric mantle of the Pannonian Basin (Hungary) and from Jeju Island (South Korea).^[13,14]

Results and Discussion

The fluid inclusions range from 4 to 30 μm in size and have a negative crystal shape. Microthermometric behavior shows only one visible melting event at -56.6 ± 0.4 °C and homogenization to the liquid phase in the range of -52 to -20 °C. At room temperature, the Fermi diad of CO₂ was observed in the Raman spectra. All of these features are typical of high-density (1.02–1.16 g/cm³), CO₂-rich mantle fluids that show no evidence of H₂O (Fig. 1(b)).

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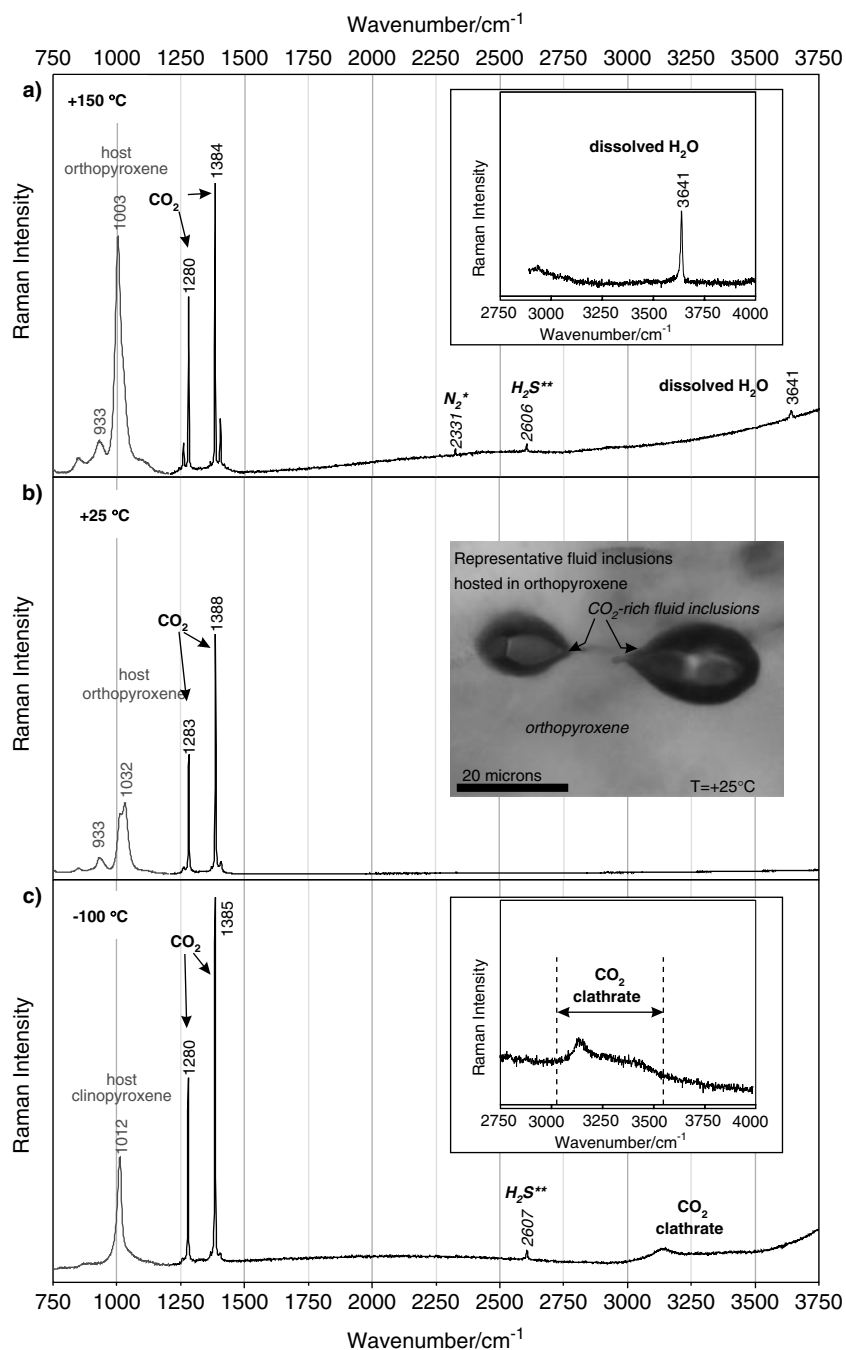


Figure 1. Summary of representative Raman spectra with laser spot focused on individual phases in fluid inclusions [photomicrograph inset on Fig. 1(b)] at (a) +150 °C: laser spot focused on the CO₂-rich phase; inset shows enlargement of the spectrum for dissolved water (peak position varies between 3638 and 3641 cm⁻¹); (b) +25 °C: laser spot focused on the CO₂-rich phase; (c) -100 °C: laser spot focused on CO₂ clathrate phase; inset shows an enlargement of the spectrum for the CO₂ clathrate with molecular water in the cage.

Note that spectra were obtained from several different inclusions hosted in clinopyroxene or orthopyroxene from spinel peridotite xenoliths from the Pannonian Basin (Hungary) and from Jeju Island (South Korea). The peaks corresponding to the host mineral are indicated by gray. Peak positions are determined by fitting with a Gaussian–Lorentzian function.

* Atmospheric nitrogen, not related to the fluid inclusions.

** H₂S was detected only in fluid inclusions from the Pannonian Basin. The presence of H₂S is probably related to the geological setting of the sub-continental lithospheric mantle, which is not discussed here.

Upon cooling, in addition to the peaks of solid CO₂, a band corresponding to CO₂ clathrate with molecular water in the cage appears (Fig. 1(c)). All low-temperature Raman spectra were obtained from solid phases (e.g., CO₂ clathrate and CO₂ ice), and therefore the distribution of the CO₂–H₂O components inside

the fluid inclusion at -100 °C is not homogeneous, excluding quantitative determination of the CO₂/H₂O ratio.

Upon heating, as H₂O-rich and CO₂-rich phases homogenize into a single phase,^[15,16] the Fermi diad of CO₂ is present and the peak for dissolved H₂O generally appears on spectra taken between 120

Table 1. Advantages and disadvantages of Raman spectroscopic techniques for H₂O detection at different temperature conditions

Method	Temperature	Advantage	Disadvantage
High-T	100–200 °C	<ul style="list-style-type: none"> • CO₂ and H₂O are homogeneously distributed in the CO₂-rich phase: the location of the laser spot within the fluid inclusion is not critical • Semi-quantitative: the CO₂/H₂O ratio of the fluid inclusion can be determined 	<ul style="list-style-type: none"> • Moderate risk of decrepitation during heating to higher T • Fluorescence may interfere with the Raman signal
Room-T	20–25 °C	<ul style="list-style-type: none"> • No cooling/heating stage is required • No risk of decrepitation • Analysis is relatively fast 	<ul style="list-style-type: none"> • H₂O cannot be identified unless the CO₂/H₂O ratio is low • Fluorescence may interfere with the Raman signal
Low-T	–100 °C (complete freezing)	<ul style="list-style-type: none"> • Solid materials produce higher intensities than their liquid or vapor counterparts under the same run conditions • May decrease fluorescence • No risk of decrepitation 	<ul style="list-style-type: none"> • Due to the small size of the solid CO₂ and/or clathrate phases in frozen inclusions, it may be difficult to focus the laser on these small phases in the inclusion • Qualitative analysis only • Time-consuming

to 150 °C (Fig. 1(a)). Even though the complete homogenization of the fluid inclusion cannot be recognized, at high temperature the distribution of dissolved H₂O in CO₂ is presumably uniform, which allows (semi-) quantification of spectra of the CO₂-rich phase according to the method of Ref. [17]. At 150 °C, the calculated H₂O content ranges from 0.04 to 6 mol% (with one exception at 11.7 mol%) and shows an average value at 3.6 mol% ($n = 39$). Note that the H₂O content of the CO₂-rich phase equals the bulk H₂O content only in homogenized fluid inclusions analyzed at high temperature. Advantages and disadvantages of the different methods of analysis are listed in Table 1.

Results of this study suggest that fluid inclusions trapped under deep lithospheric mantle conditions contain small but significant amounts of H₂O. This conclusion, in turn, has important implications concerning the geochemical and geodynamic evolution of the Earth's deep lithosphere. Therefore, the assumption of a pure CO₂ (H₂O-free) fluid in this environment must be reconsidered, as the room-temperature Raman spectroscopy and microthermometry alone are not suitable for detecting H₂O in such fluid inclusions.

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