IR Spectroscopy of Olivine from Kimberlitic Magma

Cameron A. Hughes, Department of Geology, University of Wisconsin-Eau Claire

Phillip D. Ihinger, Department of Geology, University of Wisconsin-Eau Claire

Abstract

Olivine, the most common mineral in the upper mantle, represents a major component in most mafic magmas. Olivine crystals derived from mantle xenoliths contain hydroxyl impurities and are thought to represent the major reservoir for water in the high-pressure mantle environment. However, olivine crystals sampled from tholeiitic basalts do not contain measurable water. Non-stoichiometric water is observed in a variety of nominally anhydrous crustal minerals, such as quartz and feldspar. Incorporation of water into these minerals is generally attributed to kinetic effects associated with non-equilibrium growth. Silica-poor magmas are typically volatile-rich and have extremely low viscosities promoting rapid crystal growth during transport and emplacement. Here, we test the hypothesis that olivine crystals formed in silica-undersaturated, water-rich magmas incorporate measurable hydrous impurities due to their rapid growth. Olivine crystals from Haystack Butte, MT were analyzed using micro-FTIR spectroscopy. Petrographic analyses revealed numerous spherical vapor bubbles oriented along healed fractures within some crystals. Analyses of bubble-rich and bubble-free regions of crystals showed no absorption in either of the two hydroxyl-bearing regions documented in mantle-derived olivines (3600-3450 cm^{-1}, 3450-3300 cm^{-1}). The bubble-rich regions showed prominent absorption at ~3690 cm^{-1}, indicating presence of serpentine on surfaces of spherical inclusions, likely formed from deuteric alteration.

Background

In the olivine formula unit $(Mg,Fe)_2SiO_4$, oxygen atoms are bonded in a tetrahedral formation to three (Mg,Fe) atoms and one Si atom. Thus, water is not intrinsic to olivine. However, numerous studies show that crystals of olivine derived from the mantle often incorporate hydrous impurities into their crystal lattice (Beran and Libowitzky, 2006; Keppler and Bolfan-Casanova, 2006; Mosenfelder et al., 2011). Water contents in mantle olivines range from 4 to 400 wt ppm, with an average of ~150 wt ppm H_2O. Hydrous impurities occur when a site within the tetrahedron is vacant, allowing water as OH^- to orient itself within the mineral structure. Multiple mechanisms for introducing OH^- into the olivine structure exist. Studies suggest either that OH^- fills a vacant Si site within the tetrahedron or OH^- proton pairs substitute for magnesium in the M1 or M2 sites. (Smyth, 2006; Beran and Libowitzky, 2006;Keppler and Bolfan-Casanova, 2006).

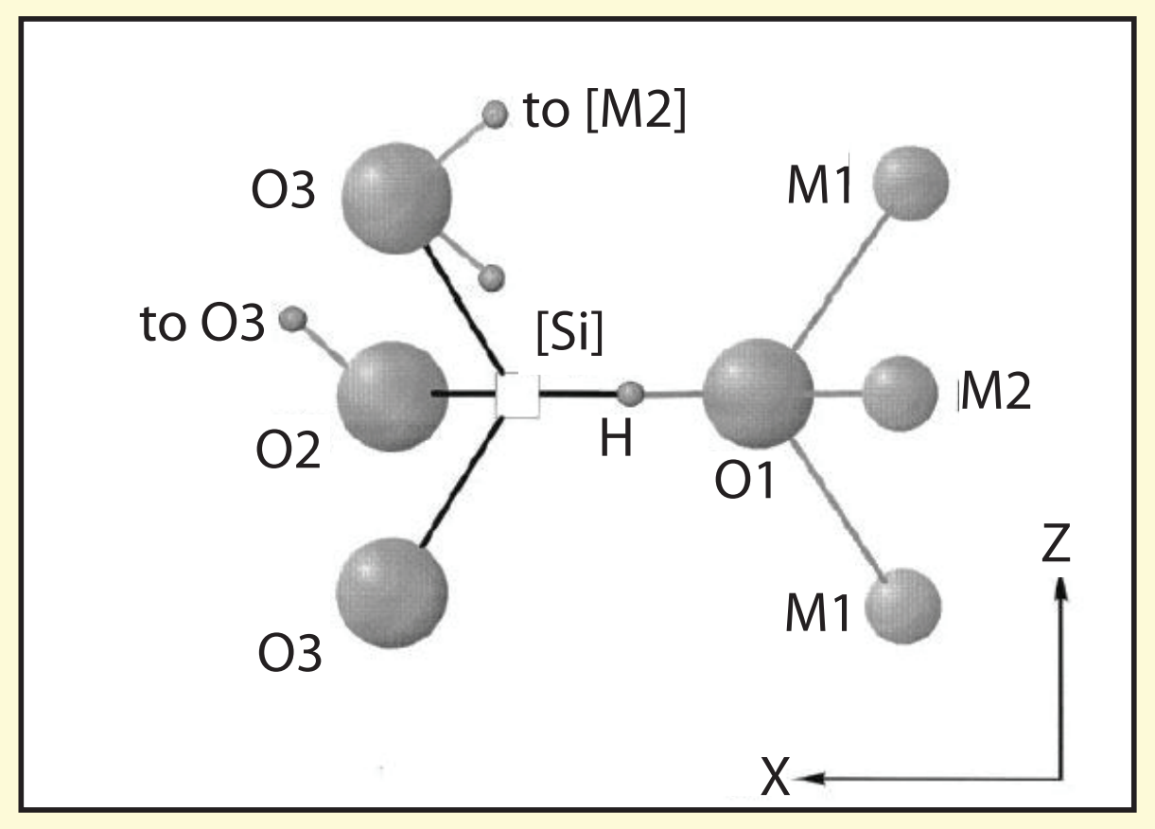


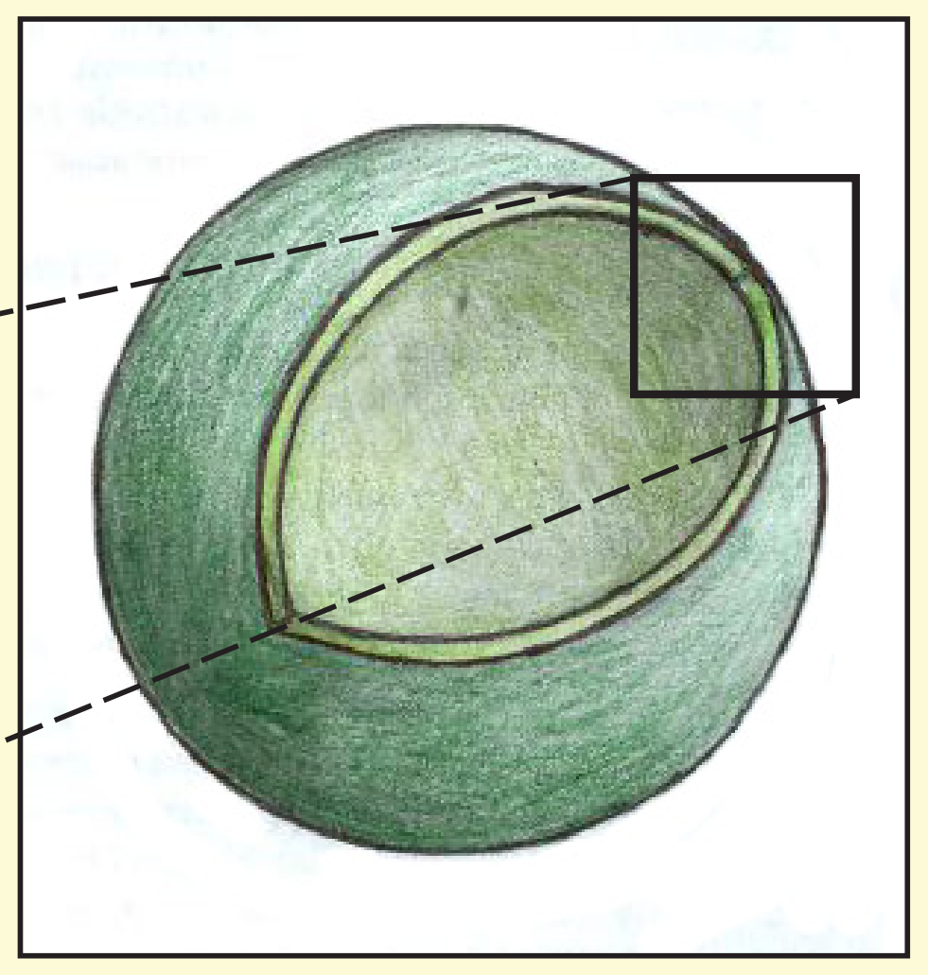
Figure 1. Diagram of possible orientations of hydrous impurities associated with Si vacancy in olivine structure (from Beran and Libowitzky, 2003).

Through hydrous impurities, nominally anhydrous minerals (NAMs) function as a reservoir for water in the mantle (Bell and Rossman, 1992). Inclusion of OH^- into NAMs impacts the physical properties of the mineral and the mantle.
Such properties include:

- mechanical strength of the host mineral
- internal diffusion rate in the host mineral
- host mineral weathering rate
- electrical conductivity in the mantle

Interpretations and Conclusions

- Absorption spectra from clean olivine crystals do not exhibit characteristics of the OH^- bands in mantle olivine spectra.
- Absorption spectra from bubble-rich regions of olivine crystals show higher water concentrations than bubble-free regions.
- Our results show that water-free olivine grew from water-rich, kimberlitic melt in the Haystack Butte, MT intrusion that crystallized at low pressure. More studies are required to demonstrate whether this result holds universally for olivine growth in low-pressure, water-rich magmas.
- The spectra from bubble-rich regions demonstrate the formation of serpentine on the walls of included bubbles. This suggests that the OH^- impurities are not intrinsic to the olivine crystal lattice. Rather, they represent the product of a low-temperature reaction of water vapor with olivine to form a serpentine rind at the contact between the two phases.



$$2Mg_2SiO_4 + 2H_2O \longrightarrow Mg_3Si_2O_5(OH)_4 + MgO$$

Figure 12. Proposed model for serpentine shell formation. The outer layer of the sphere (dark green) represents the contact of the vapor phase with the olivine crystal. Serpentine (light green) formed by the reaction of water vapor with the olivine lattice under sub-solidus cooling conditions in a process known as deuteric alteration.

Acknowledgments

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Question

Do olivine crystals grown in hydrous magma incorporate measureable amounts of water?

Motivation

- Significant quantities of water are found in high-pressure olivine, demonstrating that hyroxyl groups readily partition into the olivine crystal lattice.
- Olivines from hydrous basaltic melt show a correlation of hydroxyl absorption energies (as measured with IR spectroscopy) to silica saturation in the melt, with higher wavenumbers correlating to lower silica content (Matveev et al., 2005).
- It follows that olivine crystals grown from high-water, low-silica magmas (i.e., kimberlite) can incorporate water into their mineral structure.
- Variations in the abundance of hydroxyl impurities in other NAMs (such as quartz) have been exploited to discern new insights into their morphologic evolution and post-crystallization thermal evolution (Ihinger and Zink, 2000). Similar insights may be gained by investigating olivine crystals.

Sample

Figure 2. Photograph of sample source: Haystack Butte, MT

Figure 3. Photograph of polarized thin-section from Haystack Butte at 20x magnification.

Methods

- Doubly polished ~ 300 μm thin sections
- Located and mapped olivine crystals for analysis with petrographic microscope
- Divided crystals into bubble-rich and 'clean' crystals based on visible spherical inclusions within crystal
- Measured sample thicknesses using a digital dial indicator
- Obtained infrared spectra of mapped bubble-rich and clean crystals using Fourier Transform infrared spectrometer (FTIR)

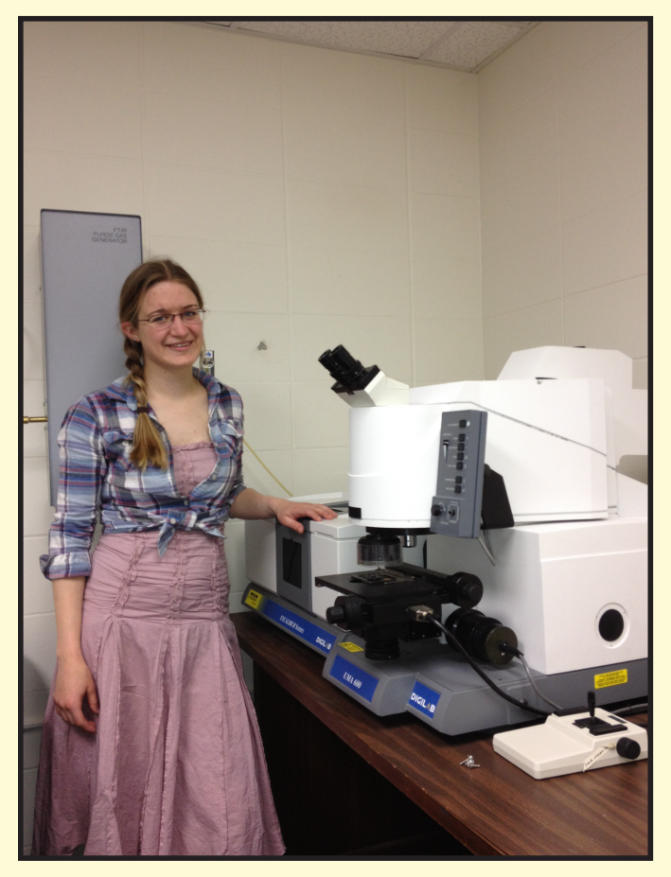

Figure 4. High resolution Fourier Transform infrared spectrometer.

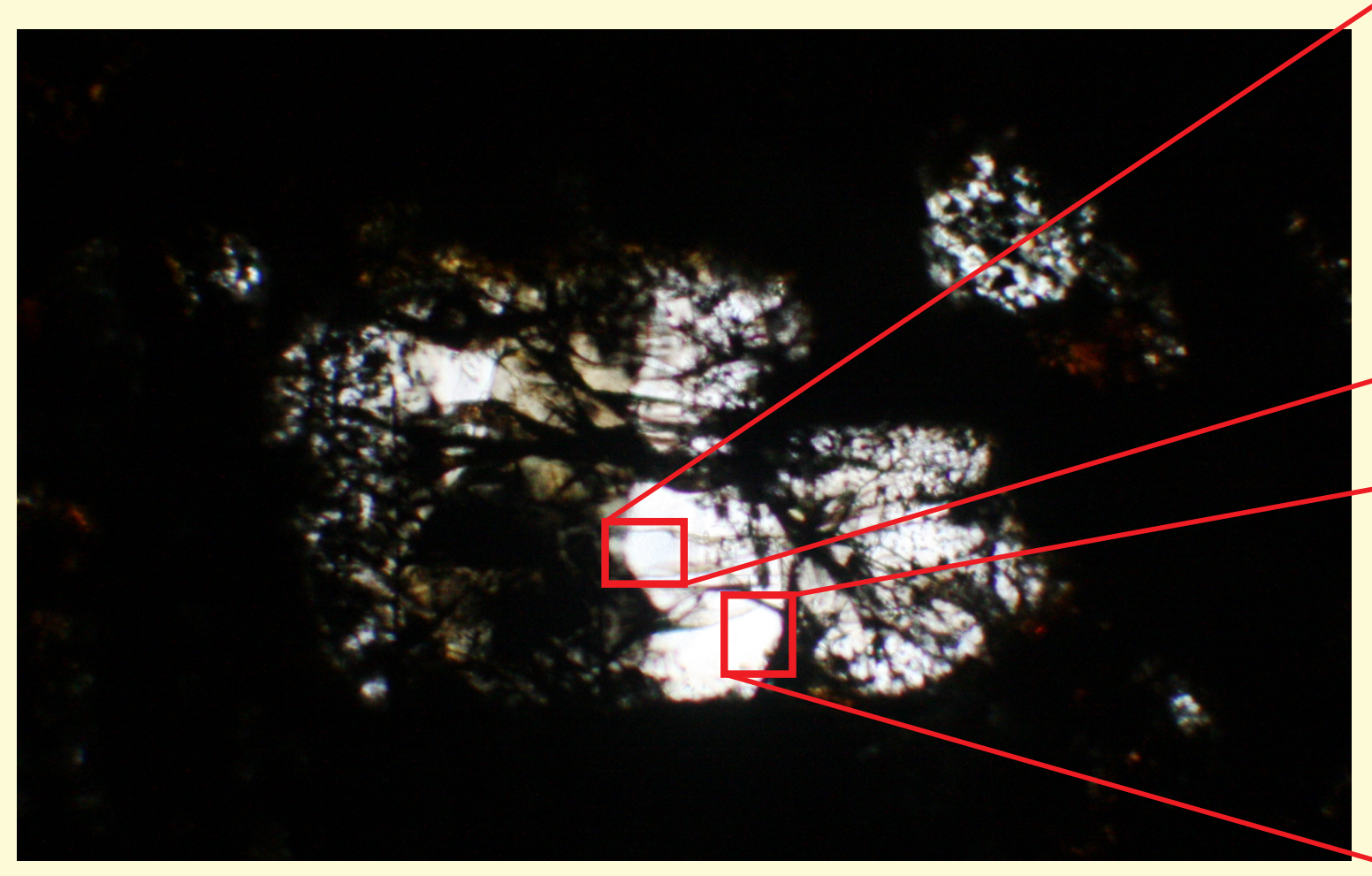

Figure 5. Olivine crystal at 20x magnification under unpolarized light.

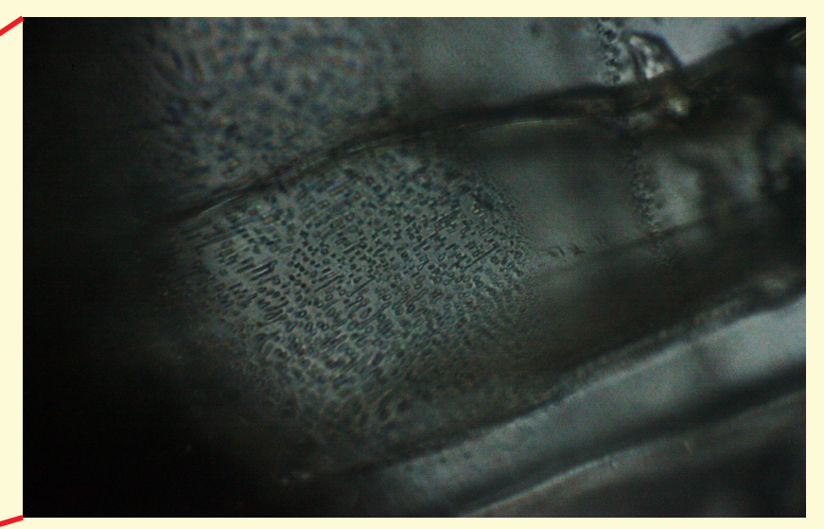

Figure 6. Photograph of healed fracture containing bubbles at 400x magnification.

Figure 7. Photograph of clean portion of olivine crystal at 200x magnification (rotated 90° clockwise from Figure 3).

Results

Clean Olivine

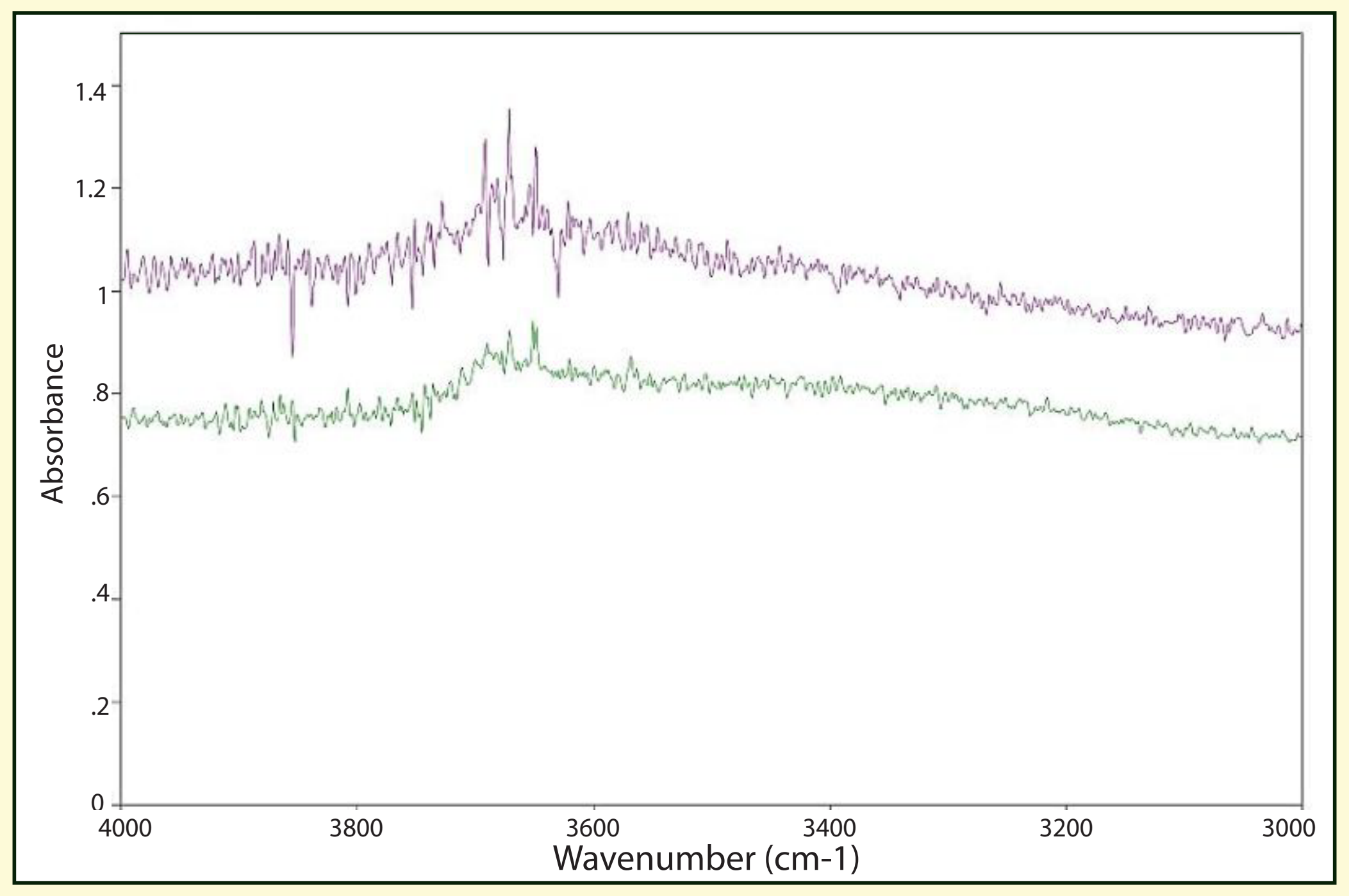

Figure 8. FTIR absorption spectra from clean portion of olivine crystals. The absorption spectra do not show the same complexity as olivines grown from the mantle.

Bubble-Rich Olivine

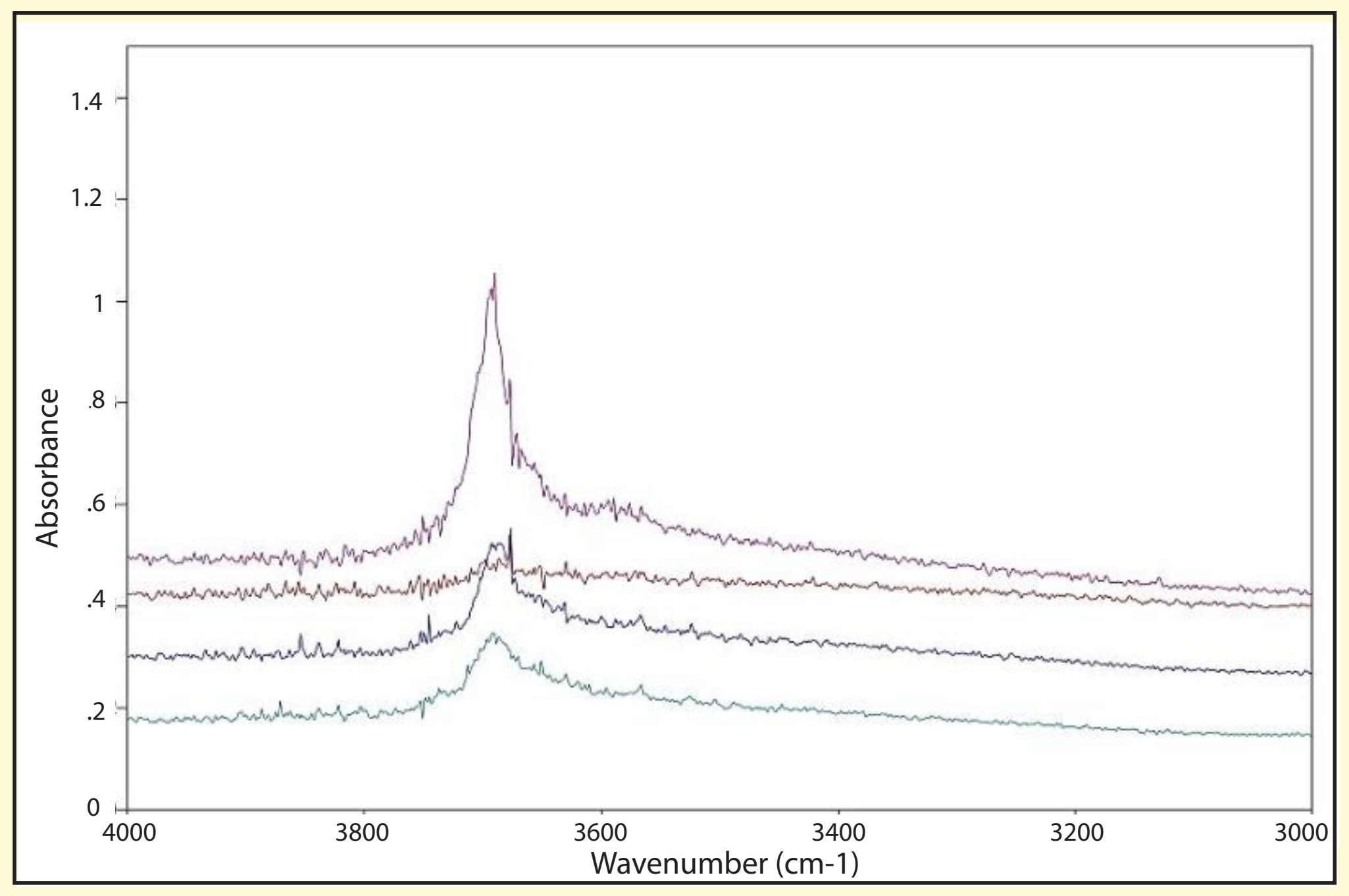

Figure 9. FTIR absorption spectra of bubble-rich healed fractures in olivine crystals. OH^- absorption bands in the 3680 to 3690 range suggest the prescence of serpentine.

Mantle Olivine

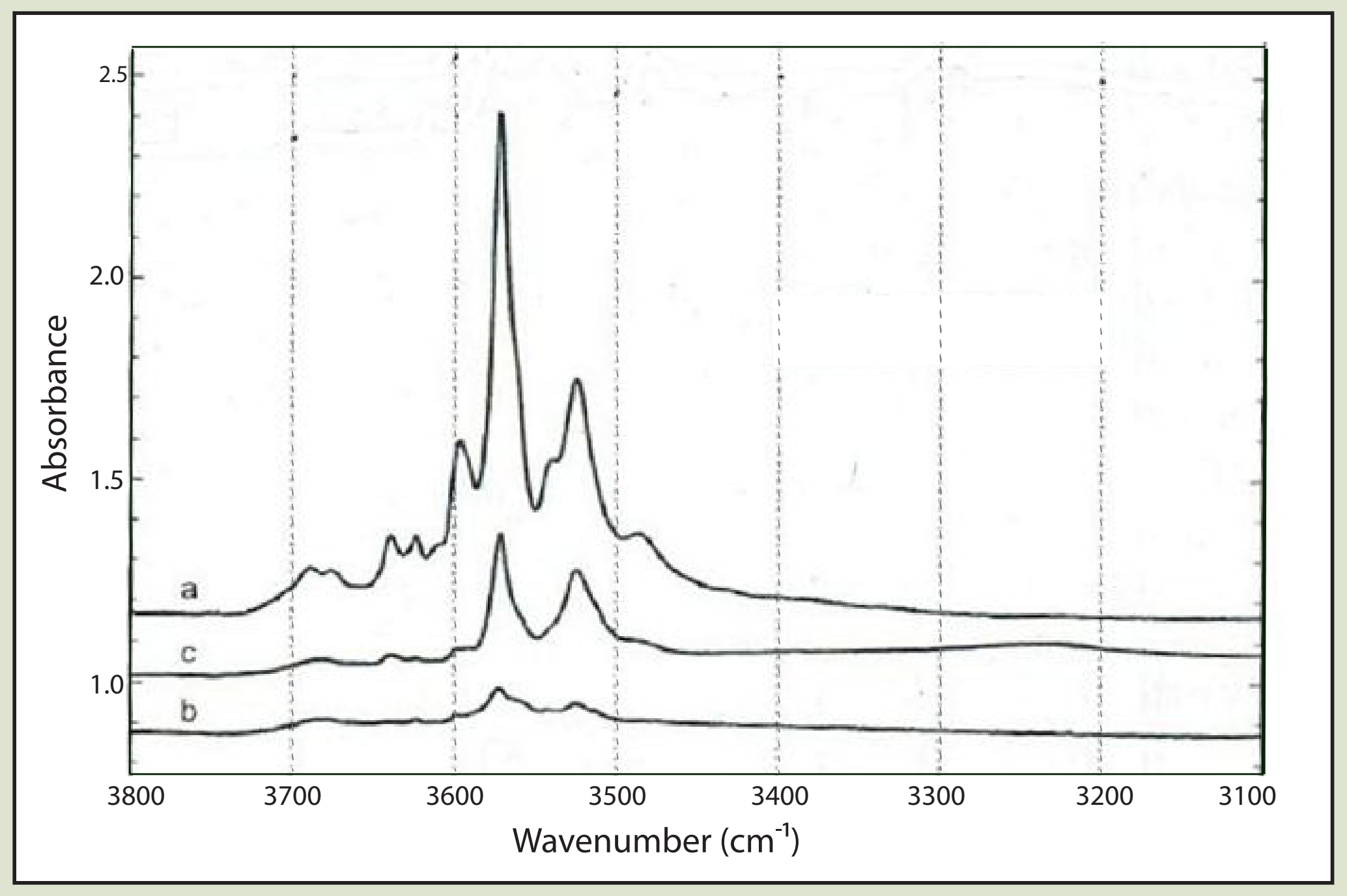

Figure 10. Polarized IR absorption spectra of mantle olivines from South American kimberlitic xenoliths (from Beran and Libowitzky, 2006).

Serpentine

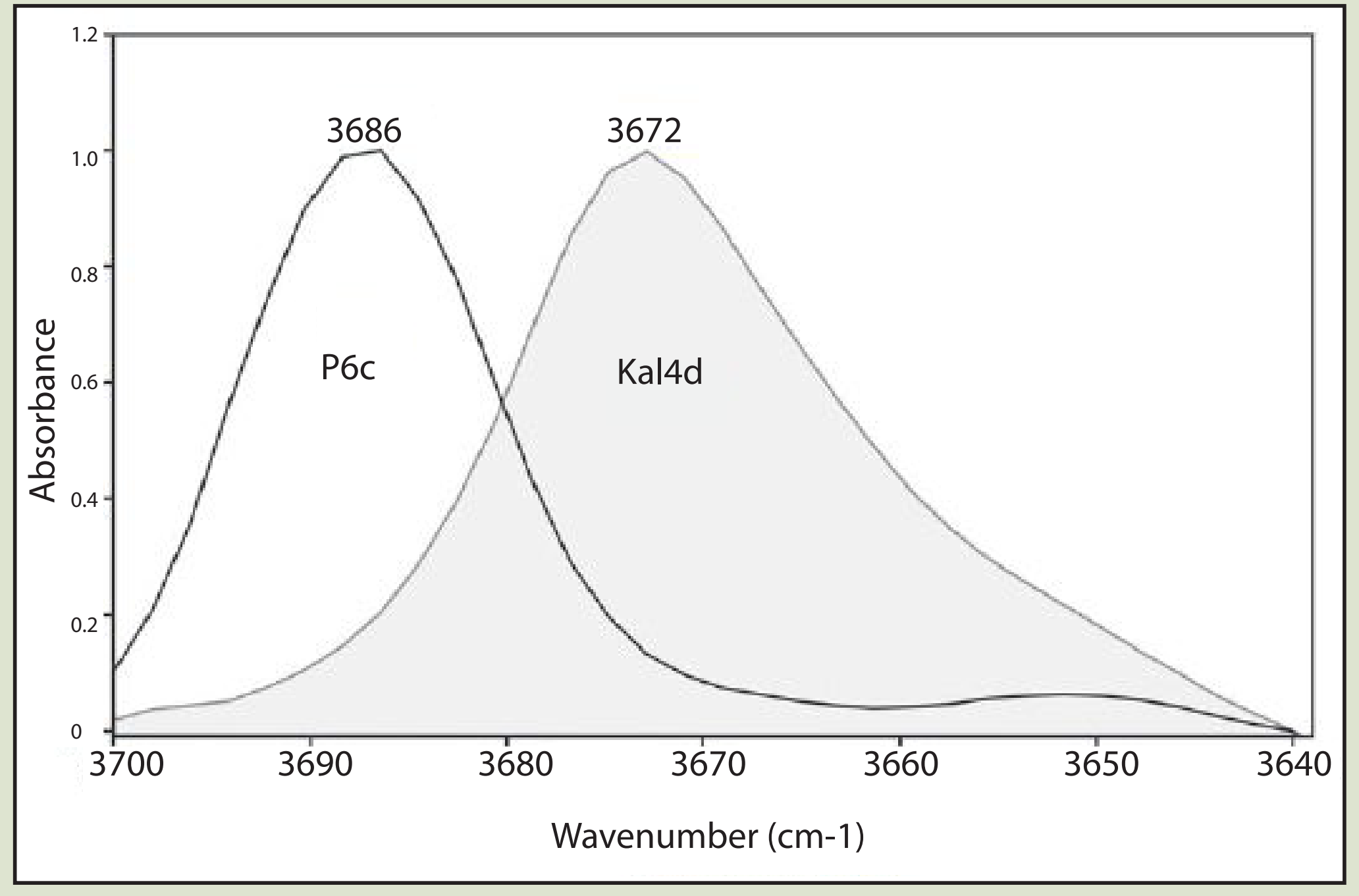

FIgure 11. IR absorption spectra of antigorite (grey: Kal4d) and lizardite (black: P6c) serpentine group samples (from Bernardini et al., 2011).

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