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Limitations of FTIR Spectroscopy for Detection of Water in Spinel Group Minerals, When $^{IV}\text{Fe}^{2+}$ is Incorporated into the Crystal Structure

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Abstract: Fourier-transform infrared (FTIR) spectroscopy can be used for detection of low hydrogen abundances as well as for finding information on hydrogen speciation in nominal anhydrous minerals (NAMs). A Perkin-Elmer 1760 X FTIR plus micro-FTIR spectrometer was used to apply this established method to natural spinel phases in order to detect water that is possibly incorporated into the crystal structure. Here, the limits of FTIR are assessed for detection of OH, when only traces of iron are incorporated into the crystal structure of natural spinel group minerals. A problem occurred because of the high intensity of the iron absorption bands, which absorb at similar wavenumbers to OH absorption bands.

Keywords: FTIR spectroscopy, hydrogen, iron, limiting factor, spinel group minerals

INTRODUCTION

IR spectroscopy is a useful tool in manifold ways. One can detect OH contents in diverse crystals and use them in many different scientific areas such as biology, chemistry, mineralogy, and so forth. IR spectroscopy institutes the possibility, in particular in the mineralogical sector, to achieve new insights into the OH defects of nominal anhydrous minerals (NAMs) from the upper mantle.^[1] The range of minerals in the earth, which are capable of hosting

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water in the form of H₂O and/or OH, ranges from ice to nominally anhydrous silicate phases. In the past 30 years, there have been many approaches and studies on NAMs such as olivines, pyroxenes.^[2,3]

The mineral spinel was chosen because, to the author's current knowledge, there exists no explicit work on the analysis of water content in spinel group minerals (SGMs) by IR spectroscopy. SGMs are of special interest because they are present in most types of geologic environments from the crust to the upper mantle.

Why would it be interesting to detect water in the SGMs? Because the earth's mantle could hold many times more water than in all the world's oceans. Earth's oceans make up just 0.02% of the planet's total mass (Fig. 1). Although the global hydrogen cycle is not completely understood yet, estimates show that subduction zones deliver up to four to six times more water to the mantle by dehydrating a slab than is released by island-arc volcanoes near subduction zones. If water is present in the earth's interior, it will influence the physical and chemical properties of the mantle such as its viscosity, melting temperature, rate of ionic diffusion, and grain growth. Previous experimental studies showed that, for example SGMs, which are likely to occur in the transition zone of the earth's mantle, contain essential amounts of water in form of OH groups. The g-Mg₂SiO₄ phase is reported to contain up to 27,000 wt. ppm H₂O.^[4]

EXPERIMENTAL

Sample Preparation

The sample selection includes representative natural SGMs such as gahnite, franklinite, and also spinel endmember. Large optical clear crystals of these diverse SGMs were used as analyzing material. These samples were prepared as parallel plates, polished on both sides. The final thickness of

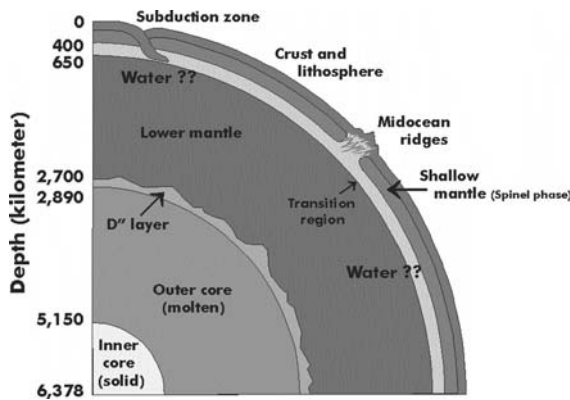


Figure 1. Division in the earth's interior (modified after Ref.^[11]).

each sample depended mainly on the concentration of iron because iron darkens the samples and increases its absorption. Therefore, the samples were thinned until the maximum absorbance bands occurring between 2500 and 6000 cm^{-1} did not exceed an absorbance of 2. Finally, the thickness of the crystals ranges between 50 and $300\text{ }\mu\text{m}$. The accuracy of the thickness measurements is estimated to be within $\pm 1\text{ }\mu\text{m}$. Unpolarized, room-temperature Fourier-transform infrared (FTIR) spectra were obtained from 20 single crystals. The FTIR spectra were recorded in the range $2500\text{--}6000\text{ cm}^{-1}$ with 64 to 256 scan-cycles and a spectral resolution of 4 cm^{-1} , using a Perkin-Elmer 1760 X FTIR plus micro-FTIR spectrometer.

Limiting Factors for IR Spectrometry

A series of measurements with a Jeol electron microscope with EDX for analyzing elements has shown that most spinel phases either possess iron stoichiometrically in their chemical formula such as franklinite (ZnFe_2O_4) or iron is incorporated as defects in the structure of crystals (up to 4 wt.% iron in gahnite and spinel). The original idea had been to detect possible water defects in spinel phases from the lower and deeper crust to achieve new insights about the quantity of water stored in spinel-alike structures and to link the results later on to the spinel phases that occur in the upper mantle showing spinel structure but that belong chemically rather to olivines. As it turned out, FTIR spectrometer was the limiting factor for detection of OH defects as soon as iron occurred in the spinel structure. Then, it was impossible to detect potential weak absorption bands of OH embedded into the spinel structure due to the high intensity of iron absorption bands absorbing at similar wavenumbers as OH (Figs. 2–4).

Broad, intense spin-allowed dd bands of tetrahedral coordinated Fe^{2+} , originating from ${}^5\text{E} \rightarrow {}^5\text{T}_2$ transition, appear in the spectral range $3000\text{--}7000\text{ cm}^{-1}$. In previous optical absorption studies of SGMs containing iron up to 4 wt.%, an intense band at $4500\text{--}5200\text{ cm}^{-1}$ was assigned to a spin-allowed electronic $d\text{--}d$ transition (${}^5\text{E} \rightarrow {}^5\text{T}_2$) in tetrahedral coordinated Fe^{2+} .^[5,6] Spectra of SGM extending into the IR range reveal additional absorption bands down to approximately 3600 cm^{-1} , which have been explained in terms of dynamic Jahn–Teller effects as well as phonon-coupling.^[5,7] The spontaneous Jahn–Teller effect is the spontaneous distortion of geometry in an electronically excited state, which results when levels are split to reduce the energy of the overall system (see <http://scienceworld.wolfram.com/chemistry/Jahn-TellerEffect.html>). A problem now arises because the peak caused by the incorporated iron into the SGM structure occurs at $\sim 3600\text{ cm}^{-1}$, an energy where normally one would expect to find bands from OH defects in the mineral spectra. Thus, the principal handicap to achieve accurate measurements of hydrogen in low-concentration phases is hereby the high intensity of iron absorbance overlapping the water absorption bands in the spectra.

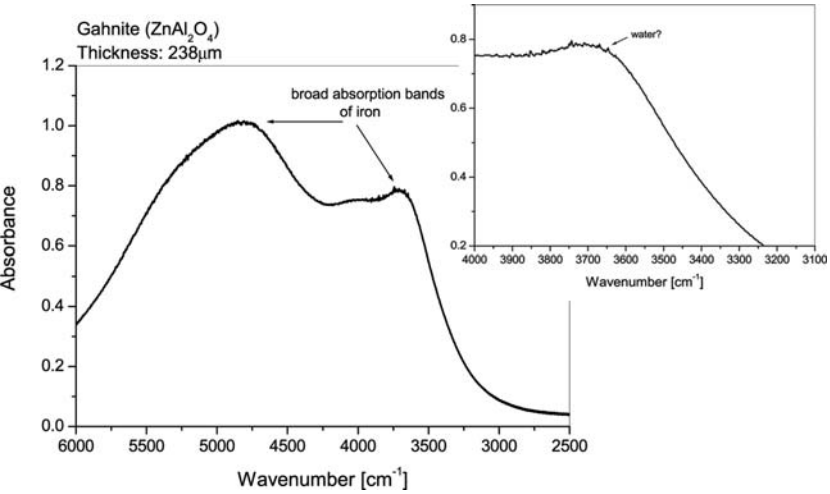


Figure 2. Gahnite FTIR spectra showing two broad absorption bands due to iron. The zoom in plot indicates possible weak peaks for water absorption.

RESULTS

In the spectra of all samples studied, broad, intense absorption bands caused by electronic, spin-allowed *dd* transitions of Fe^{2+} (${}^5\text{E} \cdot {}^5\text{T}_2$ transition in T_d -symmetry) are intense spectroscopic bands and can enwomb a potential

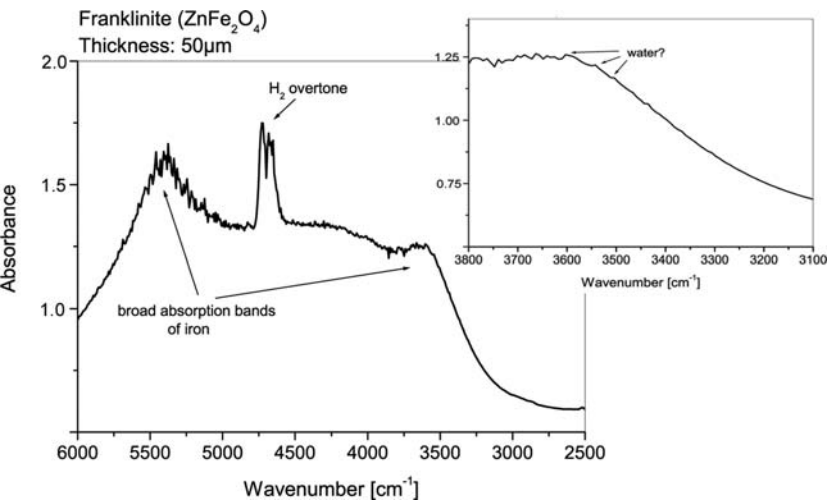


Figure 3. Franklinite FTIR spectra showing broad absorption bands due to iron. The zoom in plot indicates possible weak peaks for water absorption.

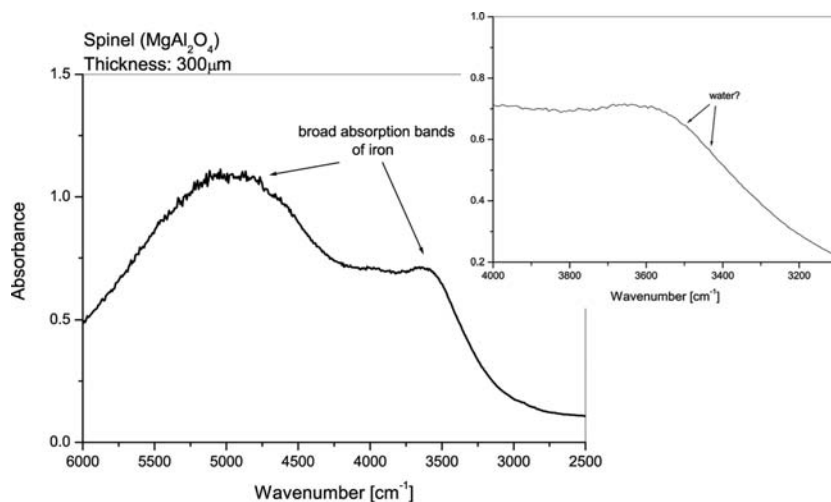


Figure 4. Spinel FTIR spectra showing two broad absorption bands due to iron. The zoom in plot indicates possible weak peaks for water absorption.

content of OH in the spinel phases. The splitting could be either the result of a dynamic Jahn–Teller effect or local clustering of Fe^{2+} .^[8]

It is interesting to note that the IR spectra (Figs 2–4) of the samples show exactly the same shape as those spectra obtained by optical spectroscopy from Rossman and Taran.^[9] Thus, the explanation for the bands is similar: X-ray structure refinements of MgAl_2O_4 ^[10] indicate that the T site is a regular tetrahedral site with T_d point symmetry. A perfect tetrahedral site ideally shows only a single absorption band, caused by the ${}^5E \rightarrow {}^5T_2$ transition in ${}^{\text{IV}}\text{Fe}^{2+}$. This is easily explained by the fact that the spinel structures are best described by a slightly distorted cubic array with free ($u u u$) oxygen fractional coordinates. Variations of u (i.e., of oxygen position along the $[1\ 1\ 1]$ direction), determines modifications of T–O and M–O bond distances and allows for accommodation of various chemical components and/or cation ordering.^[8]

CONCLUSIONS

IR spectroscopy is not suitable for minerals, such as SGMs, which are supposed to hold only traces of water (in 1 ppm range) in the structure. Once there is iron involved in the crystal structure, it will be impossible to distinguish between the weak OH peaks and noise. The samples from the crust had no manifest evidence of well-defined water detected by IR spectroscopy.

For future analyses, one has to add a technique that combines an analytical procedure for hydrogen including a low detection limit and high spatial

resolution. A sustainable instrument would be an ion probe because it offers these advantages. So, this could lead to the goal to analyze small “hidden” quantities of hydrogen at high spatial resolution to prove if the feasible water peaks are truly caused by OH absorbance.

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