SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

Quantification of CO₂ concentration in apatite

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ABSTRACT

We have calibrated the infrared (IR) method for determining CO_2 concentrations in apatite with absolute concentrations obtained through nuclear reaction analysis (NRA). IR data were obtained on double-polished apatite wafers using polarized transmission IR spectroscopy. Due to the various sites and orientations of CO_{3}^{2-} in apatite, the IR spectra are complicated and do not have the same shape in different apatite samples. Hence, simple peak heights are not used to characterize CO₂ concentrations in apatite. The total absorbance (A_{total}) was derived using the integrated area under the curves in a given polarized spectral region. Then A_{total} is calculated as $A_{E/c} + 2A_{E\perp c}$. The calibration has been carried out for two wavenumber regions, one with high sensitivity and the other applicable to apatite with high CO₂ concentrations. The first calibration is for the fundamental asymmetric CO_2^{2-} stretching at wavenumbers of $1600-1300 \text{ cm}^{-1}$, and the CO₂ concentration in parts per million can be obtained as $(0.0756 \pm 0.0036) A_{\text{total}}/d$ where d is sample thickness in centimeters. The fundamental stretching bands are strong and hence sensitive for measuring low CO₂ concentrations in apatite, down to parts per million level. The second calibration is for the CO_{3}^{-} bands at wavenumbers of 2650–2350 cm⁻¹, and the CO_2 concentration in parts per million is $(9.3 \pm 0.6) A_{total}/d$ where d is sample thickness in centimeters. These bands are weak and hence are useful for measuring high CO₂ concentrations in apatite without preparation of super-thin wafers. The anisotropy is significant. The difference between $A_{\rm E/e}$ and $A_{\rm E1e}$ can reach a factor of 2.73. Hence, for high accuracy, it is best to use polarized IR to determine CO_2 concentrations in apatite. For rough estimation, unpolarized IR spectra may be used by estimating A_{total} = $3A_{unpol}$, where A_{unpol} is the integrated absorbance from unpolarized spectra.

Keywords: Carbonate in apatite, IR spectroscopy, nuclear reaction analysis, NRA

INTRODUCTION

The mineral apatite is a common biomineral and is also an accessory mineral found in terrestrial, martian, and lunar rocks (e.g., McCubbin and Nekvasil 2008; Boyce et al. 2010; McCubbin et al. 2010a, 2010b, 2012). It has the ability to take numerous elements, including most volatile elements, into its structure, depending on the composition of the surrounding milieu (Elliott 1994; Pan and Fleet 2002; Hughes and Rakovan 2015). The formula of apatite is $M_5(ZO_4)_3X$, in which the M site is dominated by Ca2+, but can also contain Sr2+, Ba2+, Pb2+, Na+, and light rare earth elements. The Z site is dominantly P⁵⁺, but can also contain As5+, Si4+, C4+, and S6+, and the X site is a mixture of F^- , OH^- , Cl^- , and/or CO_3^{2-} . Because of this, apatite serves as a good indicator of the conditions of the magmatic environment, especially volatile conditions, from which it forms (Webster and Piccoli 2015). In particular, CO₂ concentration in apatite may be able to indicate the CO₂ concentration or fugacity in terrestriallunar-martian magmas and metamorphic rocks. For this potential to be realized, it is essential to analyze CO_2 concentrations in small apatite crystals as well as zoning of CO₂ in apatite. The focus of this study is on the quantification of CO2 concentrations in apatite by Fourier transform infrared spectroscopy (FTIR).

 CO_2 enters the apatite structure as the carbonate ion CO_3^{2-} in several ways, resulting in a series of complicated infrared (IR) peaks originating from CO₃²⁻ in apatite (Elliott 1994; Pan and Fleet 2002; Tacker 2008). The CO_3^{2-} ion is a triangular plane ion, and may substitute into two different sites in apatite: the OH- ion site and the PO₄³⁻ site. The former is referred to as the A site and the latter is referred to the B site for carbonate substitution (Fleet and Liu 2003, 2007; Fleet 2009). In the OH⁻ site, CO_3^{2-} may be oriented such that the bisector of the triangular CO_3^{2-} ion is parallel to the **c**-axis of apatite (called type A1), or such that the bisector is perpendicular to the c-axis (called type A2) (Tacker 2008). Based on IR spectra, Tacker (2008) also identified two different sites of CO_3^{2-} ion in B site, and interpreted them to be due to alignment of the 3 O atoms of CO₃²⁻ onto O atoms of the different triangular faces of the PO₄³⁻ tetrahedron (see also Ivanova et al. 2001). Charge balance can be achieved in several ways, such as one CO3- substituting for two OH-, or CO3- plus Na+ substituting for PO₄³⁻ plus Ca²⁺, etc. Each of these different substitutions results in slight changes in the apatite structure as well as shifts in both the Raman and the IR bands. In addition, these substitutions are not mutually exclusive, and often occur in combination within the same crystal. This multitudinous substitution is most evident in the wavenumber region 1600-1300 cm⁻¹. These substitutions are so complex that the IR signal from a single crystal can elicit

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as many as 7 peaks in this region (Tacker 2008).

There are several methods for assessing CO₂ concentrations in apatite (e.g., Gulbrandsen et al. 1966; Johnson and Maxwell 1981; Santos and Clayton 1995; Cassella et al. 2000; Marks et al. 2012; Grunenwald et al. 2014). Note that even though carbon in apatite is present as the carbonate ion, the concentration here is conventionally referred to as the amount of CO₂ (wt% or parts per million) that would be released if apatite were heated up to release all the volatiles. Previous methods are mostly the bulk method. These include total carbon titration or total CO₂ release (Santos and Clayton 1995; Grunenwald et al. 2014), FTIR spectra from a dispersion in a KBr pellet (Santos and Clayton 1995; Marks et al. 2012; Grunenwald et al. 2014), and vapor phase FTIR spectra obtained by reacting 50 mg of apatite with HCl (Cassella et al. 2000). These methods typically require large samples, and even the most recent powder FTIR method by Grunenwald et al. (2014) still requires 1-2 mg of apatite. Apatite crystal specimens are not always available in such large quantities. For example, in available lunar samples, apatite crystals are often in the range of tens of micrometers in size (Boyce et al. 2010; McCubbin et al. 2010). In addition, the powder or vapor FTIR methods (Santos and Clayton 1995; Cassella et al. 2000; Marks et al. 2012; Grunenwald et al. 2014) are destructive and not enough for the determination of heterogeneities at the 1000 µm scale. As demonstrated by Elliott (1994) and Wang et al. (2011), polarized IR signals of OH and carbonate from single apatite crystals are often very strong. Hence, the FTIR microbeam method on single apatite crystals has a high sensitivity and precision in determining the OH and carbonate concentrations once calibrated. Elliott (1994) used polarized FTIR analyses to determine the structural setting and orientation of the carbonate ion in apatite, whereas Wang et al. (2011) focused on polarized FTIR analyses of H₂O concentrations.

In this work, we use polarized micro-FTIR to quantify CO₂ concentrations in apatite. Although FTIR can be used to detect specific ion clusters (and specific sites and orientations) in the crystal with high sensitivity and precision, conversion of the resulting peak intensities to concentrations requires an absolute concentration technique for calibration. The creation of a calibration curve, using large apatite crystals of varying concentrations, would allow for future quantification of concentrations in smaller samples (Wang et al. 2011). Nuclear reaction analysis (NRA) is an effective way to determine the absolute concentrations of carbonate in large crystals (Mathez et al. 1987; Cherniak et al. 2010). The purpose of this project was to compare FTIR data with NRA quantification of carbonate in apatite from various sources to build a calibration curve for the FTIR signatures in these crystals. However, one difficulty in using single-crystal FTIR to quantify CO₂ concentrations in apatite is that the fundamental absorption bands are often too strong so that sometimes wafers, which are impractically too thin, must be prepared. To overcome this difficulty, appropriate combination bands that are orders of magnitude weaker can be used to determine CO₂ concentrations in apatite when the concentration is relatively high.

In addition to the high sensitivity and precision, another advantage of using polarized FTIR, and assessing spectra when the E-vector is parallel or perpendicular to the c-axis of the crystal, is the improved accuracy in quantification of concentrations as well as revealing structural information (Libowitzky and Rossman 1996). It is interesting that with all the discussion of the importance of the alignment of the CO₃ ion with the **c**-axis of the apatite crystal (Fleet and Liu 2003; Fleet et al. 2004; Tacker 2008; Fleet 2009), IR analysis of apatite parallel and perpendicular to the **c**-axis is quite rare (Elliott 1994; Suetsugu et al. 1998). Because of the different orientations of the carbonate ion, it is likely that the use of polarized FTIR will provide greater detail regarding the variety of substitutions, with some more prevalent when \mathbf{E}/\mathbf{c} , and others more prevalent when $\mathbf{E}\perp\mathbf{c}$, as well as more accurate quantification of CO₂ concentrations in apatite.

METHODS

Samples

Four apatite samples were obtained from various locations: Durango, Mexico (Cerro); High Atlas Mountains, Morocco (HAM); Faraday Township, Ontario (ROM); and one from an unknown location purchased from an online vendor (GEM). The Durango apatite has been extensively studied and is often used as a reference material (e.g., Young et al. 1969; McDowell et al. 2005). Two of these samples (Cerro, HAM) were characterized in our laboratory by electron microprobe (Henderson 2011) and used to calibrate the IR method to analyze H₂O concentrations (Wang et al. 2011). Apatite from the same ROM sample batch (Royal Ontario Museum No. M14821) was studied by Gulbrandsen et al. (1966). The compositions of the apatite single crystals, as determined by electron microprobe by Henderson (2011) for Cerro and HAM and in this study for ROM and GEM, are reported in Table 1. All the apatite crystals used are fluorapatite with F/(F+OH+Cl) > 0.7, with Ca dominating the M site (\geq 98% of the M site), P dominating the Z site (\geq 96% of the Z site), and all other elements (e.g., S, Si, Mg, Sr, Ba, REE, and Cl) totaling less than 3 wt%.

All samples were mounted on glass slides with crystal bond and cut parallel to the c-axis with a diamond wafering saw. Cerro and HAM are high-quality gem crystals with a euhedral shape and were easy to cut into oriented wafers. The ROM and GEM crystals were more difficult to mount and cut into oriented wafers because

TABLE 1. Chemical composition of apatite crystals used in this study	y
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Sample	ROM	GEM	HAM	Cerro						
Number of analyses	9	10	18	20						
P ₂ O ₅	40.36(13)	40.27(54)	40.72(68)	41.04(68)						
As ₂ O ₅	0.04(2)	0.04(4)	0.01(2)	0.08(2)						
SO3	0.02(1)	1.09(5)	0.46(4)	0.44(4)						
SiO ₂	0.09(2)	0.41(3)	0.62(2)	0.32(2)						
CaO	54.32(13)	54.50(29)	54.95(54)	54.22(53)						
SrO	0.11(3)	0.11(2)	0.13(1)	0.09(1)						
Na ₂ O	0.10(1)	0.30(3)	0.10(2)	0.28(2)						
Y ₂ O ₃	0.19(4)	0.00(3)	0.05(1)	0.09(1)						
La ₂ O ₃	0.08(8)	0.06(4)	0.25(2)	0.43(2)						
Ce ₂ O ₃	0.25(3)	0.15(4)	0.36(2)	0.62(2)						
Pr ₂ O ₃	0.04(2)	0.05(4)	0.02(3)	0.05(3)						
Nd ₂ O ₃	0.14(2)	0.07(3)	0.11(2)	0.18(2)						
F	3.93(6)	2.83(6)	2.51(8)	3.40(9)						
Cl	0.033(5)	0.04(1)	0.33(2)	0.46(2)						
H ₂ O	0.043(8)	0.24(1)	0.44(1)	0.085(14						
CO ₂	0.66(6)	0.18(4)	0.14(3)	0.03(1)						
–O=F,Cl	-1.66	-1.20	-1.13	-1.535						
Total	98.74	99.15	100.072	100.35						
Number of ions normalized to M = the sum of mono-, di-, trivalent										
cations = 5										
Р	2.908	2.881	2.875	2.925						
S	0.001	0.069	0.029	0.028						
Si	0.008	0.034	0.052	0.028						
C	0.077	0.021	0.016	0.002						

0.077 0.021 0.016 0.003 Ca 4.953 4.935 4.950 4.898 1.057 0.756 0.696 0.922 OH 0.024 0.135 0.245 0.048 CI 0.005 0.005 0.045 0.057 Notes: Data for ROM and GEM are from this study, and data for HAM and Cerro are from Henderson (2011). V2O5, Al2O3, FeO, MgO, MnO, PbO, BaO, K2O, Sm2O3,

G₂O₃, Dy₂O₃, ThO₂, and UO₂ are also measured for HAM and Cerro, but their concentrations are at or below detection limit. H₂O and CO₂ concentrations are from IR (Wang et al. 2011; this study).

TABLE 2. NRA and FTIR data on apatite from this study

Apatite	H ₂ O wt%	CO ₂ wt%	A ₁₄₄₀ E⊥c	A ₁₄₄₀ E //c	A ₁₄₄₀ Total	A ₂₅₀₀ E⊥c	A ₂₅₀₀ E //c	A ₂₅₀₀ Total
ROM	0.043 ± 0.008	0.664 ± 0.055	37250	17380	91870	323 ± 17	125 ± 3	772 ± 34
GEM	0.24 ± 0.01	0.181 ± 0.040	8890 ± 52	6590 ± 263	24380 ± 159	64.5 ± 1.3	27.5 ± 0.7	157 ± 3
HAM	-	0.142 ± 0.034	5018 ± 270	5438 ± 134	15474 ± 674	43.7 ± 1.3	31.6 ± 1.3	119.1 ± 1.2
Cerro	-	0.028 ± 0.012	683	1868	3234	-	-	-

Notes: (1) H_2O concentration is based on IR measurement in this study using the calibration of Wang et al. (2011). (2) CO_2 concentration is based on NRA analyses in this study, except for Cerro, for which the CO_2 concentration was estimated using the relationship between total absorbance of Cerro and the total absorbance of HAM (see text). Because of this, the CO_2 values of Cerro are not used in the calibration. (3) The absorbances are integrated absorbances per centimeter thickness (that is, A/d in Eq. 2). For Cerro, the CO_2 concentration is low and hence A_{2500} cannot be determined well.

the original crystal surfaces are not obvious. ROM was cut from a triangular prism crystal. GEM was originally nearly spherical so the resulting wafer was an oval with a long diameter of 5.2 mm and a short diameter of 3.1 mm. The accuracy of the orientation of the wafers was checked by polarized OH spectra (see below). These samples were further cut into two pieces. One piece was used for NRA analysis and the other was used for polarized micro-FTIR. For each of ROM and GEM, another section was prepared for electron microprobe analyses.

Electron microprobe

The electron microprobe analyses for two polished apatite crystal wafers (ROM and GEM) followed the procedure of Henderson (2011). As discovered by Stormer et al. (1993), the $FK\alpha$ intensity in apatite varies with time, especially when the analyzed section is perpendicular to **c**-axis. Henderson (2011) showed that accurate analyses may be obtained by analyzing the apatite section parallel to **c**-axis using a defocused or rastered beam of 5 to 10 µm in diameter. We used a 10 µm defocused beam at 15 kV and 10 nA on the apatite (100) sections. Full analyses conditions can be found in Henderson (2011).

FTIR

For FTIR, samples were doubly polished at least three separate times to thicknesses ranging from 1.4 mm to 20 μ m. Sample thickness was determined using a Mitutoyo digital micrometer (with a precision of ±1 μ m and an accuracy of ±2 μ m). For samples with a thickness <100 μ m, interference fringes in the FTIR spectra were used to verify and determine the thickness using the equation:

$$d = 1/(2n\Delta\omega) \tag{1}$$

where d is the thickness of the sample, n is the refractive index, and $\Delta \omega$ is the period of the interference fringes in terms of wavenumbers. A refractive index of 1.65 was used.

Polarized spectra were obtained for both E/c and $E\perp c$ on the single wafer cut parallel to the c-axis using a Perkin-Elmer Spectrum GX FTIR spectrometer at the University of Michigan with a microscope attachment that was purged with N₂ gas. Spectra were acquired with a mid-IR source, KBr beamsplitter, KRS-5 IR wire grid polarizer and a liquid nitrogen cooled MCT detector. An aperture of 50 µm by 50 µm was used. Data were recorded from 7800–700 cm⁻¹, with a resolution of 1 cm⁻¹.

The orientation to the c-axis was verified in each sample using the spectra near the wavenumber 3540 (OH peak), which is zero when $E\perp c$ and maximal when E/c (Levitt and Condrate 1970; Wang et al. 2011). The peaks in apatite attributed to CO_{3}^{2-} were compared with polarized FTIR spectra of a double-polished crystal of calcite (CaCO₃).

Nuclear reaction analysis (NRA)

We used Nuclear reaction analysis (NRA) to determine absolute carbon concentrations in apatite (Mathez et al. 1987; Proust et al. 1994; Cherniak et al. 2010). The nuclear reaction is ${}^{12}C(d,p){}^{13}C$ (i.e., ${}^{12}C + {}^{2}H \rightarrow {}^{13}C + {}^{1}H$) (Proust et al. 1994; Wang and Nastasi 2009; Csedreki et al. 2014). A high-energy beam of deuteron (²H) particles bombards the target material (polished apatite crystal). As the particles go into the target, some ${}^{2}H$ particles react with the target nucleus (${}^{12}C$) converting the target nucleus to a new nucleus (${}^{13}C$) and releasing a reaction product (${}^{1}H$) with a specific amount of energy. The released ${}^{1}H$ ion, with a different energy, is detected in the NRA proton spectrum at different energy channels.

The samples prepared for NRA were polished with SiC sandpaper and 0.3 μ m alumina powder on cloth. Samples were about 50 mm² in area and 1–3 mm thick. All NRA measurements were carried out at the Michigan Ion Beam Laboratory (MIBL) at the University of Michigan with the 1.7 MV tandem accelerator. The deuteron beam energy was selected to be 1.31 MeV to maximize the ${}^{12}C(d,p){}^{13}C$

nuclear reaction cross section (Wang and Nastasi 2009; Csedreki et al. 2014) and hence the signal in the spectrum used to quantify the carbon concentration in the sample. A Si charged-particle detector with 15 keV energy resolution was used to acquire the spectrum. The detector was placed at a scattering angle of 135°. For the acquisition of the sample spectra, a 17.7 μ m thick polyimide (H₁₀C₂₂N₂O₃) foil was placed in front of the detector to filter out backscattered deuterons of low energy (<1.1 MeV). This allowed us to increase in the deuteron current on the sample and decrease the acquisition times. The acquisition times were 500 s with a deuteron current on the sample of 130 nA. During the acquisition of the spectrum the direction of the deuteron beam is normal to the sample surface. The depth of the apatite sample being probed was estimated using the SIMNRA software (Mayer 1999) to be ~6 μ m.

Atomic carbon concentration was determined through NRA spectrum modeling also using the SIMNRA program (Mayer 1999). The NRA method is an absolute method and no independent calibration is necessary. Nonetheless, we verified the procedure by analyzing a calcite (CaCO₃), and obtaining a carbon concentration of 19.3 \pm 1.3 at%, which is in agreement with the stoichiometric concentration of carbon of 20 at%.

RESULTS

The NRA spectra and modeling curves are shown in Figure 1. The peak at 2980 keV reflects surface carbon contamination and the data from 2600-2940 keV indicate carbon in the interior of the crystal. There is significant background in the NRA spectra and the detection limit of the NRA method is 0.113 wt% CO₂. Therefore, carbon concentration in some apatite cannot be well resolved from NRA alone. For example, for Cerro, the NRA signal at 2600-2940 keV is indistinguishable from the background (Fig. 1). Hence, for Cerro, the fitting quality is low and the uncertainty in modeling the carbon concentration is large. To determine concentrations better, we used constraints from FTIR spectra, which have a high sensitivity to estimate the background in NRA and subtract the same background counts from the NRA signals for all samples. Based on IR spectra in the v₃ region (see later sections), the integrated absorbance A_{total} (see Eq. 2) for Cerro is $\sim \frac{1}{5}$ of that for HAM. Because A_{total} is proportional to the carbon concentration, we hence assigned a background to all the NRA spectra so that carbon concentration in Cerro is $\sim \frac{1}{5}$ of that for HAM. The resulting carbon concentration and error in ROM, GEM, HAM, and Cerro are listed in Table 2. Note that the new error estimates reported in Table 2 are achieved by combining the IR constraints of Cerro and HAM with the NRA data, and are smaller than the error based on the NRA data alone. The CO₂ concentration in the ROM apatite grain that we analyzed by NRA is 0.66 ± 0.06 wt% (1 σ error) based on NRA analysis, similar to the 0.57 wt% obtained by Gulbrandsen et al. (1966), who analyzed bulk apatite crystals from the same location.

Typical IR spectra with the **E** vector parallel and perpendicular to the **c**-axis are shown in Figure 2. Band identifications were taken from Regnier et al. (1994) and Koleva and Petkova (2012). The bands due to PO_4 at ~1000 cm⁻¹ are typically over-



FIGURE 1. NRA spectra of four samples. The points are data and the curves are modeling of the data using the SIMNRA software (Mayer 1999).

saturated. Oversaturation is indicated when the peak is at high absorbance values and when the peak region is not smooth, but shows a lot of "noise." These data are not useable for quantification. The bands at ~2000 cm⁻¹ are due to overtones of PO₄. The OH band at 3540 cm⁻¹ is highly anisotropic, with zero intensity when $E \perp c$, and is used to verify the orientation of the samples. The carbonate peaks in apatite at higher wavenumbers can be assigned by comparison with assignments of peaks in carbonate minerals (e.g., Gunasekaran et al. 2006) although the shapes of the carbonate peaks in apatite are more complicated than in calcite and dolomite due to the lifting of the double degeneracy and the multiple sites and orientations for the substitution of the CO3 group into the apatite structure. Following the assignments of Gunasekaran et al. (2006), the bands between 1700 and 1800 cm^{-1} are due to v_1+v_4 , those between 2400 and 2600 cm^{-1} are due to $2v_2+v_4$, and those between 2800 and 2950 cm⁻¹ are due to $2v_3$. The band at 1650 cm⁻¹, with a shoulder at 1620 cm⁻¹, does not change with the CO₂ or H₂O concentration, and appears to be due to a v_3+v_4 combination of PO₄³⁻.

Among the fundamental carbonate vibrational modes, v_3 (double-degenerate antisymmetric stretch in the region of 1600–1300 cm⁻¹) is well separated from other bands and hence well suited for the quantification of the CO₂ concentration. The v_2 mode (out-of-plane bend in the region of 850–900 cm⁻¹) is close to the main and oversaturated PO₄ bands, making it difficult to use. There are numerous carbonate v_3 and v_2 bands in apatite due to different carbonate substitution (A1, A2, B1, and B2, Tacker 2008). The v_1 mode is IR-inactive and v_4 (at ~720 cm⁻¹) is not always present. Hence, among the fundamental vibration modes, the v_3 bands are calibrated in this study. The v_3 IR bands are strong and easily oversaturated. For our study, we specifically chose some apatite with high CO₂ concentration because NRA requires high concentrations. Hence, to avoid oversaturation of the IR bands, the samples had to be very thin, and the thinnest sample is only 20 µm thick for ROM, which has the highest CO₂ concentration. That is, these IR bands have high sensitivity and are good for obtaining low CO₂ concentrations in apatite once calibrated but are



FIGURE 2. Two polarized FTIR spectra for an apatite crystal from High Atlas Mountain (HAM), one for $E \perp c$ and one for E//c. The thickness of the crystal is 65 μ m. (Color online.)



FIGURE 3. Polarized FTIR spectra at 1600–1300 and 2650–2350 cm⁻¹ collected from single apatite crystals. Note the difference in this thickness of each sample, especially between wavenumber region of 1600–1300 and of 2650–2350 cm⁻¹. To avoid oversaturation, the spectra at 1600–1300 cm⁻¹ must be collected on very thin wafers. To get significant signal, the spectra at 2650–2350 cm⁻¹ must be collected on thick wafers. The different shapes are due to different proportions of carbonate ions in A1, A2, B1, and B2 substitutions (see text). (Color online.)

not convenient for quantifying high CO_2 concentrations (e.g., ≥ 1000 ppm). To overcome this difficulty, we also calibrated the combination bands for carbonate in apatite in the region of 2650–2350 cm⁻¹. The bands in this region are about two orders of magnitude weaker than those in 1600–1300 cm⁻¹, can only be clearly resolved when the samples are greater than 0.5 mm thick (Fig. 3), and, hence, are well suited when the CO₂ concentration is high in apatite. The use of combination bands to determine high species concentrations is similar to that in studying H₂O in glasses (Newman et al. 1986).

To view the IR bands more clearly, the left three panels of Figure 3 illustrate the spectra in the region of $1600-1300 \text{ cm}^{-1}$ for the **E** vector parallel or perpendicular to the **c**-axis of the apatite crystal. The shapes of the peaks are variable from one apatite crystal to another, with major and minor peaks. For ROM and GEM apatite crystals, there are major double peaks at 1455 and

1428 cm⁻¹. When $\mathbf{E}\perp\mathbf{c}$, the two peaks are nearly identical, and when $\mathbf{E}//\mathbf{c}$, these peaks become uneven in height. The spectra of ROM are similar to the polarized IR spectra of francolite from Cornwall, England (Elliott 1994). The right three panels of Figure 3 show the same information in the region of 2650–2350 cm⁻¹. Often the absorbance for $\mathbf{E}\perp\mathbf{c}$ is larger than that for $\mathbf{E}//\mathbf{c}$, but for Cerro, the opposite is true. It can be seen that the spectra shape in the region of 2650–2350 cm⁻¹ is similar to that in the region of 1600–1300 cm⁻¹.

The shape of the spectra is related to the relative abundances of CO_3 groups in different sites and orientations, and is variable for different apatite crystals (e.g., comparing ROM with HAM). Therefore, the simple approach of using linear absorbance of main peaks (e.g., Wang et al. 2011) would not work well, and we used the integrated absorbance over each region to quantify the CO_2 concentration in apatite.

Calibration

The data in Table 2 are used to calibrate the FTIR technique for the analysis of CO_2 concentrations in apatite. The calibration is based on Beer's law describing the relationship between the CO_2 concentration and the FTIR absorbance as:

$$C = \alpha A_{\text{total}} / d \tag{2}$$

where *C* is the CO₂ concentration, A_{total} (= $A_{\text{E/c}} + 2A_{\text{ELe}}$ because there are two principal axes that are perpendicular to the **c**axis and one that is parallel to the **c**-axis) is the total integrated absorbance of the IR band in the wavenumber region of either 1600–1300 or 2650–2350 cm⁻¹, with the total mean summation over three crystallographic directions; *d* is the sample thickness; and α is a constant that contains the molar mass of CO₂, the density of apatite, and the integrated molar absorptivity in a specific spectrum region. The unit of A_{total} is the same as that of the wavenumber (cm⁻¹). The unit for *d* is chosen to be centimeters. The unit of *C* is chosen to be parts per million CO₂ (*C* = 1 means 1 ppm CO₂). Hence, the unit of α is ppm·cm².

Because of the multiple possible peaks due to variations in the substitution of the CO₃⁻ ion (Regnier et al. 1994; Fleet and Liu 2004; Fleet et al. 2004), we used the integrated area between the curve and the baseline as the characteristic to represent the CO₂ concentration in apatite. To obtain the baseline, a regression line was created that formed a tangent across the lowest point on either side of the bands defining the peaks in the wavenumber range (1600-1300 or 2650-2350 cm⁻¹) (Fig. 4). For the 1600-1300 cm⁻¹ region, the lowest points are near 1580 and 1360 cm⁻¹ (with some variability), respectively. For the 2650–2350 cm⁻¹ region, the lowest points are near 2580 and 2405 m⁻¹. Then the baseline was subtracted from the spectrum. The total area of all the bands in a region between the two tangential points was obtained by the numerical integration $\int Ad\omega$ from one tangential point to the other. This was done for both the $\mathbf{E} \perp \mathbf{c}$ spectrum to obtain $A_{\mathbf{E} \perp \mathbf{c}}$ (the integrated absorbance for $E \perp c$), and for the E//c spectrum to obtain $A_{E/c}$ (the integrated absorbance for E/c). Then A_{total} was calculated as $A_{E/e} + 2A_{E\perp e}$. The values of $A_{E\perp e}$, $A_{E/e}$, and A_{total} for all samples are listed in Table 2. For convenience, the integrated absorbance in the 1600–1300 cm⁻¹ region is referred to as A_{1440} , and that in the 2650–2350 cm⁻¹ region is referred to as A_{2500} . It can be seen that per sample thickness, A_{total} in the 2650–2350 cm⁻¹ region is about 0.8% of that in the 1300–1600 cm⁻¹ region.

Figure 5 illustrates the calibration curve for NRA (wt%) vs. the integrated area of the FTIR signal at wavenumbers 1600–1300 cm⁻¹ (Fig. 5a) and wavenumbers 2650–2350 cm⁻¹ (Fig. 5b). The data are fit by Equation 2 (i.e., the intercept is forced to be zero) to obtain α using the York algorithm (York 1969), but forcing the intercept to be zero. The Cerro sample is plotted but not used in the fitting because it has already been used in estimating the background for NRA. For the 1600–1300 cm⁻¹ region (v₃ bands), the fit value and 1 σ error for the slope α (Fig. 5a) is:

 $\alpha_{1600-1300} = 0.0756 \pm 0.0036 \text{ ppm} \cdot \text{cm}^2$, MSWD = 0.88. (2a)

For the 2650–2350 cm⁻¹ region, the fit (Fig. 5b) gives:

$$\alpha_{2650-2350} = 9.3 \pm 0.6 \text{ ppm} \cdot \text{cm}^2$$
, MSWD = 2.64. (2b)



FIGURE 4. Illustration of baseline fitting for a polarized FTIR spectra at the v_3 region (1600–1300 cm⁻¹) for **E**//c of a single apatite crystal ROM. (Color online.)

The mean square weighted deviation (MSWD) is larger than 1 for the second calibration, probably reflecting the difficulty of integrating the smaller peaks over a wide range of wavenumbers.

On the basis of 2σ reproducibility of the IR spectra, the detection limit of the integrated absorbance is on the order 1 cm⁻¹. Therefore, the detection limit for IR measurement of CO₂ in apatite, using the v₃ bands, can be sub-parts per million for 1 mm thick apatite samples. For 0.1 mm thick apatite crystals, the detection limit is about 8 ppm. That is, the v₃ bands are very sensitive for quantitative measurements of CO₂ in apatite using polarized IR on oriented crystals, but very thin wafers must be prepared when the CO₂ concentration is >0.1 wt%. On the other hand, for a 1 mm thick apatite crystal, the detection limit, using the bands in the 2650–2350 cm⁻¹ region, is about 100 ppm, and wt% level CO₂ concentrations can be measured using these bands.

H₂O concentration in the apatite samples

The IR data also provide information on the H_2O concentration using the calibration of Wang et al. (2011). All the spectra show a dominant peak at 3540 cm⁻¹ for OH in apatite, and hence a simple linear absorbance can be used to obtain the H_2O concentration. For HAM and Cerro, the peak at 3540 cm⁻¹ was oversaturated (the samples were not thin enough for the OH peak because no special effort was made to obtain OH concentrations). Wang et al. (2011) reported H_2O concentrations of 0.44 and 0.085 wt% for HAM and Cerro, respectively. For ROM and GEM, the H_2O concentrations obtained are shown in Table 2. It can be seen that ROM has the lowest H_2O but the highest CO₂ concentration among the samples. The GEM crystal used in this study has a lower H_2O concentration than the Gem3 and Gem4 crystals used in Wang et al. (2011).

DISCUSSION

The various peaks in the v₃ region

The substitution of CO_3^{2-} into the apatite crystal is complex (Elliott 1994; El Feki et al. 1999; Comodi and Liu 2000; Ivanova et al. 2001; Leventouri et al. 2001; Fleet and Liu 2003, 2004, 2005; Fleet et al. 2004; Antonakos et al. 2007; Koleva

and Petkova 2012). As summarized by Tacker (2008), CO₃²⁻ can substitute on the OH (or Cl or F) site (Type A) as well as on a PO₄³⁻ site (Type B). Type A substitutions occur in two different forms (Fleet et al. 2004). Using X-ray structural analysis, Fleet and Liu (2003) and Fleet et al. (2004) discovered an A-type substitution ordered along the apatite channel, which they labeled A1 because they also identified a second Type A substitution in a "stuffed" position, which may act as a charge balance for a B-type substitution (A2). The different Type A substitutions are reflected by different bands in the IR spectrum, with A1 bands at 1541 and 1449 $\rm cm^{-1}$ and A2 bands at 1563 and 1506 $\rm cm^{-1}$ (Fleet et al. 2004). The Type B substitutions also occur in two different forms. According to Tacker (2008), the B1 substitution is on one face of the PO₄ ion, while the B2 substitution is on a different face with resulting IR spectral bands at 1450 and 1409 cm⁻¹ (B1) and 1460 and 1427 cm⁻¹ (B2). One benefit of using polished single crystals and polarized spectra is the ability to pull out the details from these differing substitutions.

The utility of using polarized vectors parallel and perpendicular to the **c**-axis of the crystal is evident in Figure 6. When $\mathbf{E} \perp \mathbf{c}$,



FIGURE 5. Calibration line for IR measurements of CO_2 in apatite. The integrated IR absorbances are plotted on the horizontal axis. CO_2 concentrations determined by NRA are plotted on the vertical axis. The Cerro sample is plotted but not used in the fitting because it has already been used in estimating the background for NRA.



FIGURE 6. Polarized spectra illustrating the different peaks when $E \perp c$ and when E//c. A1 is the CO₂ substitution at the OH site and parallel to the **c**-axis of the crystal, A2 is perpendicular to the **c**-axis. B1 and B2 substitutions are on different faces of the PO₄ ion (see text). (Color online.)

the two major peaks are similar in height. When E//c, the band at 1428 cm⁻¹ is smaller in height relative to the band at 1455 cm⁻¹. This would imply that the band at 1428 cm⁻¹ (B2) is reflecting the activity of a substitution that is at a high angle to the **c**-axis and thus decreases when the energy is parallel to \mathbf{c} . The band at ~1406 cm⁻¹ has been identified as a B1 signal, which corresponds to "v3a" in Fleet et al. (2004), parallel to the c-axis. There are other subtle differences between the perpendicular and parallel spectra, with small shoulders appearing at the wavenumbers identified by Tacker (2008) as the four substitution sites. For example, the A1 substitution is stronger at 1455 cm⁻¹ (combined with the B2 substitution) and disappears at higher wavenumbers. The A1 substitution at these higher wavenumbers is evident only when E//c. The A2 substitution is visible only when $E \perp c$, which is consistent with integration in the columnar anion (F-, Cl⁻, OH⁻) perpendicular to the c-axis (Fleet et al. 2004; Tacker 2008). The IR bands for the B1 and B2 substitutions are at lower wavenumbers than those for the A1 and A2 substitutions.

In addition to being able to identify the multiple substitutions of CO_3^{2-} into apatite, which is aided by the use of spectra from both parallel and perpendicular energy bands, the integrated area of the entirety from these wavenumbers can be used to quantify the amount of CO_3^{2-} in the crystal using a calibration curve. An implicit assumption is that all the subspecies have the same integrated molar absorptivity. Note these are all subspecies of CO_{3}^{2-} , not chemically different species, such as CO_{3}^{2-} and CO_{2} , or OH and H₂O. Even for major species of the same element, the integrated molar absorptivities are similar. For example, Newman et al. (1986) estimated that for two major species of H (hydroxyl group OH- and neutral molecule H₂O) in rhyolitic glasses, the integrated molar absorptivity for OH is 1.67 times that for H₂O at the 3550 cm⁻¹ band, and 0.83 times that for H₂O at the 4000 cm⁻¹ band, and 1.16 times that for H₂O at the 7100 cm⁻¹ band. On the other hand, Leschik et al. (2004) cautioned that it is difficult to verify whether the results in Newman et al.

(1986) are due to differences in the molar absorptivities or due to structural variations, meaning that molar absorptivities of different H species may be roughly identical. Furthermore, it is expected that the integrated molar absorptivities of differently positioned or oriented CO_3^2 are more similar than the different chemical species of OH⁻ and H₂O. Hence, the assumption that the differently sited or oriented CO_3^2 subspecies have the same integrated molar absorptivity is reasonable. Considering that even the difference or similarity of the molar absorptivities at the same band region for major hydrous species, H₂O molecules and hydroxyl groups, is still not resolved, the resolution of possible small differences in the integrated molar absorptivities for different CO_3^2 subspecies must await future work.

Once the various substitutions of CO_3^{2-} into apatite are understood and the peak positions well quantified, it may be possible to deconvolute the various peaks in Figure 6 and use them to quantify the concentrations of each type and subtype of CO_3^{2-} substitution in apatite (Comodi and Liu 2000). The relative concentrations of the various subspecies may depend on temperature, pressure, melt composition, (such as the availability of P and F-OH-Cl), and other ambient conditions. If the controlling factors for the different substitutions are understood, the deconvoluted concentrations of the CO_3^{2-} subspecies might be able to provide rich information on apatite formation conditions.

Using unpolarized spectra to roughly estimate CO₂ concentrations in apatite

Because apatite is ubiquitous in both geological and biological systems, the use of these calibrations may be widespread. One advantage of calibrating for both lower ($1600-1300 \text{ cm}^{-1}$) and higher ($2650-2450 \text{ cm}^{-1}$) wavenumbers is that samples with a higher carbonate content do not have to be thinned to $<100 \text{ }\mu\text{m}$ to quantify the carbonate concentration.

Often apatite crystals are small or otherwise difficult to orient. For CO_3^{2-} in apatite, at least for the four samples studied in this work, the degree of anisotropy is not very large, with the ratio of $A_{\parallel e}/A_{\perp e}$ ranging from 0.47 to 2.73 (i.e., of order 1) for the 1600–1300 cm⁻¹ bands. This is in contrast to the OH band at 3540 cm⁻¹ in apatite, which is completely anisotropic, with the ratio of A_{ll}/A_{lc} approaching infinity. The smaller degree of anisotropy means that the CO₂ concentration in apatite may be roughly estimated using unpolarized spectra on unoriented apatite crystals. Such rough estimation can be achieved by measuring a couple of unpolarized spectra on random unoriented apatite sections, finding the average integrated absorbance, multiplying it by 3 to estimate the total integrated absorbance (A_{total}) , and then using Equation 2, and the appropriate value of α , to estimate the CO₂ concentration. Consider the range of $A_{\parallel e}/A_{\perp e}$ ratios to be from 0.47 to 2.73 as observed in this study for the 1600-1300 cm⁻¹ bands. If the ratio of $A_{\parallel c}/A_{\perp c} = 0.47$, then using a single unpolarized spectrum of a random section would lead to an estimated A_{total} to be 0.57 to 1.21 times that of the true A_{total} . If the ratio of $A_{//c}/A_{\perp c}$ = 2.73, then using a single unpolarized spectrum of a random section would lead to an estimated A_{total} to be 0.63 to 1.73 times that of the true A_{total} . Combining these results, the estimated A_{total} and CO₂ content would be 0.57 to 1.73 times the true values using one unpolarized IR spectrum on a random section. Measuring and averaging two or more randomly oriented sections would reduce the uncertainty significantly. Hence, using unpolarized IR spectra on random sections to estimate CO₂ concentration is expected to produce acceptable results.

IMPLICATIONS

Polarized IR spectra on oriented apatite sections not only provide a precise method to determine CO_2 concentrations in apatite, but also contain rich details about carbonate substitutions in apatite. Such details have the potential to elucidate the formation conditions. In addition, our data, using polarized IR spectra, show that carbonate in apatite displays only a weak degree of anisotropy. Hence, unpolarized IR spectra and KBr powder IR spectra may also be used to roughly estimate CO_2 concentrations in apatite. The ability to measure CO_2 concentrations in apatite is the first step toward the determination of the partition coefficient of CO_2 between apatite and various melts, and toward the inference of the CO_2 concentration in the melt from which apatite formed.

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