Mineralogical Magazine, August 2012, Vol. 76(4), pp. 903–911

Carbon dioxide in pollucite, a feldspathoid with the ideal composition $(Cs,Na)_{16}Al_{16}Si_{32}O_{96}\cdot nH_2O$

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[*Received 27 September 2011; Accepted 7 February 2012; Associate Editor: Roger Mitchell*]

ABSTRACT

We report a single-crystal Fourier-transform infrared (FTIR) study of a sample of pollucite from Maine, USA. Prior to our work, the sample had been characterized by single-crystal X-ray diffraction, neutron diffraction and electron-probe microanalysis. It is cubic $Ia\bar{3}d$, with a crystal-chemical formula $Na_{1.93}(Cs_{10.48}Rb_{0.31}K_{0.04})_{\Sigma=10.83}(Al_{14.45}Si_{33.97})_{\Sigma=48.42}O_{96}\cdot 3.92H_2O$, and an H_2O content, determined by thermogravimetric analysis, of 1.6 wt.%. The single-crystal FTIR spectrum has a doublet of intense bands at 3670 and 3589 cm^{-1}, which are assigned to the ν_3 and ν_1 stretching modes of the H_2O molecule, respectively. A very intense and sharp peak at 1620 cm^{-1} is assigned to the ν_2 bending vibration. In the near-infrared region there is a relatively intense peak at 5270 cm^{-1}, which is assigned to a combination ($\nu_2 + \nu_3$) mode of H_2O, and a weak but well defined doublet at 7118 and 6831 cm^{-1}, which is assigned to the first overtones of the fundamental stretching modes. A relatively weak but extremely sharp peak at 2348 cm^{-1} shows that the pollucite contains CO_2 molecules in structural cavities. Mapping the sample using FTIR indicates that both H_2O and CO_2 are homogeneously distributed. Secondary ion mass spectrometry yielded an average CO_2 content of 0.09±0.02 wt.%. On the basis of this value, we determined the integrated molar absorption coefficient for the spectroscopic analysis of CO_2 in pollucite to be $\varepsilon_{iCO_2} = 11{,}000 \pm 3000$ l mol^{-1} cm^{-2}; the linear molar absorption coefficient for the same integration range is $\varepsilon_{lCO_2} = 1600 \pm 500$ l mol^{-1} cm^{-1}.

KEYWORDS: pollucite, single-crystal FTIR spectroscopy, H_2O and CO_2, molar absorption coefficients.

Introduction

POLLUCITE is a member of the 'analcime group' of feldspathoids, which includes natural and synthetic compounds; the most common natural species are analcime ($Na_{16}Al_{16}Si_{32}O_{96}\cdot 16H_2O$), leucite ($K_{16}Al_{16}Si_{32}O_{96}$) and wairakite ($Ca_8Al_{16}Si_{32}O_{96}\cdot 16H_2O$) (Gottardi and Galli, 1985; Armbruster and Gunter, 2001; Baerlocher *et al*., 2001; Gatta *et al*., 2006, 2008*a*, 2009*a*,*b*). Leucite is the only (nominally) anhydrous species in this series, although Balassone *et al*. (2006) and Della Ventura *et al*. (2008) have shown recently that leucite can trap a few tenths of a percent of H_2O by weight.

Pollucite has applications as a ceramic material, particularly in nuclear technology (e.g. Kobayashi *et al*., 1997, 2006; Yanase *et al*., 1997, Gatta *et al*., 2008*b*, 2009*a*,*b*) due to its ability to host and retain large amounts of Cs (up to ~30 wt.% Cs_2O).

Carbon dioxide, which is generated by the combustion of fossil fuels, is by far the most abundant greenhouse gas and reducing its concentration in the atmosphere is a primary

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DOI: 10.1180/minmag.2012.076.4.07

environmental concern. Techniques that have been proposed to reduce the amount of CO_2 in the atmosphere include (1) forestation; (2) aquifer storage or deep sea storage; and (3) mineral carbonation, in which CO_2 is reacted with minerals to form solid carbonates. This last method of sequestration is expensive but it is considered to be the most permanent solution as carbonates are stable over geological time periods (millions of years), rather than the hundreds to thousands of years that are expected for the first two forms of sequestration.

In recent years, increasing attention has been devoted to the development of technologies that use silicate minerals as an alternative to carbonates. Many minerals contain carbon as a major to trace constituent, but in most of them the carbon is present in CO_3^{2-} ions in the structure; very few minerals contain structural CO_2. Those that do include beryl (Wood and Nassau, 1967, 1968; Aines and Rossman, 1984) and cordierite (Goldman *et al*., 1977; Aines and Rossman, 1984; Kolesov and Geiger, 2000; Komenko and Langer, 2005; Della Ventura *et al*., 2009), two minerals which have structures that are characterized by open channels running along [001]; carbon dioxide, H_2O and extraframework cations such as Na, Li or Cs can be hosted by these channels. Recent studies have shown that other silicates are able to host molecular CO_2, these include a few clay-like minerals (Zhang *et al*., 2005), some forms of hydrous silica (Kolesov and Geiger, 2003), several microporous (zeolite-type) feldspathoids (Della Ventura *et al*., 2005, 2007; Bellatreccia *et al*., 2009), and the recently described Cs-bearing mineral capranicaite (Callegari *et al*., 2011).

In this study we show that pollucite is able to trap carbon dioxide in voids within its structure. The sample that was examined had been characterized by single-crystal X-ray diffraction, neutron diffraction, electron microprobe analysis (EPMA) in wavelength-dispersive spectrometry mode (WDS), thermogravimetric analysis (TGA) and FTIR spectroscopy by Gatta *et al*. (2009*a*). Briefly, it is cubic $Ia\bar{3}d$, and the crystal-chemical formula is $Na_{1.93}(Cs_{10.48}Rb_{0.31}K_{0.04})_{\Sigma=10.83}(Al_{14.45}Si_{33.97})_{\Sigma=48.42}O_{96}\cdot 3.92H_2O$; the H_2O content, determined by TGA (in agreement with the structure refinement), is 1.6 wt.%. Structural studies by neutron diffraction revealed a disordered distribution of the water molecules in the [111] 6-membered ring channels; the water molecules are involved in weak hydrogen bonding with the surrounding oxygen atoms, which accounts for the relatively high thermal stability of the mineral even in its dehydrated state (Gatta *et al*., 2009*a*,*b* and references therein).

The single-crystal FTIR spectrum of pollucite

Single-crystal micro-FTIR spectra were collected using a Bruker Hyperion 3000 microscope equipped with a nitrogen-cooled mercury cadmium telluride (MCT-A) detector and a ZnSe gold-wire-grid IR polarizer. The nominal resolution is 4 cm^{-1} and final spectra are the average of 128 scans. Double polished sections were made from two crystal fragments. The thicker section (430 μm) was used to collect the spectrum for CO_2 and the NIR region, where the combination and overtone modes of water are found. The thinner section (55 μm) was used to collect the H_2O spectrum in the fundamental stretching region (see below). The unpolarized single-crystal FTIR spectrum of pollucite is shown in Fig. 1. There is (Fig. 1*a*) a doublet of intense bands at 3670 and 3589 cm^{-1}, which are assigned to the antisymmetric (ν_3) and symmetric (ν_1) stretching vibrations of the H_2O molecule, respectively (Gatta *et al*., 2009*a*). A very intense and sharp peak at 1620 cm^{-1} is assigned to the H_2O bending vibration (ν_2). A very weak band at 3210 cm^{-1} is assigned to the first overtone of the H_2O bending mode ($2\nu_2$). The relatively intense peak at 5270 cm^{-1} (Fig. 1*b*) is assigned to a combination mode (ν_2 bending + ν_3 antisymmetric stretching) of H_2O, and the weak but well defined doublet at 7118 and 6831 cm^{-1} is assigned to the first overtones of the fundamental stretching modes, $2\nu_3$ and $2\nu_1$, respectively. The absence of bands in the 4000−4500 cm^{-1} range indicates that hydrogen is only present in molecular H_2O.

The relatively weak and extremely sharp peak at 2348 cm^{-1} (Fig. 1*a*) is assigned to the antisymmetric ν_3 stretching vibration of CO_2 molecules, which are enclosed in structural voids in pollucite, as has been reported in similar feldspathoids (Della Ventura *et al*., 2007, 2008; Bellatreccia *et al*., 2009). The CO_2 stretching frequency is remarkably constant in all these materials, suggesting a very similar nearest-neighbouring environment in the vicinity of the carbon dioxide molecule. Polarized measurements showed that there was no change

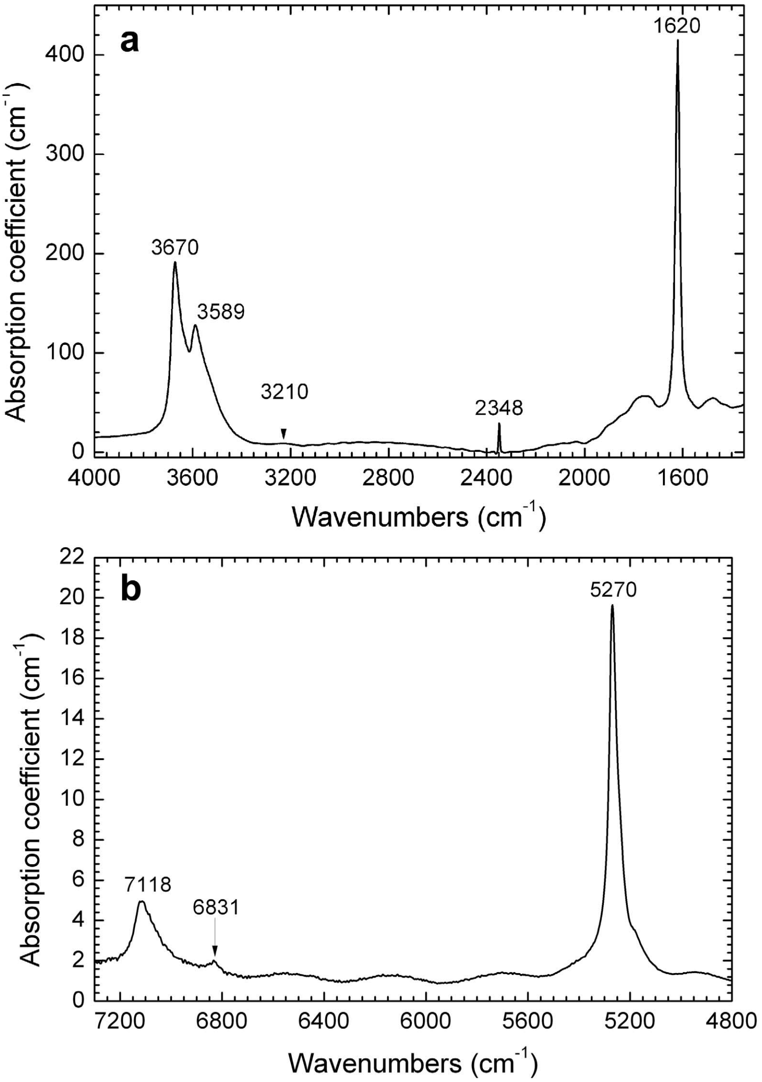

FIG. 1. Single-crystal FTIR spectra of the pollucite samples, (*a*) sample thickness 55 μm; (*b*) sample thickness 430 μm.

in the peak intensities when the electrical vector was rotated with respect the crystal.

The analysis of H and C by SIMS

Secondary ion mass spectrometry (SIMS) using a Cameca IMS4f ion microprobe at EMMAC (University of Edinburgh) was used to make independent analyses of the H and C content of the pollucite crystal. The analytical protocol was described in Harley and Carrington (2001), Thompson *et al.* (2001) and Harley *et al.* (2002). A 2.58 cm diameter analysis block incorporating cordierite standards 49528 and 81/90 (Harley *et al.*, 2002), reference Fe-richer cordierite BB3, and pollucite, was prepared, gold-coated, and inserted into the IMS4f sample change chamber for overnight pump-down prior to SIMS analysis. The negative secondary ions ^{1}H, ^{12}C and ^{28}Si were measured at an energy offset of 75 V, in an energy window of 19 eV, with 4500 V secondary beam voltage, and 8 nA and 10 kV for the primary O^- ion beam. In these conditions, the primary ion beam sputters an ellipsoidal analysis pit with a long axis of 25–30 μm and maximum depth of 3 μm. All analyses were made with a 3 minute burn-in time followed by 20 cycles of 5 s counts for each isotope. The mean isotopic ratios of $^1H/^{28}Si$ and $^{12}C/^{28}Si$ in the last 10 cycles were used to calculate the final results to avoid surface contamination. Analyses, expressed as isotopic ratios of $^1H/^{28}Si$ and $^{12}C/^{28}Si$, were converted to wt.% H_2O or CO_2 by comparison with the calibration lines produced by two standards, which were measured several times during the analytical session.

The calibration equations, fitted using linear least-squares methods to the cordierite analyses, are as follows: (1) H_2O (wt.%) = $7.26(^1H/^{28}Si) - 0.029$; and (2) CO_2 (wt.%) = $83.8(^{12}C/^{28}Si) - 0.026$. These yielded cordierite volatile contents of H_2O = 1.56±0.09 wt.% and CO_2 = 0.66±0.04 wt.% for standard AMNH, and H_2O = 0.80±0.06 wt.% and CO_2 = 1.31±0.12 wt.% for 81/90, which are consistent with accepted values. The estimated intercepts, at 0.029 wt.% apparent H_2O and 0.026 wt.% apparent CO_2, are consistent with previous measurements of backgrounds at the Edinburgh SIMS (Harley *et al.*, 2002), and these background values are also accounted for in the calibrations.

On the basis of five SIMS spot analyses on one grain, the pollucite sample appears to be homogeneous in terms of measured H/Si and C/Si ratios. To apply the cordierite calibration lines to the estimation of H_2O and CO_2 in pollucite, the calibrations have to be corrected for the differing SiO_2 contents of the cordierite standards (49.6 wt.% SiO_2) and pollucite (44.3 wt.% SiO_2), and then corrected to account for differences in the relative ion yields of H, C and Si in the different mineral matrices. Using the cordierite H_2O and CO_2 calibration lines and correcting for the difference in SiO_2 content yields apparent volatile contents of H_2O = 0.78±0.02 wt.% and CO_2 = 0.042±0.01 wt.%. These values are only indicative as they are not corrected for differences in the relative ion yields of H and C relative to Si in pollucite compared to cordierite. The ion counts for Si in pollucite were significantly higher (per wt.% SiO_2) than for cordierite, indicating that the relative ion yields for H and C in pollucite must be significantly different to those of cordierite. To correct for this, an independent estimate of the H_2O content of the pollucite is required. Thermogravimetric measurements and structural refinements by X-ray diffraction and neutron diffraction indicate that the pollucite contains 1.6 wt.% H_2O. If this value is used, a relative H/Si ion yield correction factor of 2.05 is required to bring the SIMS H_2O data into agreement with the true value (SIMS revised H_2O = 1.60±0.04 wt.%). Applying the same correction factor for the relative ion yield for C/Si, which assumes similar behaviour for H and C relative to Si in the pollucite matrix, yields an average CO_2 content of 0.09±0.02 wt.% for pollucite.

Calibration of a quantitative FTIR analysis of hydrogen and carbon in pollucite

The spatial distribution of carbon dioxide in the 430 μm thick double-polished sample was mapped using a Bruker Hyperion 3000 microscope with a computer-controlled stage. Spectra at a resolution of 4 cm^{-1} were collected using a 50 × 50 μm pinhole; the sample was displaced in steps of 50 μm along the *x* and *y* axes. As its absorbance is strong (see below), the distribution of H_2O was studied using the 55 μm thick double-polished sample with a 64 × 64 pixel focal-plane-array (FPA) detector and a 15 × objective. The IR images were acquired in the wavelength range 900–3900 cm^{-1} at a nominal resolution of 8 cm^{-1}. In these conditions, a single FPA image covers an area of 170 × 170 μm at a spatial resolution of 3–5 μm (Della Ventura *et al.*, 2010). Integration of the absorbance in the 2485–2250 cm^{-1} range for CO_2 (Fig. 2*a*) and in the 1710–1540 cm^{-1} range for H_2O (Fig. 2*b*) shows that both are homogeneously distributed. This is essential in calibrating the molar absorption coefficients (ε) required for quantitative analyses of these molecular groups in pollucite. Recent studies of a variety of microporous minerals including cordierite (Della Ventura *et al.*, 2009); leucite (Della Ventura *et al.*, 2008); cancrinite (Della Ventura *et al.*, 2007, 2010); and haüyne, nosean and lazurite (Bellatreccia *et al.*, 2009) have shown that both H_2O and CO_2 can be significantly zoned within crystals, due to geological processes such as alteration and fracturing, which occur after crystal formation.

According to the Beer–Lambert law, the concentration of a molecule in a mineral is related to the infrared absorbance via the molar absorption coefficient, ε, which is matrix

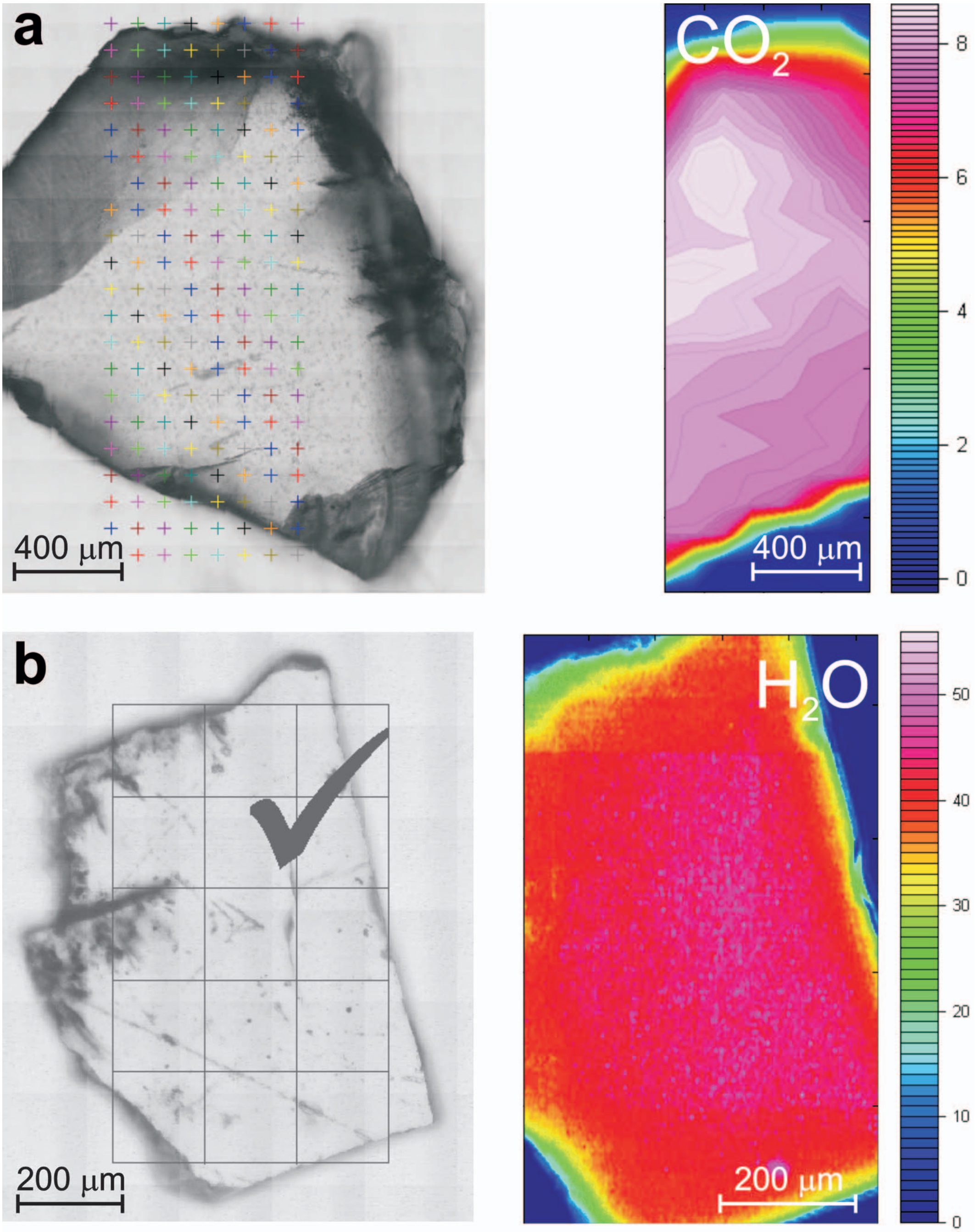

FIG. 2. (*a*) A CO_2 map of the sample shown in Fig. 1*b* using an integration in the range 2485–2250 cm^{-1}. The optical image of the crystal on the left shows the measured grid; the FTIR map is on the right. (*b*) An FPA image of the H_2O distribution in the sample shown in Fig. 1*a* using an integration in the range 1710–1540 cm^{-1}. The optical image on the left shows the area that was scanned; the FTIR image is on the right.

dependent (see Libowitzky and Rossman, 1996 for a detailed discussion of the theory of quantitative FTIR analysis in minerals). To calibrate the molar absorption coefficient, the concentration of the absorber in the mineral can either be determined by a different analytical method or it can be extrapolated from working curves such as those established by Libowitzky and Rossman (1997) for H_2O. Although a relatively large corpus of ε_{H_2O} data is available for minerals (see Libowitzky and Rossman, 1997 for a compilation) and glasses (Stolper, 1982; Ihinger *et al*., 1994; Mandeville *et al*., 2002), very few ε coefficients are available for the quantitative analysis of CO_2 in geological materials. Most of these calibrations are for natural and synthetic volcanic glasses (Fine and Stolper, 1985; Blank *et al*., 1993; Morizet *et al*. 2002; Behrens *et al*., 2004). For minerals, we know of only one ε_{CO_2}, based on single-crystal polarized-light data, for cordierite (Della Ventura *et al*., 2009). This coefficient was determined on a single sample which seemed to be relatively homogeneous with respect to CO_2, however further work on a larger set of specimens with different provenance (G. Della Ventura, unpublished data) shows that it will have to be revised.

For the pollucite samples studied here, the ε_{H_2O} and ε_{CO_2} values have been calibrated using the SIMS data to produce the following equations: $\varepsilon_{CO_2} = (4.401A)/(ctD)$, where A is the measured absorbance (a dimensionless value if it is a linear absorbance, A_l, and a value expressed in cm^{-1} if it is an integrated absorbance, A_i), c is the CO_2 concentration (in wt.%), t is the thickness (in cm), D is the density (in g cm^{-3}), and the factor 4.401 is required to convert the CO_2 concentration from mol l^{-1} to wt.%. Using a density of 2.857 g cm^{-3} (from the chemical and structural data of Gatta *et al*., 2009*a*) and integrating the intensity of the 2348 cm^{-1} band (Table 1), we obtain ε_{iCO_2} = 11,000±3000 l mol^{-1} cm^{-2}. The calculated linear molar absorption coefficient for the same integration range is ε_{lCO_2} = 1600±500 l mol^{-1} cm^{-1}.

The data reduction for H_2O is complicated by the fact that water is a major constituent in pollucite (and in many of the other hydrous minerals that are of interest in materials science). In these cases, the single-crystal spectra collected in the principal H_2O-stretching MIR region (4000−3000 cm^{-1}), have absorption bands that are systematically in error, for thicknesses that exceed few tenths of a μm. In these cases the preparation of self-supporting oriented sections suitable for polarized measurements is critical, and as a result very few ε_{H_2O} values have been reported for zeolite-like minerals. In this study two double-polished sections were prepared and calibrated using ε_{H_2O} coefficients based on the intensity of the fundamental, the combination and the overtone modes. In the NIR region, the H_2O absorption bands are much less intense (Fig. 1*b*), and thicker sections, which are much easier to prepare, can be used. If thicker sections can be used, the error introduced in the measurement of the thickness is greatly reduced. In addition, the background in the NIR region is typically linear and thus the peak area can be integrated with greater accuracy and reproducibility. As ε is wavenumber dependent (Paterson, 1982; Libowitzky and Rossman, 1997), different values are expected in the different spectral ranges. For H_2O, the molar absorption coefficient is $\varepsilon_{H_2O} = (1.802A)/(ctD)$ where the factor 1.802 is needed for the conversion of the H_2O concentration from mol l^{-1} to wt.%; substituting c_{H_2O} (wt.%) from TG and structure refinement, we obtain, by integrating the total area of the unresolved $\nu_1 + \nu_3$ stretching absorption (Table 1), ε_{iH_2O} = 28,000±4000 l mol^{-1} cm^{-2}. The linear coefficient for the ν_3 mode is ε_{lH_2O} = 220±30 l mol^{-1} cm^{-1}. These values were determined using the 55 μm thick slice. If the whole area of the ($\nu_2 + \nu_3$) combination band at 5270 cm^{-1} (on a 430 μm thick slice) is used, ε_{iH_2O} = 700±100 l mol^{-1} cm^{-2}. The linear coefficient for the same integration range is: ε_{lH_2O} = 11±2 l mol^{-1} cm^{-1}. In each case the measured absorbance (A) has been multiplied by three because the mineral is isometric (Libowitzky and Rossman, 1996). The density value used in this work was calculated based on the structural data and H_2O from TG (Gatta *et al*., 2009*a*). The final molar absorption coefficients are summarized in Table 1.

Discussion

The molar absorption coefficients calibrated in this multi-methodological study (Table 1), are compared with values reported for similar substances in Table 2. For H_2O, the only value available for a matrix similar to pollucite is that reported by Libowitzky and Rossman (1997) for analcime, ε_{iH_2O} = 36,000 l mol^{-1} cm^{-2}). This value is 30% higher than the average value we calculated based on the TGA data. However, whereas our ε_{iH_2O} for pollucite is based on

TABLE 1. Quantitative data for the IR calibration of the CO_2 and H_2O contents in pollucite.

	Absorption (cm^{-1})	A_l/t (cm^{-1})	ε_l ($l\ mol^{-1}\ cm^{-1}$)	A_i/t (cm^{-2})	ε_i ($l\ mol^{-1}\ cm^{-2}$)
CO_2	2349 (ν_3)	89	1600±500	647	11,000±3,000
H_2O	3589 (ν_1)	360	140±20	–	–
	3670 (ν_3)	549	220±30	–	–
	3589 + 3670 ($\nu_3 + \nu_1$)	–	–	71,737	28,000±4000
	3601*	–	–		37,500
	5270 ($\nu_3 + \nu_2$)	28	11±2	1696	700±100

* Calculated following Libowitzky and Rossman (1997).

analysed H_2O contents, the value reported by Libowitzky and Rossman (1997) was obtained using a stoichiometric H_2O content. The difference might also be explained by considering the effect of Cs–Na substitution in these minerals. It should also been noted that the ε_{iH_2O} obtained for pollucite is also out of the frequency–ε_{iH_2O} relationship of Libowitzky and Rossman (1997), $\varepsilon_i = 246.6(3753 - \nu)$ (where ν is the mean wavenumber of the OH stretching band, in the present case $\nu = 3601\ cm^{-1}$). Using this equation we obtain $\varepsilon_{iH_2O} = 37{,}500\ l\ mol^{-1}\ cm^{-2}$ (Table 2), which is significantly different from our value of $28{,}000 \pm 4000\ l\ mol^{-1}\ cm^{-2}$. Comparison with the ε_{iH_2O} values which have been reported for feldspars is difficult, as these values span a very large range (Table 2).

For CO_2, as discussed above, the only possible comparison is with aluminosilicate glasses with similar compositions. Again, there are large differences in both the linear coefficients and the integrated ones (Table 2).

The neutron diffraction based structure refinement of Gatta *et al.* (2009*a*) shows that there is a disordered distribution of the H_2O molecules in the [111]-channels of the pollucite framework, with several equivalent and mutually exclusive configurations. Using topological considerations, the authors suggested a 'static disorder' configuration of the molecules, rather than a 'dynamic

TABLE 2. A comparison of the molar absorption coefficients of pollucite with similar substances.

Material	Band (cm^{-1})	ε_l ($l\ mol^{-1}\ cm^{-1}$)	ε_i ($l\ mol^{-1} cm^{-2}$)	Reference
CO_2				
Pollucite	2348	1600±500	11,000±3000	This paper
Rhyolitic glass	2349	1214±78	–	Behrens *et al.* (2004)
Rhyolitic glass	–	1066	–	Blank *et al.* (1993)
Albitic glass	2352	945±45	25,200±1200	Fine and Stolper (1985)
Phonolitic glass	2351	890±250		Morizet *et al.* (2002)
H_2O				
Pollucite	3589 + 3670	–	28,000±4000	This paper
Pollucite	3601*	–	37,500	This paper
Analcime	3552	240	36,000	Libowitzky and Rossman (1997)
Nepheline	3559	27	4515	Beran and Rossman (1989)
Feldspars	2900–3600	–	107,000±5000	Johnson and Rossman (2003)

* Calculated following Libowitzky and Rossman (1997).

disorder', as: (1) the point symmetry of H_2O molecules (i.e. 2*mm*) differs from that along the [111] of the cubic structure (i.e. the $\bar{3}$-fold axis), with the molecules likely to be disordered with partial site occupancy (and a local violation of the symmetry); and (2) the small 'free diameter' of the 6-membered ring channel along [111] may hinder a dynamic disorder of the H_2O molecules. To date, there are no structural data about the orientation of CO_2 in pollucite channels. If CO_2 and H_2O molecules lie in the channels along [111], two possible orientations of CO_2 might be expected: the molecule might be oriented with C and O lying on the $\bar{3}$-fold axis, or with C lying on the triad and O on a plane perpendicular to [111]. The latter leads to a disordered distribution of the molecules along the channel, as the point symmetry of CO_2 (i.e. ∞/mm) differs from that of the [111] axis.

Acknowledgements

Critical review by A. Beran (Vienna) and G. Balassone helped to improve the clarity of the manuscript. Financial support was provided by COFIN 2009 to GDV. This manuscript is dedicated to Mark Welch, in recognition of his important contributions to mineral spectroscopy.

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