SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

Quantification of CO$_2$ 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 CO$_2$ concentrations in apatite. The total absorbance ($A_{\text{total}}$) was calculated from the integrated area under the curve in a given polarized spectral region. Then $A_{\text{total}}$ is calculated as $A_{E//} + 2A_{E\perp}$. The calibration has been carried out for two wavenumber regions, one with high sensitivity and the other applicable to apatite with high CO$_2$ concentrations. The first calibration is for the fundamental asymmetric CO$_3^{2–}$ stretching at wavenumbers of 1600–1300 cm$^{-1}$, and the CO$_2$ 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 CO$_2$ concentrations in apatite, down to parts per million level. The second calibration is for the CO$_3^{2–}$ bands at wavenumbers of 2650–2350 cm$^{-1}$, and the CO$_2$ concentration in parts per million is $(9.3 \pm 0.6) A_{\text{total}}/d$ where $d$ is sample thickness in centimeters. These bands are weak and hence are useful for measuring high CO$_2$ concentrations in apatite. For rough estimation, unpolarized IR spectra may be used by estimating $A_{\text{total}} = 3A_{\text{unpol}}$, where $A_{\text{unpol}}$ 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 $M_x(ZO_4)_yX$, in which the M site is dominated by Ca$^{2+}$, but can also contain Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Na$^+$, and light rare earth elements. The Z site is dominantly P$^{5+}$, but can also contain As$^{3+}$, Si$^{4+}$, C$^{4+}$, and S$^{6+}$, 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, CO$_2$ concentration in apatite may be able to indicate the CO$_2$ concentration or fugacity in terrestrial-lunar-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 CO$_2$ in apatite. The focus of this study is on the quantification of CO$_2$ 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 CO$_3^{2–}$ 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 PO$_4^{3–}$ 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 e-axis of apatite (called type A1), or such that the bisector is perpendicular to the e-axis (called type A2) (Tacker 2008). Based on IR spectra, Tacker (2008) also identified two different sites of CO$_3^{2–}$ in B site, and interpreted them to be due to alignment of the 3 O atoms of CO$_3^{2–}$ onto O atoms of the different triangular faces of the PO$_4^{3–}$ tetrahedron (see also Ivanova et al. 2001). Charge balance can be achieved in several ways, such as one CO$_3^{2–}$ substituting for two OH$^–$, or CO$_3^{2–}$ plus Na$^+$ substituting for PO$_4^{3–}$ plus Ca$^{2+}$, 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