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LETTER

Hydrogen-carbonate ion in synthetic high-pressure apatite

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ABSTRACT

The hydrogen-carbonate ion [$(HCO_3)^-$] has been detected by Fourier transform infrared (FTIR) spectroscopy in the *c*-axis structural channel of Na-bearing type A-B carbonate apatite synthesized under conditions of high P (0.1–1 GPa), T (800–1350 °C), and $p(CO_2)$, and accounts for up to one-third of the total complement of channel carbonate. The hydrogen-carbonate ion is only loosely bound in the apatite channel, and breaks down on aging at room temperature. Volatile decomposition products are lost from the carbonate apatite structure, with CO_2 more mobile than H_2O. The mobility of small volatile molecules points to a possible role for the apatite channel in mediating acid-base reactions in restricted surficial environments and biological systems.

Keywords: Apatite, hydrogen-carbonate ion, high-pressure synthesis, FTIR spectra, CO_2 mobility, H_2O mobility

INTRODUCTION

A prominent feature of the apatite structure (e.g., Hughes and Rakovan 2002) is the *c*-axis channel, which accommodates the X anion component of the ideal structural formula $M1_4M2_6(ZO_4)_6X_2$ (White et al. 2005) within tri-cluster rings of M2 cations (e.g., Fig. 1). Channel (X) substituents in natural apatites are essentially restricted to F^-, $(OH)^-$, and Cl^-, with $(CO_3)^{2-}$, vacancies, H_2O, and O^{2-} of lesser importance, although a wide variety of monovalent and divalent anions, as well as organic molecules, have been inserted in the *c*-axis channel of synthetic apatite-type compounds (e.g., Pan and Fleet 2002; and more recently formate in Ca-deficient apatite; Wilson et al. 2003). The accommodation of the carbonate ion in hydroxyl-apatite [$Ca_{10}(PO_4)_6(OH)_2$] has been studied extensively for a number of years (e.g., LeGeros et al. 1969; Bonel 1972; Elliott 2002; Wilson et al. 2004; Fleet and Liu 2007), because minor amounts of carbonate and sodium are important, and possibly essential, constituents of the hydroxyl-apatite of dental enamel and bone. Carbonate-bearing hydroxyl-apatite is herewith abbreviated as CAP: also, carbonate is labeled type A when present in the apatite channel and type B when substituting for the phosphate group. Recent study of a suite of Na-bearing type A-B CAP, of general composition $Ca_{10-y}Na_y[(PO_4)_{6-y}(CO_3)_y][(OH)_{2-2x}(CO_3)_x]$, $x \approx y \rightarrow 1.0$, demonstrated that the Na^+ and channel and phosphate carbonate ion defects were coupled locally by charge and spatial compensation requirements (Fleet and Liu 2007). Also, biological apatite was reinterpreted as Na-bearing type A-B CAP with channel carbonate up to 50% of total carbonate. We presently report hydrogen carbonate (bicarbonate) in the apatite channel of Na-bearing type A-B CAP synthesized under high pressure from carbonate-rich bulk compositions. The hydrogen-carbonate ion has previously been reported as an anion defect in biogenic (e.g., Bischoff et al. 1985) and room-temperature laboratory-precipitated (Feng et al. 2006) calcite. Hydrogen carbonate associated with bone is the most important agent for neutralizing acidity in the body (e.g., Bushinsky et al. 2002), but has not yet been identified as an intracrystalline component of the hydroxyl-apatite nanocrystals in bone.

EXPERIMENTAL METHODS

Sodium-bearing CAP was synthesized at 1 GPa and 800–1350 °C using a Depths of the Earth Company Quickpress piston-cylinder device with a ¾ inch assembly and platinum capsules and at 0.1 GPa and 800 °C using a cold-seal hydrothermal vessel and gold capsules. Starting compositions were prepared from analytical grade $CaHPO_4$, Na_2CO_3, $Ca(OH)_2$, and $CaCO_3$. These salts were mixed in stoichiometric proportions corresponding to a nominally ideal type B carbonate apatite formula of $Ca_{10-y}Na_y[(PO_4)_{6-y}(CO_3)_y](OH)_2$ with $y = 2$ or 3 and a fluid phase in excess. All experiments were quenched at pressure by switching off the furnaces. Further experimental details are given in Fleet and Liu (2007).

The products were characterized by optical microscopy, powder X-ray diffraction (XRD; Rigaku D/MAX-B system; Co$K\alpha$ X-radiation), and Fourier transform infrared (FTIR) spectroscopy (Nicolet Nexus 670 FTIR spectrometer). Infrared spectra were obtained for both hand-separated CAP crystals and bulk samples using KBr pellets (Figs. 2 and 3). We also collected a spectrum for sodium hydrogen carbonate (Fig. 2) using analytical grade $NaHCO_3$ (synthetic nahcolite). About 10 mg of sample was first ground to a powder, then diluted in an agate mortar with 1 g of KBr and ground under an infrared heating lamp to a grain size of <25 μm; transparent pellets were made under vacuum at a pressure of 200 kg/cm².

RESULTS AND DISCUSSION

The present FTIR spectrum of sodium hydrogen carbonate (Fig. 2) corresponds closely to the IR spectrum in White (1974; his Fig. 12.16), taking into account the much greater band widths in the earlier study. Our interpretation and band assignments

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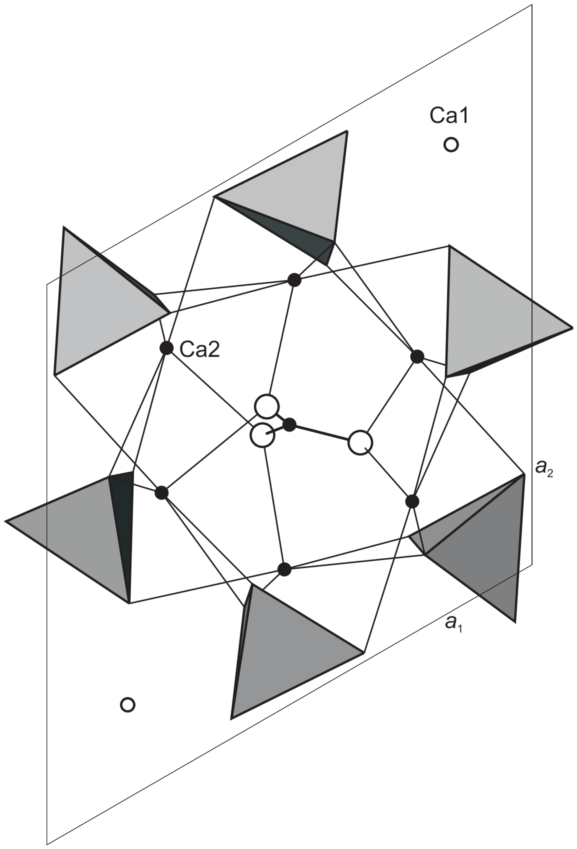

FIGURE 1. Structure of type A carbonate apatite showing location of $(CO_3)^{2-}$ ion in apatite channel, centered at $z = 1/2$ and bonded to triclusters of Ca2 (M2) cations at $z = 1/4$, $3/4$; note that precise location and orientation of carbonate ion are dependent on bulk composition.

follow Novak et al. (1963), Ross (1972), and White (1974). The structure of sodium hydrogen carbonate is based on infinite chains of cross-linked planar $(HCO_3)^-$ ions (e.g., Sharma 1965). The hydroxyl oxygen is O3, and the hydrogen bond is to O2. C-O3 is essentially a single bond, but C-O2 is only marginally longer than the formally double-bonded C-O1. A recent unpublished X-ray refinement of this structure in our laboratory has resulted in the following bond distances (Å): C-O1 = 1.255, C-O2 = 1.262, C-O3 = 1.338, H-O3 = 1.00, and H-···O2 = 1.60. Because the hydrogen-carbonate ion in $NaHCO_3$ has two strongly bonded C-O distances, it can be considered to have the same molecular structure as $CO_2(OH)^-$. This greatly simplifies assignment of the internal vibration modes since the spectrum of CO_2 can be used as a template (Ross 1972). Based on these assumptions, the $NaHCO_3$ spectrum of Figure 2 indicates that: $\nu\nu_4$ and $\nu\nu_2$ are C-O antisymmetric and symmetric stretching, respectively, $\nu\nu_1$ is C-OH symmetric stretching, and $\nu\nu_6$ is CO_3 out-of-plane bending; a weak (but apparently characteristic) band at 1696 cm^{-1}, as well as $\nu\nu_3$ and $\nu\nu_5$, are left unassigned. The strong H-···O2 hydrogen bonding displaces the OH stretching mode to lower wavenumbers and, with delocalization of the H atom, results in a prominent broad band at 2750–2250 cm^{-1}. The C-O-H in-plane bending band occurs at about 1300 cm^{-1} and is the dominant feature of the $NaHCO_3$ IR spectrum; the C-O-H out-of-plane bending band occurs at 1000 cm^{-1} and is also relatively strong.

The FTIR spectrum for hand-separated crystals of carbonate apatite from experiment LM003 (also reported in Fig. 2) includes contributions from: (1) hydroxyl ions (X) in the apatite channel, (2) types A and B carbonate, and (3) the phosphate group. This spectrum is reproduced from Fleet and Liu (2007) who noted additional bands (marked by asterisks in Fig. 2) consistent with minor amounts of the hydrogen-carbonate ion and, in the absence of a more thorough investigation, tentatively attributed them to admixed sodium hydrogen carbonate. Hydrogen-carbonate ion bonded to Na is readily identified in this spectrum by the good agreement with the reference FTIR spectrum for $NaHCO_3$, specifically with the bands for $\nu\nu_4$, $\nu\nu_6$, $\nu\nu_5$, and $\nu\nu_3$, and the C-O-H in-plane bending band at 1309 cm^{-1}: note that $\nu\nu_2$ and $\nu\nu_1$ are obscured by bands for antisymmetric stretching of carbonate and phosphate ions in CAP, respectively. The C-O-H in-plane bending band for this hydrogen-carbonate-bearing CAP is greatly reduced in intensity relative to the C-O antisymmetric stretching bands at 1658–1619 cm^{-1}, but is nevertheless more useful than the latter for characterizing small amounts of hydrogen carbonate due to possible interference from bands for in-plane bending of molecular water in the apatite channel near 1644 cm^{-1}.

Powder XRD patterns indicated that the bulk products for all of the experiments yielding hydrogen-carbonate-bearing CAP were essentially single phase apatite (Table 1[1]); $NaHCO_3$ (synthetic nahcolite) was not present, even at the minor-trace level of abundance. Hydrogen-carbonate-bearing CAP appears to be associated only with CO_2-rich synthesis experiments (cf. Table 1 of Fleet and Liu 2007), and is independent of temperature (800–1350 °C), pressure (0.1–1 GPa), and run duration (8–48 h).

The characteristic FTIR bands for hydrogen carbonate disappear with either prolonged dry storage at room temperature (RT) or heating in air at 110 °C; the results for LM003 are shown in Figure 3. Spectrum 3a represents the quenched material and was collected after 75 days storage at RT. Unfortunately, we did not obtain a spectrum immediately after opening the capsule, and consider it likely that spectrum 3a represents CAP with partially decomposed hydrogen carbonate. Spectrum 3b represents crystals heated at 110 °C for 7 h only after RT storage for 283 days and indicates a trace amount of hydrogen carbonate, whereas for spectrum 3c the crystals were heated for 55 days after RT storage for 283 days, and no hydrogen-carbonate bands are evident. Spectrum 3d represents bulk sample stored for 367 days at RT and is likewise devoid of hydrogen-carbonate bands. Sodium hydrogen carbonate is well known to have a limited thermal

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[1] Deposit item AM-07-032, Table 1. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of the recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

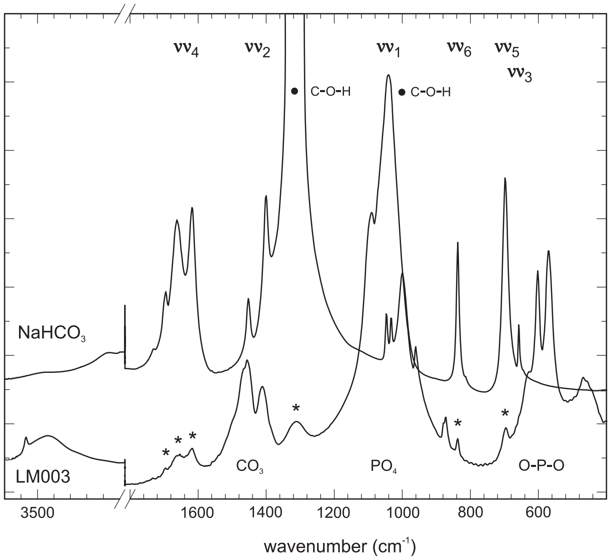

FIGURE 2. FTIR spectra for hand-separated crystals of a hydrogen-carbonate-bearing CAP (LM003; 1200 °C, 1.0 GPa, 8 h) and sodium hydrogen carbonate salt: asterisks flag characteristic hydrogen-carbonate bands in CAP. The band for the C-O-H in-plane bend vibration is dominant in the salt but relatively weak in the CAP.

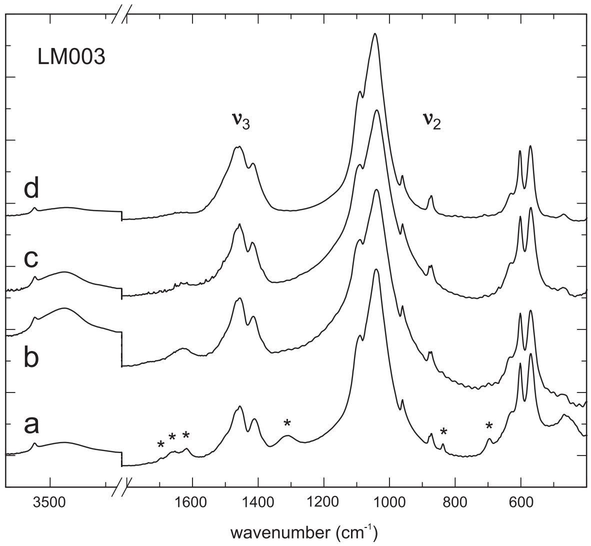

FIGURE 3. FTIR spectra for aged and heat-treated samples of the hydrogen-carbonate-bearing CAP LM003: (**a**) quenched material after 75 days storage at room temperature (RT; hand separated CAP crystals); (**b**) 283 days at RT, 7 h at 110 °C (crystals); (**c**) 283 days at RT, 55 days at 110 °C (crystals); (**d**) 367 days at RT (bulk); ν_3 and ν_2 identify bands for antisymmetric stretching and out-of-plane bending of the $(CO_3)^{2-}$ group in CAP, respectively. Note increase in area of bands for carbonate (at 1550–1350 cm^{-1}) and O-H in molecular water (at 3600–3300 cm^{-1}) in **b** and **c**.

stability; e.g., Dei and Guarini (1997) found that the commercial salt decomposes in air at about 85 °C with the simultaneous evolution of water and CO_2. Their results were consistent with the decomposition reaction:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2 \quad (1)$$

Consistent with this reaction, the spectra for the aged and heated CAP products in Figure 3 do show an increase in water content, particularly 3b, but the evidence for molecular CO_2 hosted by CAP is ambiguous with only 3c showing a weak band at about 2350 cm^{-1}.

Charge compensation requirements suggest that the hydrogen-carbonate ion is hosted in the apatite channel, since it is unlikely that a monovalent anion complex would substitute for $(PO_4)^{3-}$. This conclusion is supported by comparison of the absorption intensity for the antisymmetric stretching bands of carbonate in CAP (Fig. 3) and the apparent ease with which CO_2 and H_2O are lost from aged and heat-treated samples of CAP. Fleet and Liu (2007, Fig. 2 therein) noted that the intensities of the ν_3 and ν_2 carbonate bands for three of their CAP crystal products increased in proportion to the analyzed amounts of total carbonate. However, the hydrogen-carbonate-bearing sample LM003 was apparently anomalous in this respect because the ν_3 (Fig. 2 of Fleet and Liu 2007) carbonate band intensity at about 1550–1350 cm^{-1} was low relative to a total carbonate content of 6.2 wt% CO_3. This anomaly is accounted for in this study by comparing band intensities for the three crystal products (Figs. 3a–3c). When these spectra are normalized for differences in areas of the phosphate antisymmetric bend mode bands, the ν_3 carbonate band areas reveal an increase in carbonate content of up to about 25% for the two aged and heat-treated samples (Figs. 3b and 3c). For the decomposition reaction 1, this increase represents one-half of the original hydrogen-carbonate content. Therefore, the ν_3 carbonate band area of LM003 actually represents a carbonate content of about 4.1 wt% CO_3, which is consistent with the systematic increase in band area with increase in total carbonate content noted in Fleet and Liu (2007). Based on this reasoning LM003 contains about 4.1 wt% carbonate and 2.1 wt% hydrogen carbonate (reported as CO_3), although these estimates are only semi-quantitative. The relative carbonate band area for the aged bulk sample of LM003 (spectrum 3d) is greater than that of the corresponding crystal products (Figs. 3b and 3c), because carbonates are low-melting components in the synthesis experiments and tend to be enriched in the late-crystallizing product.

The FTIR spectra for the aged and heat-treated samples of LM003 show that the volatile decomposition products of hydrogen carbonate are not retained by CAP. Although decomposition of hydrogen carbonate proceeds much faster than the loss of volatiles, the latter are progressively lost from the apatite channel, with CO_2 more mobile than H_2O. Spectrum 3b suggests that much of the water is retained in the channel after just 7 h heating at 110 °C, but essentially all of it is lost after prolonged aging (spectrum 3d).

Charge compensation and packing considerations point to local coupling of Na and hydrogen carbonate in the channel of CAP (cf. Fleet and Liu 2007); i.e., there must be a strong preference for Na^+ cations on Ca2 (M2) sites to cluster about the $(HCO_3)^-$ ions. Indeed, the lack of significant shifts in hydrogen-carbonate band positions suggests that the hydrogen-carbonate ions are only loosely bound in the apatite channel and exist essentially as

$NaHCO_3$ entities. Infrared spectra for hydrogen carbonate that is more strongly bound to substrates (e.g., oxide surfaces; Lercher et al. 1984; Su and Suarez 1997) show significant departure from the spectrum for sodium hydrogen carbonate salt in the region of the $\nu\nu_2$ mode (CO_3) and C-O-H in-plane vibrations.

However, the pronounced decrease in intensity of the C-O-H in-plane vibration of the LM003 product (Fig. 2) does indicate minor change in the steric environment of the hydrogen-carbonate ion, and supports our conclusion that the hydrogen-carbonate ion is hosted by the CAP crystals. The relative band areas in Figure 2 are 192, 29, 73, and 644+ for the sodium hydrogen carbonate salt and 22, 2, 4, and 14 for hydrogen carbonate in CAP for the $\nu\nu_4$, $\nu\nu_6$, $\nu\nu_5$, and C-O-H in-plane vibrations, respectively.

The present observations suggest that the hydrogen-carbonate ion is incorporated in CAP under the conditions of synthesis [high P-T-$p(CO_2)$] but is unstable at ambient P and T. In respect to high-pressure phase relations in the Na_2O-CO_2-H_2O system, nahcolite is stable up to at least 10 GPa at room temperature (Kagi et al. 2005) but is unstable above about 300 °C at 1 GPa in the presence of excess H_2O fluid (Liu and Fleet, work in progress). Although the carbonation of hydroxyl-apatite at high $P(CO_2)$ and T is well known (Bonel 1972), this study has shown that both water and CO_2 are mobile in the apatite structure under ambient conditions. Thus, hydrogen-carbonate CAP is a potential pH buffer for restricted surficial environments. Perhaps more intriguingly, it seems probable that the channel constituents of biological apatites would influence acid-base reactions in bone cells and blood.

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