Equation of state of carbonated hydroxylapatite at ambient temperature up to 10 GPa: Significance of carbonate

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ABSTRACT

The incorporation of the carbonate ion into the crystal structure of hydroxylapatite results in the creation of vacancies, oxygen-loss, and disorder, with consequent changes in physical and chemical properties. High-pressure experimental investigation up to 10 GPa of two synthetic carbonated hydroxylapatite samples with up to 11 wt% \( \text{CO}_3 \), using a diamond-anvil cell and synchrotron powder X-ray diffraction, provides the first rigorous assessment of the mechanical behavior of the carbonated hydroxylapatite. The pressure-volume data suggest that the isothermal bulk modulus of these carbonated hydroxylapatites has been significantly decreased by the presence of the carbonate (up to about 15%), which in turn will affect all the carbonated apatite-related reactions in the geosystem. Since hydroxylapatite is one of the major components of the bones and teeth, the incorporation of the carbonate in the hydroxylapatite weakens teeth and bones not only chemically, but also physically.

KEYWORDS: Carbonated hydroxylapatite, isothermal bulk modulus, equation of state, synchrotron X-ray diffraction

INTRODUCTION

Apatite commonly occurs in sedimentary, igneous, and metamorphic rocks (e.g., Walters and Luth 1969; McClellan 1980; Lang et al. 1995; Santos and Clayton 1995; Comodi and Liu 2000), and it has been regarded as the tenth most abundant mineral on the Earth (McClellan and Lehr 1969; Hughes and Rakovan 2002). In most geological settings, it is present as an accessory phase, but in some other cases it can appear as a major phase; for example, its proportion in the pyroxenite of the Triassic-Jurassic silica-undersaturated alkalic intrusions in the Cordillera of British Columbia is about 10% (Lang et al. 1995). Due to its ubiquitous geological presence and crystal-structure chemical characteristics, such as extensive anion/cation substitution and volatile content (Hughes and Rakovan 2002; Pan and Fleet 2002), apatite has numerous useful geological applications, especially in dating and petrogenesis (e.g., Li et al. 2000; Filiberto and Treiman 2009).

The general chemical formula of apatite can be written as \( \text{A}_{10}(\text{BO}_4)\text{X}_5 \), where \( A = \text{Na}^+, \text{Ag}^+, \text{Ca}^{2+}, \text{Pb}^{2+} \), and rare-earth elements (REE\(^{3+}\)), \( B = \text{P}^{5-}, \text{C}^{3-}, \text{S}^{6-}, \text{Si}^{4+}, \text{As}^{5+}, \text{and} \text{V}^{5+} \), and \( X = \text{F}^{−}, \text{Cl}^{−}, \text{CO}_3^{2−}, \text{HCO}_3^{−}, \text{OH}^{−}, \) neutral molecules like \( \text{H}_2\text{O} \), and vacancies (Pan and Fleet 2002; Fleet and Liu 2007a). The geochemically important species of apatite are fluoroapatite [ideal formula \( \text{Ca}_{10}(\text{PO}_4)_3\text{F}_2 \)], hydroxylapatite [ideal formula \( \text{Ca}_{10}(\text{PO}_4)_3(\text{OH})_2 \)], chlorapatite [ideal formula \( \text{Ca}_{10}(\text{PO}_4)_3\text{Cl}_2 \)], and carbonated apatite with variable formula. The structural details of fluorapatite, hydroxylapatite, and chlorapatite have been generally well established (e.g., Hughes et al. 1989) while those of carbonated apatite have not been fully disclosed, as outlined below. It has been experimentally shown that apatite can be stable up to the \( P-T \) conditions of the upper mantle of the Earth (about 12 GPa; Murayama et al. 1986), so that the equation of state of apatite could be very important. So far, compression experiments have been carried out to investigate the compressibility of fluorapatite, hydroxylapatite, and chlorapatite (Brunet et al. 1999; Comodi et al. 2001; Matsukage et al. 2004), but no comparable work has been done on the carbonated apatite. Additional closely-related experimental studies include Liu et al. (2008) [lead fluorapatite \( \text{Pb}_6(\text{PO}_4)\text{F}_2 \)] and Fleet et al. (2010) (lead fluorapatite), and Zhai et al. (2009) \( \gamma \)-tricalcium phosphate \( \gamma-\text{Ca}_3(\text{PO}_4)_2 \), the main breakdown product of apatite.

As mentioned above, the formula of carbonated apatite is highly variable, and this is mainly because carbonate can substitute for both the channel anion and the phosphate ion: the former carbonate is referred to as type A while the latter is type B (e.g., LeGeros 1965; Trueman 1966; LeGeros et al. 1969; Elliott et al. 1980; Regnier et al. 1994; Nathan 1996). Due to the importance of the carbonated hydroxylapatite in biomineralization (Elliott 1994, 2002), the incorporation of carbonate in apatite and its resulting physical-chemical changes have been actively explored and intensely debated (e.g., Wilson et al. 1999; Leventouri et al. 2000, 2001; Fleet and Liu 2003, 2004, 2005, 2007a, 2008a, 2008b, 2009; Fleet et al. 2004; Wilson et al. 2004; Fleet 2009). In particular, it has been shown that the incorporation of carbonate into the structure of apatite can enhance the solubility of apatite (LeGeros 1991). Here we investigate the effect of the carbonate ion on the compressibility of the apatite.

EXPERIMENTAL METHODS

The materials used in the high-pressure experiments reported here were samples LM006 \( ([\text{Ca}_{10}(\text{Na}_{5.4})(\text{CO}_3)_{0.5}]_{(\text{OH})}_{1.5}]_{(\text{CO}_3)_{1.9}}; 4.8 \text{ wt\% CO}_3 \) and LM005 \( ([\text{Ca}_{10}(\text{Na}_{5.4})(\text{CO}_3)_{0.5}]_{(\text{OH})}_{1.5}]_{(\text{CO}_3)_{1.9}}; 11.2 \text{ wt\% CO}_3 \) (Fleet and Liu 2007b). These two samples have been characterized previously by