



High pressure experimental studies on $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ and $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$: Extensive pressure behaviors of carbonophosphates family

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ABSTRACT

Carbon-bearing phases in the Earth's interior have profound implications for the long-term Earth carbon cycle. Here we investigate high-pressure behaviors of carbonophosphates $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ and $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ in diamond anvil cells up to ~ 12 GPa at room temperature. Modifications in *in situ* synchrotron X-ray diffraction patterns and Raman spectra confirm the structural stability of carbonophosphates within the pressure region. Fitting the third-order Birch-Murnaghan equation of state to the volume compression curve, the isothermal bulk modulus parameters are obtained to be $K_0 = 56(1)$ GPa, $K_0' = 3.3(1)$, $V_0 = 303.3(3) \text{ \AA}^3$ for $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ and $K_0 = 54(1)$ GPa, $K_0' = 3.4(1)$, $V_0 = 313.4(2) \text{ \AA}^3$ for $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$. Crystallographic axes exhibit an elastic anisotropy with a more compressible *c*-axis relative to the *ab*-plane. An inverse linear correlation between the K_0 value and the ionic radius of M^{2+} ($\text{M} = \text{Mg}, \text{Fe}, \text{Mn}$) is well determined for carbonophosphates. The pressure-dependence responsiveness of $[\text{PO}_4]$ and $[\text{CO}_3]$ in carbonophosphates show a negative relationship to the M^{2+} radius. We also discussed the effect of $[\text{PO}_4]$ group on the structural variations and high-pressure behaviors of carbonates. Furthermore, the geochemical properties of carbonophosphates hold implications to diamond genesis.

1. Introduction

There has long been considerable interest in the stability of carbonates under high pressure and high temperature conditions, because they represent the major carbon-bearing phases that are recycled into the Earth's interior [1]. They are also considered as potential carbon-hosts inside the Earth due to the low solubility of carbon in silicates in the mantle [2]. Since the 1980s, a barrage of carbonate associations including calcite CaCO_3 , magnesite MgCO_3 , dolomite $\text{CaMg}[\text{CO}_3]_2$ and eitelite $\text{Na}_2\text{Mg}[\text{CO}_3]_2$ has been identified within natural diamonds from the lower part of the transition zone and the lower mantle [3–10]. It provides credible evidence for the presence of carbonates in the Earth's deep interior and, holds implications of genetic relationship between the carbonate associations and the diamond hosts [11]. Long-range studies on geochemical behaviors of carbonates is fruitful [12–27], but the fate of carbon-bearing phases with complex chemistry is still poorly known.

Indeed, in addition to carbonates, $[\text{CO}_3]$ -bearing polyanionic

minerals could be concerned proxy of carbon inside the Earth; the presence of additional anion group e.g. $[\text{SiO}_4]$, $[\text{PO}_4]$ and $[\text{OH}]$ would greatly affect the structure, the property and the phase diagram of carbonates under mantle conditions. Gao et al. [28] has reported effect of pressure on local structure of three typical silicate-carbonate minerals: spurrite $\text{Ca}_5(\text{SiO}_4)_2(\text{CO}_3)$, galuskinitite $\text{Ca}_7(\text{SiO}_4)_3(\text{CO}_3)$ and tilleyite $\text{Ca}_5(\text{Si}_2\text{O}_7)(\text{CO}_3)_2$, up to ~ 30 GPa. An array of exploration on geochemical behaviors of carbonate-rich apatite is on-going well [29–31]. Recently, a high-pressure study on azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ has discussed the effect of $[\text{OH}]$ on structural stability of carbonates under mantle pressures up to ~ 16 GPa [32]. Having a knowledge of high-pressure behaviors of $[\text{CO}_3]$ -bearing polyanionic phases would constitute the missing link to complete our knowledge of the Earth carbon cycle.

Carbonophosphates, first reported in the 1980s [33], is an interesting model family of $[\text{CO}_3]$ and $[\text{PO}_4]$ coexistent phase. It has a general formula of $\text{A}_3\text{M}(\text{CO}_3)(\text{PO}_4)$ ($\text{A} = \text{Li}$ or Na ; $\text{M} = \text{Mg}, \text{Fe}, \text{Mn}$, etc.) with four members discovered naturally so far, including bradleyite

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$\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)$, bonshtedtite $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$, sidorenkite $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ and crawfordite $\text{Na}_3\text{Sr}(\text{PO}_4)(\text{CO}_3)$. Several new members have been synthesized successfully in the laboratory afterwards [34,35]. These members are isostructural with a space group of $P2_1/m$ and $Z = 2$. They are featured with a double-layered framework constituted by “[MO_6]-octahedron-[PO_4]-tetrahedron” chains and the “[NaIO_7]-[NaIO_7]” polyhedron chains along the b -axis. These layers are bridged by the coplanar [CO_3]-triangles and the isolated [NaIO_6] polyhedron. Carbonophosphates family has attracted much attention due to their promising application as rechargeable battery material [34–36] and the references therein). Only limited attempts, however, have been made to characterize their thermodynamical stability [33], the local structural features of $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ [37], the high-pressure behavior of $\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)$ [38] and the vibrational spectral signature of $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ [39]. Little of our knowledge is far short to acquire geochemical properties of carbonophosphates. Here we conduct *in situ* high-pressure experiments to probe into the structural modifications and the compression behaviors of carbonophosphates bonshtedtite $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ and sidorenkite $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ above ~ 12 GPa. Combined with the results of $\text{Na}_3\text{Mg}(\text{PO}_4)(\text{CO}_3)$ from Gao et al. [38], we make a well-rounded summary on the high-pressure behaviors of carbonophosphate family. The geochemical properties of carbonophosphates compared with that of carbonates, and the effect of [PO_4] on the structural variations of carbonates at extreme conditions is also discussed.

2. Materials and methods

2.1. Sample preparation

The carbonophosphate samples $\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$ (referred to as Fe hereinafter) and $\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$ (Mn) were synthesized from modified hydrothermal solutions. Details of similar synthetic method were reported in Huang et al. [35]. A typical synthesis route is described below using the Fe version as an example. First, 4 mmol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 50 mg citric acid were dissolved in 10 ml water/ethylene glycol (EG) mixed solution (volume ratio: $\text{H}_2\text{O}/\text{EG} = 3/1$) to form a clear solution A. Separately, 4 mmol $(\text{NH}_4)_2\text{HPO}_4$ and 4 g Na_2CO_3 were dissolved in 20 ml $\text{H}_2\text{O}/\text{EG}$ mixed solution (volume ratio: $\text{H}_2\text{O}/\text{EG} = 3/1$) to form a clear solution B. Solution A was then added to solution B after a vigorous stirring, and the mixture slurry was kept stirring for half an hour. Then the mixture products were transferred into a 40 ml stainless steel autoclave and heated at 180°C for 70 h. Later the products were washed by distilled water five times, followed by drying in a vacuum oven at 80°C overnight. To synthesize Mn, the metal source in the raw materials was changed to be $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ while $(\text{NH}_4)_2\text{HPO}_4$ and Na_2CO_3 are kept as phosphorus and carbon sources. The synthetic products were characterized for phase purity ($P2_1/m$, $Z = 2$) by X-ray diffraction (XRD) measurement. The refined lattice parameters are $a_0 = 8.9354(5)$ Å, $b_0 = 6.6402(2)$ Å, $c_0 = 5.1559(3)$, $\beta = 90.45(1)^\circ$ for Fe, and $a_0 = 8.9913(3)$ Å, $b_0 = 6.7595(2)$ Å, $c_0 = 5.1598(2)$, $\beta = 90.15(1)^\circ$ for Mn (Table 1).

Fine sample powder was compressed into a slice of ~ 20 μm in thickness, and loaded into a symmetric diamond anvil cell (DAC) equipping with beveled diamonds of 300 μm culets. A rhenium gasket was preindented to ~ 45 μm and drilled to make a hole of ~ 120 μm in diameter as the sample chamber.

2.2. Angle-dispersive powder XRD

The angle-dispersive powder XRD measurements were performed at 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF). The monochromatic X-ray beam wavelength was 0.6199 Å. Diffraction patterns were reordered using a Mar345 imaging panel detector with exposure times of 300 s per pattern. Geometrical parameters for radial integration of two-dimensional data and the sample-detector distance

Table 1

Pressure dependence of lattice constants of Fe and Mn calculated from XRD data. The number in the parentheses represents one standard deviation in the right-most digit. The data labeled by* are referred to [34] for comparison.

Pressure (GPa)	a (Å)	b (Å)	c (Å)	V (Å ³)	β (°)
$\text{Na}_3\text{Fe}(\text{PO}_4)(\text{CO}_3)$					
0.0001*	8.95	6.61	5.16	305.25	90.4
0.0001	8.9354(5)	6.6402(2)	5.1559(3)	302.57(2)	90.45(1)
0.5	8.891(1)	6.598(2)	5.115(2)	300.0(1)	90.5(1)
1.5	8.842(1)	6.565(2)	5.077(2)	294.7(1)	90.7(1)
2.7	8.802(1)	6.532(2)	5.040(2)	289.7(1)	90.8(1)
3.8	8.768(1)	6.501(2)	5.004(2)	285.2(1)	91.2(1)
5.0	8.726(1)	6.466(2)	4.963(2)	280.0(1)	90.9(1)
6.3	8.688(1)	6.421(2)	4.930(2)	275.0(1)	91.3(1)
7.8	8.634(1)	6.383(2)	4.890(2)	269.5(1)	91.1(1)
9.0	8.602(1)	6.346(2)	4.868(2)	265.7(1)	91.2(1)
10.1	8.581(1)	6.308(2)	4.838(2)	261.8(1)	91.0(1)
11.3	8.559(1)	6.288(2)	4.810(2)	258.8(1)	91.4(1)
$\text{Na}_3\text{Mn}(\text{PO}_4)(\text{CO}_3)$					
0.0001*	8.99	6.74	5.16	312.65	90.1
0.0001	8.9913(3)	6.7595(2)	5.1598(2)	314.72(2)	90.15(1)
1.4	8.941(2)	6.717(3)	5.153(1)	309.5(1)	90.8(1)
2.4	8.908(2)	6.680(3)	5.112(1)	304.2(1)	90.6(1)
3.8	8.854(2)	6.632(3)	5.065(1)	297.3(1)	91.3(1)
4.9	8.813(2)	6.596(3)	5.025(1)	292.1(1)	91.0(1)
6.0	8.778(2)	6.563(3)	4.999(1)	287.9(1)	91.1(1)
6.9	8.742(2)	6.539(3)	4.969(1)	284.0(1)	91.3(1)
8.2	8.711(2)	6.505(3)	4.933(1)	279.4(1)	91.6(1)
9.4	8.681(2)	6.471(3)	4.895(1)	274.9(1)	91.2(1)
10.4	8.650(2)	6.449(3)	4.868(1)	271.5(1)	91.4(1)
11.4	8.632(2)	6.425(3)	4.848(1)	268.8(1)	91.4(1)

were calibrated with a CeO_2 standard [40]. The intensity versus 2θ spectra were processed with FIT2D code [41]. Refinements were performed by Unitcell program [42]. Argon was adopted as pressure transmitting media (PTM), and the pressure was calculated from the volume determined by Pt (111) diffraction line [43].

2.3. Raman spectroscopy

In situ Raman experiments were conducted on Reinshaw 1000 laser Raman spectrometer in Peking University, China. This system uses a 514.5 nm Ar^+ laser excitation line with an on-sample intensity of 2 mW. The laser light was focused using a Leica microscope with a 50 × microscope objective to a beam size of ~ 1.5 μm in-diameter. Acquisitions were obtained with 2400 l/mm grating and 100 cm^{-1} cut-off edge filter. A piece of single-crystal silicon was used to calibrate the wave number of the Raman shifts. We collected Raman spectra of Mn with increasing pressure up to ~ 14 GPa (the Raman signal of Fe is too weak in intensity to be identified). All the spectra were recorded in the backscattering geometry, and the collection time for each spectrum was 60 s. Raman spectra were fitted to the Lorentzian profile through Peakfit software. Silicone oil was used as PTM [44]. The pressure was calibrated by ruby fluorescence method [45].

3. Results

In Fig. 1 we present integrated XRD patterns of Fe and Mn at selected pressures up to ~ 12 GPa. The evolution of XRD data shows continuous shifts to higher angles, without any sign of a phase transition. We determined pressure-induced lattice parameters and cell volumes by labeled diffraction peaks. All the calculated results are listed in Table 1. Linear regression analyses were applied to describe the axial compression (Fig. 2a and b), with the compression coefficient (δ) of $\delta_a = -3.5(1) \times 10^{-3}$, $\delta_b = -4.4(1) \times 10^{-3}$, $\delta_c = -5.6(1) \times 10^{-3} \text{ Å GPa}^{-1}$ for Fe, and $\delta_a = -3.6(1) \times 10^{-3}$, $\delta_b = -4.7(1) \times 10^{-3}$, $\delta_c = -5.8(1) \times 10^{-3} \text{ Å GPa}^{-1}$ for Mn. The elastic anisotropy of Fe can be thus expressed as $\delta_a:\delta_b:\delta_c = 1:1.25:1.60$ and of Mn as $1:1.31:1.61$. Axial angle β increases from 90.5° to 91.5° with somewhat fluctuations during the compression process (Fig. 2c), which indicates a reduction tendency

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