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Natural high-pressure polymorph of merrillite in the shock veins of the Suizhou meteorite

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Abstract—A new high-pressure polymorph of merrillite with the structure of trigonal γ -Ca₃(PO₄)₂ was found in the shock-produced veins of the Suizhou meteorite, where it coexists with ringwoodite, majorite, NaAlSi₃O₈-hollandite, and majorite-pyrope garnet. The crystallographic nature of this natural γ -Ca₃(PO₄)₂ phase was characterized by Raman spectroscopy and X-ray diffraction, and all data compare favorably to the same data obtained from γ -Ca₃(PO₄)₂ synthesized at 14 GPa and 1400°C. The cell parameters of this new high-pressure mineral are $a = 5.258(1)$ angstroms and $c = 18.727(3)$ angstroms, space group R-3m, and density = 3.447 (g/cm³), where the number in parentheses are standard deviations in the last significant digits. The natural occurrence of the γ -Ca₃(PO₄)₂ phase together with other high-pressure minerals constrains the pressure of the shock veins at about 23 GPa. The Suizhou meteorite provides the first naturally occurring example of γ -Ca₃(PO₄)₂ polymorph. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Merrillite (Ca₉MgNa(PO₄)₇), whitlockite (Ca₆MgH(PO₄)₇) and apatite (Ca₅(PO₄)₃(F, OH, Cl)) are among the most important phosphate minerals found in lunar samples, meteorites, and terrestrial rocks (Griffin et al., 1972; Nash, 1984; Buchwald, 1984; Lundberg et al., 1988; Frondel, 1941; Keppler, 1965; Gopal and Calvo, 1972; Prewitt and Rothbard, 1975; Dowty, 1977; Rubin, 1997). Merrillite and whitlockite have slightly different structures. The structure of merrillite is essentially identical to that of synthetic β -(Ca₃(PO₄)₂), whereas in natural and synthetic whitlockite, one of tetrahedral PO₄ groups is inverted (Gopal and Calvo, 1972; Calvo and Gopal, 1975; Rubin, 1997). Merrillite, the anhydrous Ca-phosphate, usually has an extraterrestrial origin, whereas whitlockite is found in the terrestrial rocks (Rubin, 1997). The volatile element-bearing apatite is stable at shallower horizons of upper mantle. At higher pressures and temperatures in the deep upper mantle, where volatile components might become less abundant (Beswick and Carmichael, 1978), apatite could initially coexist with whitlockite and then eventually decompose to merrillite. Since the mantle of the Earth has a chondritic composition with ~0.26 wt.% P₂O₅ (Mason, 1966), the behavior of phosphate minerals at depths in the terrestrial mantle where neither whitlockite (or merrillite) nor apatite exists stably is of great interest for understanding the behavior of rare earth elements (REE) and other large lithophile elements. A polymorph of phosphate stable at deeper mantle pressures and temperatures could act as an important host of REE, Na, Sr and Ba (Griffin et al., 1972; Beswick Carmichael, 1978; Dowty, 1977; Murayama et al., 1986; Sugiyama and Tokonami, 1987).

The compound Ca₃(PO₄)₂ has four polymorphs: α -, α -, β -, and γ -phases. The β -phase is stable at ambient conditions, the γ -phase is stable at high pressure, and the α - and α -phases are stable at high temperatures (Sugiyama and Tokonami, 1987). The trigonal γ -Ca₃(PO₄)₂ is a dense phase isostructural with

Ba₃(PO₄)₂ (Roux et al., 1978), which is 13% denser than β -Ca₃(PO₄)₂ (Murayama et al., 1986; Roux et al., 1978). Thermodynamic computations indicate that whitlockite transforms to γ -Ca₃(PO₄)₂ at pressures above 2.5 GPa at 1000°C (Murayama et al., 1986), and that whitlockite has a relatively low density making it unstable at higher pressures. Multi-anvil high-pressure experiments using hydroxylapatite and fluorapatite as starting materials revealed that apatite decomposes to γ -Ca₃(PO₄)₂ at pressures above 12 GPa and temperatures from 1100 to 2300°C (Murayama et al., 1986; Roux et al., 1978). Chen et al. (1995) reported that chlorapatite in shock veins of the Sixiangkou meteorite was transformed to an unknown high-pressure polymorph. Thus far, no high-pressure polymorph of merrillite has been positively identified in any terrestrial or extraterrestrial rocks. Here we report the first natural occurrence of the high-pressure polymorph of merrillite with the structure of γ -Ca₃(PO₄)₂ in the Suizhou meteorite.

2. SUIZHOU METEORITE

The Suizhou meteorite fell on April 15, 1986, in Dayanpo, which is located 12.5 km southeast of Suizhou in Hubei, China. A total of 270 kg of the Suizhou meteorite was collected, and the largest fragment, weighing 56 kg, is now preserved in the City Museum of Suizhou. This meteorite was classified as an L6 chondrite (Wang and Li, 1990), and its shock classification stage is S3 to S4 (Xie et al. 2001a).

The chondritic host of Suizhou consists of the rock-forming minerals olivine, low-Ca pyroxene, plagioclase, FeNi-metal and troilite, and accessory components merrillite, chlorapatite, chromite and ilmenite. Compared to other L6 chondrites with thick shock veins up to several millimeters (Chen et al., 1996; Price et al., 1979; Rubin, 1985), this meteorite contains only a few, very thin shock-produced black melt veins ranging from 0.02 to 0.09 mm in width. The shock vein is chondritic in composition and consists of two distinct high-pressure mineral assemblages that have been identified by electron microprobe and microRaman spectroscopic techniques (Xie et al., 2001b): (a) coarse-grained polycrystalline ringwoodite, majorite, and

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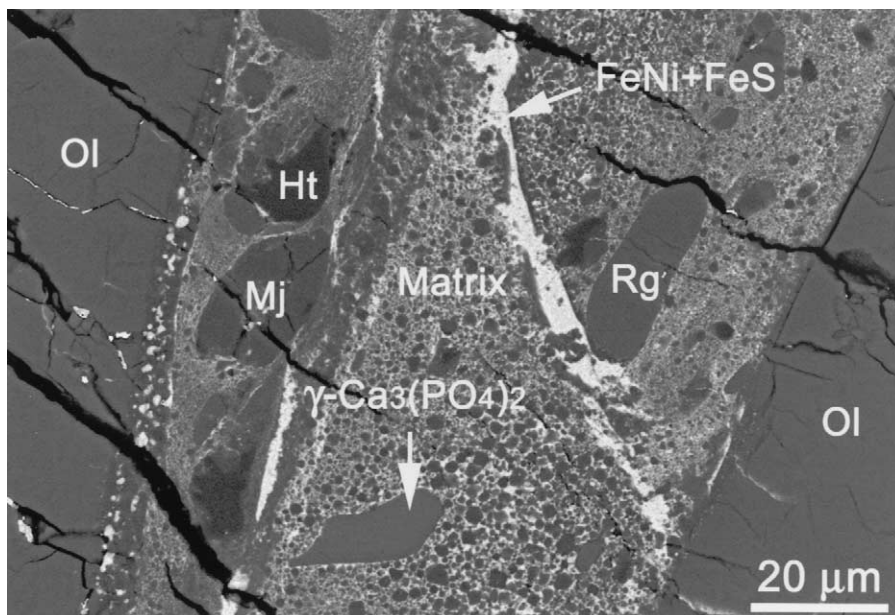


Fig. 1. Back-scattered electron image of a shock melt vein in the Suizhou meteorite, indicating that the high-pressure minerals in the veins include ringwoodite (Rg), majorite (Mj), $\text{NaAlSi}_3\text{O}_8$ -hollandite (Ht), $\gamma\text{-Ca}_3(\text{PO}_4)_2$, and fine-grained garnet. Garnet with FeNi-metal and troilite make up the matrix of the vein. The vein intersects the chondritic region consisting of intact olivine (Ol), pyroxene, metal and troilite. Melted metal-troilite veinlets (FeNi+FeS) are also observed in the shock vein.

$\text{NaAlSi}_3\text{O}_8$ -hollandite that are formed either through the solid state transformations of or from the crystallization of monomineralic melts of olivine, low-calcium pyroxene and plagioclase, respectively; and (b) fine-grained majorite-pyroxene garnet that crystallized at high pressures and temperatures from shock-produced dense chondritic melt (Fig. 1). Fine-grained garnet together with FeNi-metal and troilite make up the matrix of the vein. Most plagioclase in the chondritic region was transformed into maskelynite, a dense plagioclase glass (Xie et al., 2001a; Chen and El Goresy, 2000).

3. EXPERIMENTAL METHODS

Polished thin sections were prepared from fragments of Suizhou that contain black shock-induced veins. The petrology and compositions of the samples were investigated by optical microscopy using a Hitachi S-3500N scanning electron microscope in back scattered electron mode at the Guangzhou Institute of Geochemistry and a Cameca SX-51 electron microprobe with 15 kV accelerating voltage and 10 nA beam current at the Institute of Geology, Chinese Academy of Sciences. Raman spectra of natural phosphate minerals were recorded with a Renishaw R-1000 Raman microscope (Ar^+ laser, 514 nm line) at the Beijing Institute of Non-ferrous Metals.

X-ray diffraction data of a phosphate phase present in the Suizhou shock veins were obtained by the synchrotron X-ray diffraction technique. Polished thin sections of samples were probed by energy dispersive X-ray diffraction using the synchrotron beam line X17c (operating at 2.584 GeV and 300 to 100 mA) at the National Synchrotron Light Source, Brookhaven National Laboratory. The size of the X-ray beam was collimated to $15 \times 15 \mu\text{m}$, and was focused on a phosphate grain $10 \times 20 \mu\text{m}$ in size. Owing to the extremely small size and thickness of the probed grain and the influence of the very strong diffraction lines from the surrounding and underneath fine-grained matrix minerals, we only resolved the strongest diffraction peaks belonging to the unknown phosphate phase ($\text{Ca}_3(\text{PO}_4)_2$).

To uncover the crystal structure of this unknown phosphate phase in Suizhou, we carried out multi-anvil experiments at 14 GPa and 1400°C,

using $\text{Ca}_3(\text{PO}_4)_2$ powder as the starting material. The starting material was stored in a drying oven at 100°C before the experiment. The choice of the experimental pressure and temperature was guided by the findings of Murayama et al. (1986). To achieve the pressure and temperature necessary to create the high-pressure $\text{Ca}_3(\text{PO}_4)_2$ polymorph, a multi-anvil apparatus at the Geophysical Laboratory of the Carnegie Institution of Washington was utilized following the method of Bertka and Fei (1997). The sample was housed in a 10/5 assembly containing a Re heater and a $\text{W}_5\text{Re-W}_{26}\text{Re}$ thermocouple was used to monitor sample temperature. The sample was first brought up to the final pressure of 14 GPa and then brought up to the final temperature of 1400°C. The sample was held for 24 h at 14 GPa and 1400°C, was quenched by shutting off the power to the heater and was then decompressed. For analysis of the experimentally produced high-pressure $\text{Ca}_3(\text{PO}_4)_2$ polymorph, the charge containing the experimental product was partially ground away to reveal sample.

The Raman spectrum of the synthesized $\gamma\text{-Ca}_3(\text{PO}_4)_2$ was first obtained with a micro-Raman system (Ar^+ laser, 514 nm line) at the Geophysical Laboratory. Powder X-ray diffraction data for the synthetic high-pressure $\text{Ca}_3(\text{PO}_4)_2$ phase were then collected with a Rigaku PSpC-MDG2000 X-ray microdiffractometer equipped with an imaging plate detector system, also at the Geophysical Laboratory. Structure refinements were performed using the program package GSAS (A.C. Larson and R.B. von Dreele, Report LAUR 86 to 748, Los Alamos National Laboratory, 1986).

4. RESULTS

4.1. Natural High-Pressure $\text{Ca}_3(\text{PO}_4)_2$ Phase

The Suizhou meteorite contains ~2 vol.% merrillite and 1 vol.% chlorapatite. These two phosphates occur in the chondritic region as single crystals up to 150 μm in grain size. The phosphates in the shock veins are less than 20 μm in grain size.

Our study indicates that the merrillite in the chondritic region of Suizhou is usually fractured but its crystal structure is undisturbed. Table 1 lists the composition of this merrillite,

Table 1. Compositions of merrillite and γ -Ca₃(PO₄)₂ phase (γ -phase) in the Suizhou meteorite from microprobe analyses.

	Oxides (wt.%)										Totals
	TiO ₂	FeO	MgO	CaO	NiO	Na ₂ O	K ₂ O	Cr ₂ O ₃	P ₂ O ₅		
merrillite	0.06	0.28	3.27	46.62	0.08	2.57	0.03	0.03	47.67	100.61	
γ -phase	0.04	0.38	3.58	46.14	0.05	2.80	0.07	0.00	47.16	100.22	
	Number of cations (oxygen=28)										Totals
	Ti	Fe	Mg	Ca	Ni	Na	K	Cr	P		
merrillite	0.00	0.07	0.91	8.82	0.00	0.88	0.00	0.00	7.14	17.82	
	Number of cations (oxygen=8)										Totals
	Ti	Fe	Mg	Ca	Ni	Na	K	Cr	P		
γ -Phase	0.00	0.03	0.28	2.51	0.00	0.28	0.00	0.00	2.02	5.12	

Standard deviations of analyses (1σ in %) are 0.02 (TiO₂), 0.05 (FeO), 0.02 (MgO), 0.27 (CaO), 0.03 (NiO), 0.02 (K₂O), 0.01 (Cr₂O₃), 0.03 (P₂O₅).

which is similar to merrillite in many other ordinary chondrites and achondrites, but distinct from REE-rich merrillite found in lunar rocks and hydrogen-bearing whitlockite in terrestrial samples (Dowty, 1977; Prewitt, 1975). Raman spectroscopic investigation indicates that the spectrum of this merrillite consists of intense peaks at 956 and 972 cm⁻¹, less intense peaks at 408, 445 and 1080 cm⁻¹, and weak peaks at 178, 550, and 1026 cm⁻¹ (Fig. 2a). The two strongest peaks at 956 and 972

cm⁻¹ can be assigned to the ν_1 symmetric stretching vibration of PO₄ tetrahedra (Jolliff et al., 1996). The Raman spectrum of the chondritic region merrillite is similar to the Raman spectra of merrillite in the Sixiangkou meteorite (Chen et al., 1995) and synthetic REE-poor whitlockite (Jolliff et al., 1996), where all the spectra contain a well-resolved strong doublet from 950 to 976 cm⁻¹.

In the shock vein of Suizhou, we found a phosphate phase of unknown structure that coexists with high-pressure phases such as ringwoodite, majorite, NaAlSi₃O₈-hollandite, and majorite-pyrope garnet (Fig. 1). The shock vein phosphate phase is smooth, occurs as unfractured grains up to 10 × 20 μ m in size, and is surrounded by fine-grained matrix minerals. Electron microprobe analyses indicate that the composition of this phosphate is identical to that of the merrillite outside the shock vein (Table 1). No chlorine was detected from this phosphate phase. Thus, the compositional character of the phosphate phase in the shock veins of Suizhou suggests that it is related to merrillite, and not chlorapatite, in the Suizhou chondritic region.

The Raman spectrum of the shock vein phosphate phase displays only one intense peak at 974 cm⁻¹, two less intense peaks at 410 and 577 cm⁻¹, and four weak peaks at 192, 640, 997 and 1095 cm⁻¹ (Fig. 2b). The single strong peak at 974 cm⁻¹, induced from ν_1 symmetric stretching vibrations of the PO₄ group, differs from the strong doublet of REE-poor merrillite (and whitlockite) from 950 to 976 cm⁻¹ (Chen et al., 1995; Jolliff et al., 1996) and from the asymmetric single peak or the very poorly resolved doublet from REE-rich whitlockite (Jolliff et al., 1996). Since both this phosphate phase and the merrillite outside the shock veins have the same composition, and the shock vein is full of high-pressure minerals, the compositional and structural data suggest that a phase transformation from merrillite to its high-pressure polymorph took place in the shock veins.

We also obtained X-ray diffraction data of the phosphate phase in the Suizhou shock veins on a thin section by using synchrotron X-radiation with an energy dispersive diffraction technique. We observed nine diffraction peaks at 2.892 Å, 2.628 Å, 2.427 Å, 2.073 Å, 2.048 Å, 2.008 Å, 1.945 Å, 1.732 Å, and 1.567 Å which can be assigned to the hkl indices of (-105), (-120), (11-3), (-108), (-204), (1-26), (02-5), (0-10), and (2-35), respectively, of the trigonal high-pressure phase. These diffraction lines can also be indexed from the X-ray diffraction pattern of the synthetic γ -Ca₃(PO₄)₂ phase (Fig. 3). The unit cell parameters for the phosphate trigonal

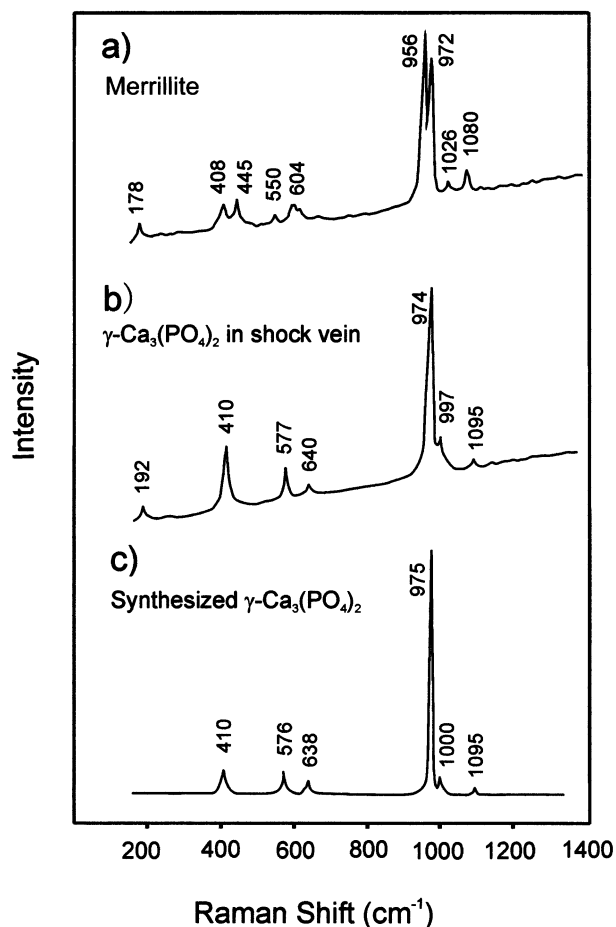


Fig. 2. Raman spectra of (a) merrillite in the Suizhou meteorite, (b) γ -Ca₃(PO₄)₂ phase in the shock vein of Suizhou meteorite, (c) γ -Ca₃(PO₄)₂ phase synthesized at 14 GPa and 1400°C.

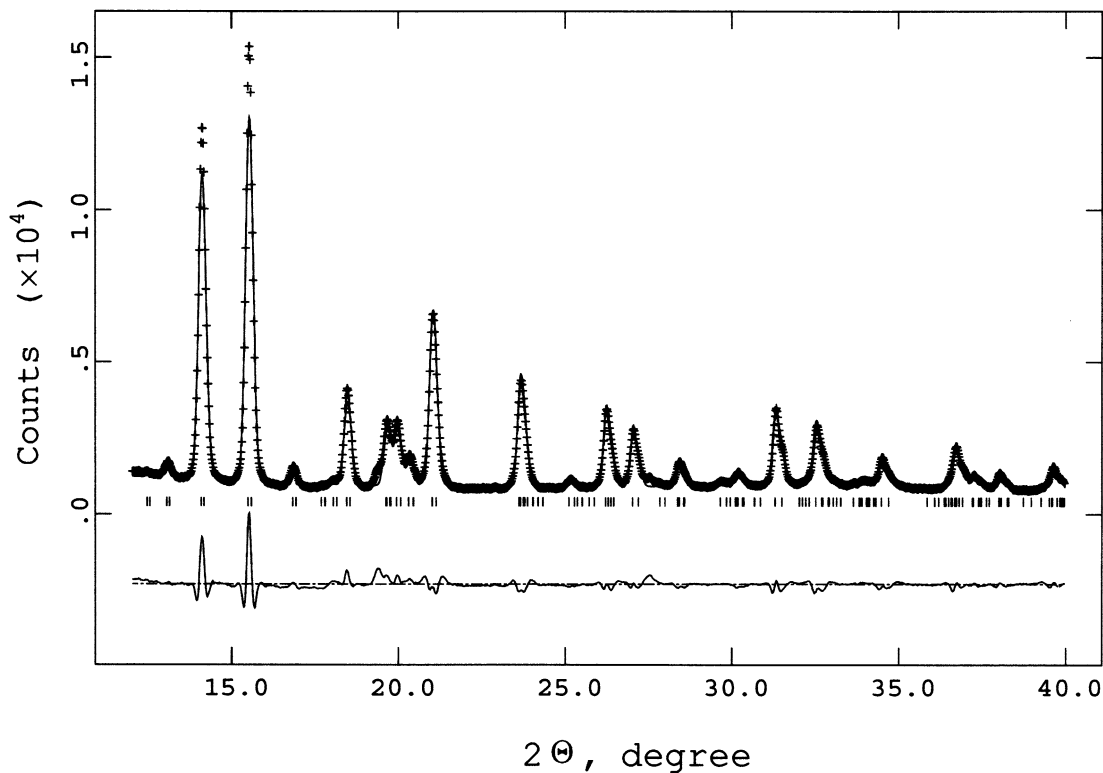


Fig. 3. Observed (crosses) and calculated (solid line) X-ray diffraction pattern for the synthesized $\gamma\text{-Ca}_3(\text{PO}_4)_2$ high-pressure phase. The observed data were collected with a wavelength of 0.70926 Å (Mo). Tick marks for the peak positions of the high-pressure phase are shown below the pattern. The difference curve is shown at the bottom. The refinement is based on the space group $R\text{-}\bar{3}m$ with trigonal cell parameters, $a = 5.2576(2)$ Å and $c = 18.7049(13)$ Å.

phase in the Suizhou meteorite are $a = 5.258(1)$ Å, $c = 18.727(3)$ Å, space group $R\text{-}3m$, and density (calc.) = 3.447 (g/cm^3), where the numbers in parentheses are standard deviations in the last significant digits (Table 2). The structure refinements are based on crystal structural model for the $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase proposed by Sugiyama and Tokonami (1987).

4.2. Synthesized High-Pressure $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase

The run product of multi-anvil experiments contains a single phase with stoichiometric $\text{Ca}_3(\text{PO}_4)_2$ composition. We ob-

tained a Raman spectrum of this synthetic phase, which consists of one intense peak at 975 cm^{-1} , two less intense peaks at $410, 576\text{ cm}^{-1}$, and three weak peaks at $638, 1000$ and 1095 cm^{-1} (Fig. 2c). It indicates that the Raman spectrum of the synthesized $\text{Ca}_3(\text{PO}_4)_2$ phase is identical to the unknown phosphate phase in the shock vein of Suizhou (cf. Fig. 2). The x-ray diffraction data revealed that the synthetic $\text{Ca}_3(\text{PO}_4)_2$ phase has a trigonal unit cell with cell parameters of $a = 5.2576$ Å and $c = 18.7049$ Å, and density (calc.) = 3.452 (g/cm^3) (Table 2). The synthetic phase is identical to the high-pressure $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase found as a decomposition product of apatite

Table 2. Cell parameters of synthesized and natural $\gamma\text{-Ca}_3(\text{PO}_4)_2$ and natural $\beta\text{-Ca}_3(\text{PO}_4)_2$.

	Synthesized $\gamma\text{-Ca}_3(\text{PO}_4)_2$ [¶]	Synthesized $\gamma\text{-Ca}_3(\text{PO}_4)_2$ [†]	Natural $\gamma\text{-Ca}_3(\text{PO}_4)_2$ [†]	Natural $\beta\text{-Ca}_3(\text{PO}_4)_2$ [‡]
Space group	R-3m	R-3m	R-3m	R-3c
a (Å)	5.2487(6)	5.2576(2)	5.258(1)	10.37
c (Å)	18.6735(36)	18.7049(13)	18.727(3)	37.19
Volume (Å ³)	445.5(1)	447.7(6)	448.3(6)	
Chemical composition	$\text{Ca}_5(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2$	$\text{Ca}_3(\text{PO}_4)_2$
Z*	3	3	3	21
Density (calc.) (g/cm^3)	3.469	3.452	3.447	3.12
Density (meas.) (g/cm^3)	3.462	—	—	3.12

* Molecular number in the unit cell.

¶ Sugiyama and Tokonami (1987).

† Present study.

‡ Gopal et al. (1974).

at high pressure and temperature (Murayama et al., 1986; Sugiyama and Tokonami, 1987). Figure 3 shows the X-ray diffraction pattern for the synthetic high-pressure $\text{Ca}_3(\text{PO}_4)_2$ phase ($\gamma\text{-Ca}_3(\text{PO}_4)_2$). The structure refinements are also based on crystal structural model for the $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase proposed by Sugiyama and Tokonami (1987). The calculated pattern agrees very well with the observed X-ray diffraction data (Fig. 3).

5. DISCUSSION

It is obvious that the unit cell parameters for the trigonal phosphate phase in the Suizhou meteorite shock veins are comparable to the cell parameters of the synthetic high-pressure $\text{Ca}_3(\text{PO}_4)_2$ phase. On the basis of the Raman spectroscopic measurements and the X-ray diffraction data, we conclude that the phosphate phase in the shock veins of Suizhou has the same crystal structure as the synthesized $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase. Evidently, it is the first natural occurrence of the high-pressure $\gamma\text{-Ca}_3(\text{PO}_4)_2$ polymorph.

Although the shock veins are poorly developed in the Suizhou meteorite, the shock-induced P-T conditions in the thin veins were adequate to result in the formation of a series of high-pressure phases. The phase transition from plagioclase to the hollandite structural polymorph constrains the pressure and temperature in the shock vein to ~ 23 GPa and 2000°C (Xie et al., 2001b; Liu, 1978; Yagi et al., 1994; Gillet et al., 2000), although it is possible that the meteorite and shock veins experienced much higher pressures during the compression phase (Langenhorst and Poirier, 2000). Such P-T conditions developed in the veins were also available for the phase transformations of olivine to ringwoodite and pyroxene to majorite. The $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase in Suizhou resulted from the transformation of merrillite in the meteorite, as indicated by the compositional similarities of the high-pressure phase and the merrillite in the chondritic portion of Suizhou. Even though the phase diagrams in Murayama et al. (1986) indicate that the $\gamma\text{-Ca}_3(\text{PO}_4)_2$ forms at as low as 12 GPa, it would still be present at 20 GPa or higher. The P-T condition suggested by the phosphate phase is consistent with the P-T conditions indicated by the other high-pressure phases.

Like the Suizhou meteorite, the shock veins of the Sixiangkou meteorite contain abundant high-pressure minerals including ringwoodite, majorite, $\text{NaAlSi}_3\text{O}_8$ -hollandite, fine-grained majorite-pyrope garnet and magnesiowüstite, which set an upper bound for the P-T regime of the shock vein at 20 to 24 GPa and $\sim 2000^\circ\text{C}$ (Chen et al., 1996; Gillet et al., 2000). The high-pressure polymorph of chlorapatite in the shock veins of Sixiangkou has an identical compositions of chlorapatite in the Sixiangkou chondritic host and the high-pressure phase in the shock veins (Chen et al., 1995). The similarity of compositions of the host and shock vein chlorapatite indicates that chlorapatite was not devolatilized in the shock event. One might expect that the merrillite in the Sixiangkou should also have been transformed into a high-pressure polymorph. However, no phase transition from merrillite to the $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase is observed in the Sixiangkou shock veins (Chen et al., 1995). Experiments indicate that the transformation from whitlockite to $\gamma\text{-Ca}_3(\text{PO}_4)_2$ takes place at a pressure lower than 20 GPa (Murayama et al., 1986; Sugiyama and Tokonami, 1987). It,

therefore, shows that the shock-induced pressures both in the shock veins of Suizhou and Sixiangkou are sufficient for the phase transition from merrillite to $\gamma\text{-Ca}_3(\text{PO}_4)_2$. Considering that Sixiangkou was more severely shock-metamorphosed than Suizhou, and that the Sixiangkou shock veins are thicker and more abundant than those in Suizhou, we suggest that shock vein cooling history plays a key role in the quenching of the high-pressure polymorph of merrillite. Evidently, the thin shock veins in Suizhou cooled rapidly and preserved nearly all the shock-induced high-pressure phases, whereas a back transformation from $\gamma\text{-Ca}_3(\text{PO}_4)_2$ to merrillite took place in the slower-cooling Sixiangkou shock veins. In fact, Chen et al. (1995) observed a difference in the Raman spectra of the intact merrillite in the chondritic region and the merrillite in the shock veins of Sixiangkou, which could be a hint that $\gamma\text{-Ca}_3(\text{PO}_4)_2$ was created but then transformed back to merrillite.

The $\gamma\text{-Ca}_3(\text{PO}_4)_2$ phase has two large cation sites, a twelve-coordinated Ca (M1) site and a ten-coordinated Ca (M2) site, and the two sites are large enough for ionic substitution by larger lithophile elements deep in the terrestrial mantle (Sugiyama and Tokonami, 1987). The transformations from apatite to merrillite, and then to $\gamma\text{-Ca}_3(\text{PO}_4)_2$ are correlated positively to pressure. Apatite and whitlockite (or merrillite) are important minerals to host large lithophile elements and REE in the crust and shallower upper mantle. Thus, the discovery of natural $\gamma\text{-Ca}_3(\text{PO}_4)_2$ supports the idea that another phosphate polymorph could act as a host for larger lithophile elements such as REE, Sr and Ba in the deeper terrestrial mantle.

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