ORIGINAL ARTICLE

The discovery of TiO_2 -II, the α -PbO₂-structured high-pressure polymorph of rutile, in the Suizhou L6 chondrite

Xiande Xie¹ Xiangping Gu² · Ming Chen^{1,3}

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Abstract We report the discovery of TiO₂-II in the unmelted rock of the shocked Suizhou L6 chondrite. Natural TiO2-II was previously found in ultrahigh-pressure metamorphic and mantle-derived rocks, terrestrial impact structures, and tektite. Our microscopic, Raman spectroscopic, electron microprobe and transmission electron microscopic investigations have revealed: (1) All observed TiO₂-II grains are related with ilmenite and pyrophanite; (2) TiO₂-II occurs as needle- and leaf-shaped inclusions in ilmenite and patch-, tape-shaped body in pyrophanite; (3) The composition of TiO₂-II is identical with that of its precursor rutile; (4) The Raman spectrum of TiO₂-II is in good agreement with that of natural and synthesized α -PbO₂-type TiO₂; (5) TiO₂-II occurs mainly in the form of well-ordered nano-domains and small mis-orientation among the domains can be observed. (6) All electron diffraction reflections from TiO2-II can be indexed to a-PbO₂ structure in space group *Pbcn* with lattice parameters of a = 4.481 Å, b = 5.578 Å and c = 4.921 Å; (7) The exsolution inclusions of rutile from host ilmenite are mostly connected with an alternation process along the lamellar twinning plane of ilmenite induced by shock-

- ² School of Geosciences and Info-Physics, Central South University, Changsha 410083, China
- ³ State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

induced high pressure and high temperature; (8) The P-T regime of 20–25 GPa and 1000 °C estimated for the Suizhou unmelted rock is suitable for phase transition of rutile into TiO₂-II phase.

Keywords Rutile \cdot TiO₂-II \cdot High-pressure polymorph \cdot Shock metamorphism \cdot Suizhou meteorite

1 Introduction

Rutile is a common accessory mineral in various types of terrestrial and extraterrestrial rocks. TiO₂-II is a highpressure polymorph of rutile that was first synthesized by static compression experiment (Bendeliany et al. 1966) and by shock wave techniques (McQueen et al. 1967). The powder X-ray diffraction data show that TiO₂-II is isostructural with α -PbO₂-type TiO₂, space group *Pbcn*, synthesized by shock experiments (McQueen et al. 1967) and in-situ high-pressure experiments using a diamondanvil cell (Gerward and Olsen 1997). It was also revealed that TiO₂-II is the only high-pressure polymorph of rutile that can be recovered experimentally at ambient conditions (Wu et al. 2010).

The occurrence of natural TiO₂-II was previously reported in ultrahigh-pressure metamorphic rocks (Huang et al. 2000; Wu et al. 2005), mantle-derived rocks (Dobrzhinetskaya et al. 2009), terrestrial impact structures (El Goresy et al. 2001; Jackson et al. 2006; McHone et al. 2008; Chen et al. 2013), and tektite (Glass and Fries 2008), as well as in Neoarchean spherule layers (Smith et al. 2016), but no finding of TiO₂-II in meteorites was reported in the literature. In this paper, we report the discovery of

[⊠] Xiande Xie xdxie@gzb.ac.cn

¹ Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

 TiO_2 -II in a meteorite, namely, in the shocked Suizhou L6 chondrite.

2 Samples and analytical methods

The Suizhou L6 chondrite fell on April 15, 1986, at Dayanpo, Suizhou City, Hubei Province, China, This meteorite consists of olivine, low-Ca pyroxene, plagioclase, FeNimetal, troilite, merrillite, chlorapatite, chromite, ilmenite, pyrophanite, native copper, and shenzhuangite (Xie et al. 2001a, 2011; Xie and Chen 2016; Bindi and Xie 2017). Rutile is a very rare phase observed only inside some ilmenite and pyrophanite grains. The Suizhou meteorite was classified as a strongly shock-metamorphosed (S5) meteorite due to the presence of transformation of plagioclase to maskelynite (Xie et al. 2001a; 2011). This meteorite contains a few very thin shock-produced melt veins, and up to 14 high-pressure phases were identified inside or adjacent to these veins, among them, the ringwoodite, majorite, lingunite, magnesiowüstite and majorite-pyrope_{s s} are abundant constituent high-pressure phases, but tuite, xieite, chenmingite, wangdaodeite, hemleyite, asimowite, poirierite, hiroseite and elgoresyite are new highpressure minerals (Xie et al. 2001a, 2002, 2011, 2019; Chen et al. 2003, 2008; Ma et al. 2018; Xie and Chen 2016, Bindi et al. 2017, 2019, 2020, 2021; Tomioka et al. 2021).

Polished thin sections were prepared from fragments of the Suizhou meteorite. All observations and physical and chemical analyses are performed in-situ on thin sections. The mineral assemblages in polished sections of the samples were investigated by optical microscopy using a Leica DM2500p microscope. A Shimadzu 1720 electron microprobe (EPMA) was used to study the mineral occurrence in back-scattered electron (BSE) mode, and to quantitatively determine the chemical composition of minerals using the wave length dispersive technique at 15 kV accelerating voltage and beam current of 10 nA. Natural and synthetic phases of well-known compositions were used as standards, such as SiO₂ for Si, TiO₂ for Ti, Al₂O₃ for Al, Fe₃O₄ for Fe, and pure Mn, Nb, Ta, and the data were corrected using a ZAF program. Raman spectra of minerals in the polished thin sections were recorded with a Horiba Labram Aramis instrument. A microscope was used to focus the excitation beam (Ar+ laser, 633 nm line) to $1 \mu m$ wide spots and to collect the Raman signal. Accumulations of the signal lasted 300 s. The laser power was 2 mW. A focused ion (Ga+) beam (FIB) workstation equipped in the FEI Helios Nanolab 600i systems at the Center for Advanced Research of Central South University was used to cut a chip in sizes of 10 μ m \times 7 μ m \times 0.2 μ m, which was mounted onto the molybdenum sample holder and then sliced to a thickness of about 37 nm for transmission electron microscopy (TEM) observation. TEM and selected area electron diffraction (SAED) analyses were performed using Fei Titan G2 60–300 transmission electron microscope operated at 300 kV accelerating voltage.

3 Results

3.1 Occurrence

Rutile occurs in the Suizhou chondritic rock as acicular and leaf-shaped crystals inside ilmenite grains (Fig. 1). However, rutile grains are seldom preserved without transformation to TiO₂-II in the un-melted chondritic part of the Suizhou meteorite. Most of them have transformed to their high-pressure polymorph—TiO₂-II. Under a reflected light microscope, both rutile and TiO2-II can not be distinguished and shows a grayish color and brighter reflectance than coexisting ilmenite and pyrophanite in a specific polarized direction. Four types of occurrence of TiO₂-II, patch-shaped, tape-shaped, needle-shaped, and leaf-shaped grains are observed (Fig. 2): Fig. 2a shows two patchshaped grains of $8 \times 5 \,\mu m$ and $10 \times 4 \,\mu m$ in sizes in grain with a transition composition between ilmenite and pyrophanite. For the upper-left and the lower-right TiO₂-II grains, some lamella-like slices of TiO₂-II can be observed. Besides, a long tape-shaped grain of 20 µm in length and $2 \sim 3 \mu m$ in width is also observed in this grain. Figure 2b shows some large patch-shaped TiO₂-II grains up to $30 \times 12 \ \mu m$ in size, and a few tape-like grains of rutile. Figure 2c displays a needle-like TiO₂-II of 30 µm in length and 1-2 µm in width in a fractured ilmenite grain, and it crosses the whole ilmenite grain. Figure 2d shows two leafshaped TiO₂-II grains of 20 and 16 µm in length, and a



Fig. 1 Acicular crystal of rutile in ilmenite surrounded by kamacite, troilite, and olivine, the line with TEM indicates the position of the TEM chip

Fig. 2 Reflected light photomicrographs showing different occurrences of TiO2-II in ilmenite (Ilm) and pyrophanite (Pyn) grains. a Patch-shaped TiO₂-II grains developed on both tops of pyrophanite and ilmenite grain and a tape-like TiO2-II grain in the middle part of this grain. b Patch-shaped TiO₂-II grains in pyrophanite. c a TiO₂-II needle in an ilmenite grain. d Two leafshaped and needle-like TiO2-II grains in ilmenite. Cr = chromite, Olv = olivine,Msk = maskelvnite. FeNi = FeNi metal, Tro = troilite, Ru = rutile, Feoxide = amorphous Fe-oxide: The crosspoints with numbers 1, 2, and 3 refer to the positions of **EPMA**



needle-shaped TiO₂-II of 40 μ m in length and 1.5–2 μ m in width. Interestingly, all TiO₂-II-bearing ilmenite grains we observed in the Suizhou meteorite are surrounded by FeNi metal or FeNi metal + troilite and olivine.

3.2 Chemical composition

Quantitative analytical results of chemical compositions of TiO_2 -II are given in Table 1. The compositions of TiO_2 -II are similar to that of rutile that occurred in many meteorites (Ramdohr 1973) and Xiuyan impact crater (Chen et al. 2013). The TiO_2 -II in Suizhou meteorite contains dominating TiO_2 with minor amounts of FeO (up to 2.06 wt%), MgO (up to 0.39 wt%), MnO (up to 0.97 wt%), Cr₂O₃ (up

to 0.69 wt%) and Nb₂O₅ (up to 0.17 wt%). The empirical formula of TiO₂-II (based on total atoms = 3 *apfu*) can be written as $(Ti_{0.966}Fe_{0.023}Mn_{0.006}V_{0.006}Cr_{0.005}Mg_{0.004}Si_{0.001}Al_{0.001})_{1.013}O_{1.987}$. The simplified formula is TiO₂. This implies that TiO₂-II is formed from rutile by solid-state phase transformation under pressure.

3.3 Raman spectroscopy

Although the size of the TiO_2 -II phase in the Suizhou meteorite is small and thin, and it closely coexists with ilmenite and pyrophanite, we could obtain good enough Raman spectra of TiO_2 -II phase since this phase exhibits strong Raman scattering. Figure 3 shows the Raman

Table 1	Composition of TiO ₂ -				
II in the	Suizhou meteorite				

Sample ^a	TiO ₂	SiO ₂	Al_2O_3	Nb ₂ O ₅	V_2O_3	Cr ₂ O ₃	FeO	MgO	MnO	Total
1	92.97	0.04	0.10	0.00	0.54	0.55	3.71	0.39	0.97	99.33
2	99.41	0.06	0.08	0.17	0.61	0.21	0.94	0.00	0.21	101.68
3	95.81	0.08	0.08	0.06	0.56	0.69	1.52	0.19	0.44	99.42
Average	96.06	0.06	0.09	0.08	0.57	0.48	2.06	0.19	0.54	100.14

^aPositions of sample numbers are shown in Fig. 2a, b



Fig. 3 Raman spectra of TiO_2 minerals in the Suizhou meteorite. **a** From a patch-shaped TiO_2 -II on the up-right top of Fig. 2a with strong band of ilmenite (691 cm⁻¹) and that of rutile (612 cm⁻¹), **b** From a TiO₂-II needle shown in Fig. 2c. Note the 609 cm⁻¹ band of rutile is very strong. **c** From a leaf-shaped TO₂-II grain shown in Fig. 2d with a minor amount of ilmenite and rutile. **d** Rutile coexisting with TiO₂-II, **e** Ilmenite coexisting with TiO₂-II

spectra of TiO₂-II, rutile, and ilmenite in the Suizhou meteorite. Raman spectra of TiO₂-II in Fig. 3a, b, c display well-defined peaks at 152–154 (m), 170–174 (s), 315–317 (w), 336–341 (m), 428–431 (vs), 441–447 (vs, sh), which are distinct from that of rutile at 142 (w), 238 (m, bd), 355 (w), 450 (w) and 612 (vs) cm⁻¹ (Fig. 3d) (vs = very strong, s = strong; m = medium; w = weak; sh = shoulder, bd = broad). The spectrum of TiO₂-II is in good agreement with that of α -PbO₂-type TiO₂ found in shock-metamorphosed rutile in the Xiuyan impact crater (Chen et al. 2013) and that of TiO₂-II synthesized at static high pressures (Mammone et al. 1981). However, the presence of rutile peaks (608–612 cm⁻¹) on the Raman spectra of Suizhou TiO₂-II implies that some host rutile relict remained in TiO₂-II grains.

3.4 Crystallography

The crystal structure of TiO₂-II was determined by Filatov et al. (2007) using the single-crystal x-ray diffraction analysis, which is different from that of rutile. In both structures of TiO₂-II and rutile, chains of edge-sharing TiO₂ octahedra along the *c*-axis are connected through two vertices of each octahedron, forming the three-dimensional framework. An obvious difference in the structure between TiO₂-II and rutile lies in that the TiO₂-II structure consists of zigzag edge-sharing TiO₆ octahedral chains instead of straight edge-sharing octahedral chains as in rutile.

Since the grains of both rutile and TiO_2 -II in the Suizhou meteorite are very thin and small, we could obtain their crystallographic data only by TEM observations. The results of our observations are described as follows.

3.4.1 TEM observations of rutile

A chip of needle-like rutile embedded in ilmenite prepared from focused ion beam (FIB) thinning is observed by TEM. Representative results are shown in Fig. 4. Figure 4a is the bright field image of needle-like rutile in ilmenite shown in Fig. 1, and Fig. 4b is the selected area electron diffraction (SAED) pattern of rutile along the zone-axis [100], which shows that all reflections are elongated indicating a deformed rutile structure. All reflections from rutile can be indexed to tetragonal structure in space group $P4_2/mnm$. Figure 4c is the high-resolution transmission electron microscopy (HRTEM) image of the needle-like rutile, in which the well-developed (hk0) stacking faults are observed. Figure 4d is the fast Fourier transform (FFT) pattern of rutile along the [010] zone-axis. Fig. 4 TEM images of rutile in the Suizhou meteorite. **a** Bright field image of TiO_2 rutile needle in ilmenite. **b** SAED pattern of TiO_2 rutile along the zone-axis [100]. **c** HRTEM image of rutile. Note the well-developed (hk0) stacking faults. **d** Fast Fourier transform (FFT) pattern of rutile along [010] zone-axis



3.4.2 TEM observations of TiO₂-II

Chips of TiO₂-II phase embedded in pyrophanite prepared from focused ion beam (FIB) thinning are observed by TEM, Representative results are shown in Fig. 5. Figure 5a is the bright field image of the patch-shaped TiO₂-II grain shown in Fig. 2a, and the Fig. 5b is the SAED pattern of TiO₂-II along [010] zone-axis. All reflections from TiO₂-II can be indexed to α -PbO₂ structure in space group Pbcn with lattice parameters of a = 4.581 Å, b = 5.578 Å, $c = 4.921 \text{ Å}, V = 125.74 \text{ Å}^3, Z = 4$. The spots pointed by arrows may be from diffuse reciprocal rods of the firstordered Laue zone. Figure 5c, d are HRTEM images and FFT patterns of patch-shaped TiO₂-II along the [010] zoneaxis, respectively. On the HRTEM image nano-domains with Pbcn symmetry are clearly shown, and small misorientation among the domains can be detected. FTT image from some TiO2-II domains looks well-ordered and do not show extra spots that violate the c-glide. However, in some boundary/interface areas it shows spots that violate the c-glide.

The structure data obtained for TiO₂-II in the Suizhou meteorite using the electron diffraction method are consistent with those obtained for the shock-induced TiO₂-II in the Xiuyan impact crater using micro X-ray diffraction analyses, which showed an α -PbO₂-type *Pbcn* structure and lattice parameters of a = 4.543(1)Å, b = 5.491(9)Å, c = 4.895(2)Å, V = 122.1(4) Å³, Z = 4. (Chen et al. 2013). The slight difference in cell parameters between TiO₂-II in the Suizhou chondrite and Xiuyan impact crater can be explained by the difference in the precision of measurement.

4 Discussion and conclusion

Ramdohr (1973) reported that almost all ilmenite grains in meteorites show marked lamellar twinning caused by pressure, and they sometimes contain exsolution inclusions of another mineral, probably caused by twin lamellation, He mentioned that rutile in many normal chondrites is often associated with ilmenite and chromite, sometimes intimately intergrown, frequently as large individual Fig. 5 TEM images of patchshaped TiO₂-II in the Suizhou meteorite. **a** Bright field image of patch-shaped TiO₂-II with α -PbO₂-type *Pbcn* structure. **b** SAED pattern of TiO₂-II along [010] zone-axis, **c** HRTEM image of TiO₂-II. Note the square area on its upleft is for FFT analysis **d** FFT pattern of TiO₂-II along [010] zone-axis



grains. The inclusion of rutile in ilmenite is mostly connected with an alternation process, but very thin lamellae of rutile can be present in ilmenite without recognizable signs of an alternation. He also reported that ilmenite grains in many chondrites contain a few straight and very thin lamellae of rutile, often only one, crossing the whole ilmenite grain.

Ilmenite, FeTiO₃, is one of the accessory opaque minerals in the Suizhou L6 chondrite. It occurs in association with troilite, chromite, and FeNi metal as small grains of irregular shape with grain sizes less than 20–30 μ m. The ilmenite content in this meteorite is only about 20 ppm by volume. Our TEM study revealed that ilmenite in the Suizhou meteorite also shows marked lamellar twinning caused by shock-induced pressure, and a straight fracture in parallel with the lamellar twinning is visible. Rutile in the Suizhou chondrite is associated with ilmenite as inclusions and most rutile grains have transformed to TiO₂-II. Based on the occurrences of TiO₂-II and its close relations with ilmenite, we assume that all four types of TiO₂-II occurrence are consistent with that of rutile in many other chondrites described by Ramdohr (1973).

The replacement structure of ilmenite in Suizhou can be seen in Fig. 2a, where the two patch-shaped TiO₂-II grains show lamellar structure. This implies that the replacement process would have started at the tiny exsolution lamellae of precursor rutile. The occurrence and the form of the replacement of ilmenite by precursor rutile would presume the reaction proposed by Ramdohr (1973): 2 FeTiO₃ + C (as a hydrocarbon) = 2 Fe + 2 TiO₂ + CO₂. A similar alternation mechanism can be explained for the formation of leaf-shaped TiO₂ -II grains shown in Fig. 2d. As for the thin and straight needle-like TiO₂-II shown in Fig. 2c and the tape-like TiO₂-II shown in Fig. 2a, no signs of alternation were observed. This can be explained by the exsolution of TiO₂ along one of the rhombohedron faces (Ramdohr 1973) or in parallel with the lamellar twinning plane of ilmenite caused by shock-induced pressure and temperature.

After Bendeliany et al. (1966) first synthesized TiO_2 -II by static compression experiment, several high-pressure experiments revealed that rutile can be transformed not only into a high-pressure polymorph of TiO_2 -II (α -PbO₂), but also into baddeleyite, orthorhombic I and cotunnite

phases with increasing pressure (Nishio-Hamane et al. 2010, and references therein), and the high-pressure polymorphs of baddeleyite, orthorhombic-I, and cotunnite-type TiO₂ would reverse to TiO₂-II on decompression. Several static compression experiments succeed in the transition of rutile to TiO₂-II at a pressure range between 4 and 12 GPa and temperature between 400 and 1500 °C (Bendeliany et al. 1966; Jamieson and Olinger 1968; Akaogi et al. 1992; Olsen et al. 1999; Withers et al. 2003). Shock-loading experiments revealed that rutile transforms to TiO₂-II at peak shock pressure from 20 to 100 GPa (McQueen et al. 1967; Linde and Decarli 1969; Kusaba et al. 1988). Based on shock compression experiments, Kusaba et al. (1988) proposed a displacive mechanism of phase transition to explain the shock-produced transformation of rutile to TiO₂-II, in which rutile first transforms by shock compression to a high-pressure polymorph, and then this polymorph instantly converts to TiO₂-II structure during decompression. Based on the static and shock compression experiments, it is reasonable to assume that the transition of rutile to TiO₂-II takes place at static high pressure of 4–12 GPa and high temperature of 400–1500 °C, and peak shock pressure from 20 to 100 GPa.

Wu et al. (2010) reported that TiO_2 -II is the only highpressure polymorph that can be recovered experimentally at ambient conditions. Therefore, the presence of natural TiO_2 -II in ultrahigh-pressure metamorphic rocks, mantlederived rocks, terrestrial impact structures, and tektite is quite understandable.

The Suizhou meteorite is a heavily shocked chondrite. Most of the plagioclase grains in Suizhou unmelted chondritic rock display isotropic nature indicating these grains have transformed into maskelynite, a melted plagioclase glass. This indicates that the Suizhou unmelted rock experienced a peak shock pressure of 20–25 GPa and a temperature of 1000 °C (Xie et al. 2001b, 2011; Xie and Chen 2016). This shock-induced P-T regime in the Suizhou unmelted chondritic rock is suitable for the phase transition of rutile into the TiO₂-II phase because it falls in the P-T range of such phase transition determined by both static and shock-loading experiments.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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