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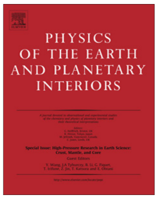

Thermodynamic investigation on β- and γ-$Ca_3(PO_4)_2$ and the phase equilibria

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ABSTRACT

γ-$Ca_3(PO_4)_2$, naturally known as tuite, is regarded as an important potential reservoir for rare earth elements and large ion lithophile elements. It is a high-pressure polymorph of β-$Ca_3(PO_4)_2$ whitlockite and a decomposed product of apatite under high-pressure and temperature. Drop-solution enthalpies of β- and γ-$Ca_3(PO_4)_2$ were obtained as 298.59 ± 3.02 and 278.74 ± 2.98 kJ/mol, respectively, by the drop-solution calorimetry with $2PbO{\cdot}B_2O_3$ solvent at 978 K. Thus the enthalpy of transition from β- to γ-$Ca_3(PO_4)_2$ at 298 K ($\Delta H^o_{tr,298}$) was 19.85 ± 4.24 kJ/mol. The isobaric heat capacities of β- and γ-$Ca_3(PO_4)_2$ were measured at temperature range of 300–770 K by differential scanning calorimetry, and compared with the results calculated from the Kieffer model. The equilibrium phase boundary between β- and γ-$Ca_3(PO_4)_2$ was calculated using present measured data combined with other available thermochemical and thermoelastic data. The calculated boundary gave a phase transition boundary with a dP/dT slope of 4.7 ± 0.2 MPa/K in the temperature range of 900–2000 K. Based on the phase relationship, the occurrences of tuite and whitlockite in meteorites are discussed.

1. Introduction

In the interiors of terrestrial planets, phosphorus usually exists as phosphate. Tricalcium phosphate ($Ca_3(PO_4)_2$), one of the most important phosphates, has four polymorphs. These polymorphs include α′-$Ca_3(PO_4)_2$, which is stable above 1430 °C, α-$Ca_3(PO_4)_2$, which is stable between 1125 and 1430 °C, and β-$Ca_3(PO_4)_2$, which is stable below 1125 °C (Nurse et al., 1959; Welch and Gutt, 1961; Fix et al., 1969). β-$Ca_3(PO_4)_2$ was initially labeled as whitlockite (Frondel, 1941) and belongs to the rhombohedral symmetry with space group of *R*3*c* (Gopal and Calvo, 1972; Prewitt and Rothbard, 1975; Dowty, 1977). It is well known that whitlockite is a common phosphate in lunar rocks and meteorites (Griffin et al., 1972; Buchwald, 1984; Delaney et al., 1984; Lundberg et al., 1988; McCoy et al., 1992; Heide and Wlotzka, 1995; Rojkovič et al., 1997; Zinovieva et al., 1999; Anand et al., 2003; Walton and Spray, 2003; Szurgot et al., 2009; Ángeles et al., 2010). The remaining polymorph, γ-$Ca_3(PO_4)_2$, is a high-pressure phase first synthesized from β-$Ca_3(PO_4)_2$ at 4 GPa and 1223 K (Roux et al., 1978). γ-$Ca_3(PO_4)_2$ was later found as a decomposed product of hydroxylapatite and fluorapatite at approximately 12 GPa and 1500 K (Murayama et al., 1986). The crystal structural refinement shows that γ-$Ca_3(PO_4)_2$ is rhombohedral with a space group of *R*-3*m* (Sugiyama and Tokonami, 1987). In Suizhou L6 chondrite, a natural γ-$Ca_3(PO_4)_2$ was discovered (Xie et al., 2001, 2002) and named tuite. It was found to form by an isochemical solid-state phase transition of whitlockite under pressure and temperature conditions of up to 23 GPa and 2273 K (Xie et al., 2003).

Since apatite and whitlockite can accommodate a large amount of rare earth elements and large ion lithophile elements, γ-$Ca_3(PO_4)_2$ is regarded as an important potential reservoir for rare earth elements and large ion lithophile elements in the deep mantle of the earth and the moon. The phase relations of apatites have been experimentally investigated and the equilibrium between β- and γ-$Ca_3(PO_4)_2$ was also approximately calculated by Murayama et al. (1986). In their calculation, the thermochemical data for γ-$Ca_3(PO_4)_2$ was deduced from assumptions because no enough thermodynamic parameters were available.

In this study, we have measured enthalpies of solution and heat capacities of β- and γ-$Ca_3(PO_4)_2$ to investigate the phase equilibrium between both phases. Based on the phase relation of β- and γ-$Ca_3(PO_4)_2$, the pressure and temperature conditions for formations of whitlockite and tuite in meteorites are discussed.

2. Experimental

2.1. Sample preparations

The samples for calorimetric and heat capacity measurements were synthesized by solid-state reaction. A powdered mixture of

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reagent-grade $CaHPO_4$ and $CaCO_3$ in a proportion corresponding to the $Ca_3(PO4)_2$ stoichiometry was ground finely and pressed into pellets with a diameter of 5 mm under a uniaxial pressure of 30 MPa. The pellets were sintered in a conventional muffle furnace at 1300 K for 48 h to form a single phase of β-$Ca_3(PO_4)_2$ which was confirmed by a powder X-ray diffractometer (Rigaku's SmartLab) equipped with a rotating Cu anode operated at 40 kV and 30 mA. Using β-$Ca_3(PO_4)_2$ as starting material, γ-$Ca_3(PO_4)_2$ was synthesized at 7 GPa and 1500 K for 24 h in the Kawai-type double-staged multianvil apparatus (USSA-5000) installed at the Institute for Study of the Earth's Interior, Okayama University. The synthesized γ-$Ca_3(PO_4)_2$ was also identified to be a single phase by powder X-ray diffraction. Following the procedure described by Ono et al. (2009), Raman spectra of β- and γ-$Ca_3(PO_4)_2$ samples were collected by JASCO NRS-3100 using a Nd:YAG laser with a wavelength of 532 nm at Gakushuin University.

Table 1
Measured drop-solution enthalpies of samples in $2PbO{\cdot}B_2O_3$ solvent at 978 K.

γ-$Ca_3(PO_4)_2$		β-$Ca_3(PO_4)_2$	
Weight (mg)	ΔH^o_{d-s} (kJ mol^{-1})	Weight (mg)	ΔH^o_{d-s} (kJ mol^{-1})
2.908	281.92	2.617	303.39
2.733	282.05	2.762	295.43
2.728	278.28	2.691	297.85
2.679	278.41	2.769	304.85
2.731	282.71	2.851	295.90
2.750	269.42	2.785	292.90
2.685	278.53	2.753	296.48
2.567	278.59	2.580	301.88
Average	278.74 ± 2.98	Average	298.59 ± 3.02

Errors are twice the standard deviations of the mean.

2.2. Enthalpy and heat capacity measurements

Drop-solution enthalpy measurements were carried out using a Calvet-type twin micro-calorimeter (Setaram HT1000) at Gakushuin University. The procedure is described elsewhere (Kojitani et al., 2009, 2012). The calorimeter temperature was kept at 978 K in the present study. A lead borate solvent of $2PbO{\cdot}B_2O_3$ (about 5 g), prepared by following the procedure of Charlu et al. (1975), was kept in a Pt crucible. The Pt crucible was put in an Inconel liner with a SiO_2 protection test tube. The assembly was inserted into the calorimetric chamber. The Ar gas bubbling method, with the flow rate of 5 cm^3 min^{-1}, was adopted for stirring the solvent well. Using a die, the powdered samples were compressed into 1.3 mm diameter pellets. In each run, a pellet sample of 2.6–2.9 mg was dropped from outside of the calorimeter (at 298 K) into the solvent in the calorimeter. Both β- and γ-$Ca_3(PO_4)_2$ samples were completely dissolved in the solvent within about 2 h. Obtained drop-solution enthalpies (ΔH_{d-s}) were calibrated by a drop-solution enthalpy of α-Al_2O_3. ΔH_{d-s} (α-Al_2O_3) of 106.67 ± 0.51 kJ/mol used as the standard value was the average of 87 measured data points (Kojitani et al., 2009) determined by a differential drop-solution method (Akaogi et al., 1995).

The heat capacity at constant pressure (*Cp*) of the samples was measured at 1 atm using a differential scanning calorimeter (Perkin Elmer, Diamond DSC). The γ-$Ca_3(PO_4)_2$ powder

Table 2
Measured heat capacities for γ- and β-$Ca_3(PO_4)_2$.

γ-$Ca_3(PO_4)_2$				β-$Ca_3(PO_4)_2$			
T (K)	*Cp* (J mol^{-1} K^{-1})	*T* (K)	*Cp* (J mol^{-1} K^{-1})	*T* (K)	*Cp* (J mol^{-1} K^{-1})	*T* (K)	*Cp* (J mol^{-1} K^{-1})
303	222.9	483	270.7	303	224.0	483	272.3
308	224.7	488	271.4	308	226.0	488	273.1
313	226.5	493	272.2	313	227.6	493	274.3
318	228.7	498	273.1	318	229.7	498	275.2
323	231.2	503	273.7	323	231.7	503	276.1
328	232.8	508	274.7	328	233.5	508	276.9
333	235.1	513	275.7	333	235.2	513	277.9
338	236.8	518	276.2	338	236.8	518	278.8
343	237.8	523	277.0	343	238.7	523	279.7
348	239.0	528	277.8	348	240.2	528	280.4
353	241.4	533	278.8	353	241.8	533	281.1
358	243.0	538	279.1	358	243.6	538	281.9
363	244.4	543	280.2	363	245.0	543	282.7
368	245.3	548	280.7	368	246.5	548	284.8
373	246.8	555	281.3	373	248.2	555	285.4
378	247.6	565	282.9	378	249.3	565	286.9
383	248.6	575	284.4	383	250.7	575	288.3
388	249.8	585	285.7	388	252.1	585	289.6
393	251.0	595	287.2	393	253.5	595	290.8
398	252.0	605	288.4	398	254.5	605	291.9
403	252.8	615	289.8	403	255.4	615	293.3
408	254.1	625	291.3	408	256.9	625	294.4
413	255.6	635	291.8	413	258.1	635	295.5
418	256.5	645	293.6	418	259.9	645	297.2
423	257.4	655	294.6	423	260.9	655	298.2
428	258.7	665	295.7	428	261.7	665	299.9
433	259.6	675	297.0	433	263.1	675	300.9
438	260.8	685	298.2	438	264.4	685	301.9
443	262.1	695	299.2	443	265.5	695	303.2
448	263.0	705	300.3	448	266.5	705	304.2
453	264.4	715	301.4	453	267.2	715	305.3
458	265.4	725	302.3	458	267.8	725	306.5
463	266.5	735	302.9	463	269.3	735	307.3
468	267.5	745	304.3	468	270.0	745	308.9
473	268.3	755	305.4	473	270.1	755	309.9
478	269.2	765	306.4	478	271.3	765	311.0