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Abstract

In situ observations of the zircon-reidite transition in $ZrSiO_4$ were carried out using a multianvil high-pressure apparatus and synchrotron radiation. The phase boundary between zircon and reidite was determined to be P (GPa) = 8.5 + 0.0017×(T-1200) (K) for temperatures between 1100-1900 K. When subducted slabs, including igneous rocks and sediments, descend into the upper mantle, zircon in the subducted slab transforms into reidite at pressures of about 9 GPa, corresponding to a depth of 270 km. Reidite found in an upper Eocene impact ejecta layer in marine sediments is thought to have been transformed from zircon by a shock event. The peak pressure generated by the shock event in this occurrence is estimated to be higher than 8 GPa.

Introduction

An understanding of the distribution of the radiogenic elements U and Th in Earth's interior is necessary for understanding the Earth's thermal history. Zircon, $ZrSiO_4$, is one of the most important host minerals for U and Th. Thus, the behavior of the high-pressure phase of $ZrSiO_4$ may provide significant information

regarding the distribution of U and Th among high-pressure phases in Earth's deep interior. Moreover, it has been recognized that the dating of zircon plays an important role in understanding a wide range of processes, including the formation of the oldest crust (Compston and Pidgeon 1986; Bowering et al. 1989), material circulation in the mantle (Pilot et al. 1998), and the origin of ultrahigh-pressure metamorphic rocks (Katayama et al. 2001). Recently, metamorphic high-pressure minerals have been observed as inclusions within zircon grains. This indicates that zircon forms a good pressure container during retrogressive pressure release (Katayama et al. 2000). As zircon has a high resistance and stability under upper mantle conditions, it is also a good container for minerals of deep mantle origin, in a similar way to diamond. Glass and Liu (2001) reported that the high-pressure phase of $ZrSiO_4$, which is named reidite (Glass et al. 2002), was discovered in an upper Eocene impact ejecta layer in marine sediments. The crystal structure of the natural reidite was confirmed as a scheelite-type structure ($I4_1/a$). However, the pressure-temperature history of the impact event, which formed the reidite, is not clear. Understanding the stability field of zircon will contribute to an understanding of all of these issues.

Large-volume press experiments (Reid and Ringwood 1969; Tange and Takahashi 2002), shock experiments (Mashimo et al. 1983; Kusaba et al. 1985),

and diamond anvil cell experiments (Liu 1979; Knittle and Williams 1993; van Westrenen et al. 2004) have demonstrated that zircon undergoes a phase transition at high pressures. At pressures higher than 20 GPa, reidite dissociates into two dioxides, ZrO_2 and SiO_2 (Liu 1979; Tange and Takahashi 2002). Recently, Ono et al. (2004) reported that the phase transition from zircon to reidite occurs at 10 GPa, based on laser-heated diamond anvil cell experiments combined with synchrotron X-ray diffraction. However, the phase boundary between zircon and reidite was not determined precisely because X-ray diffraction data was only observed for temperature-quenched samples. It is known that the sample pressure often changes during the temperature quenching because of the effects of thermal expansion. Therefore, we have directly investigated zircon and reidite at pressures from 4 to 14 GPa and temperatures from 1100 to 1900 K, equivalent to upper mantle conditions. High-pressure and high-temperature X-ray diffraction measurements using strong synchrotron radiation are highly advantageous for phase equilibrium studies compared to the conventional quenching method, because, in this method, both the phase present and the pressure conditions are determined simultaneously. We have recently developed a multianvil assembly for X-ray diffraction measurement that provides stable conditions to 25 GPa and 2000 K for a sufficient duration (Ono et al. 2001; Katsura et al. 2003a). The purpose of

the present paper is to report the results of our studies of the zircon-reidite transition, which have been obtained by *in situ* X-ray observations using the multianvil and a synchrotron radiation source.

Experimental procedure

Experiments were performed at SPring-8, using a double-stage multianvil high-pressure apparatus: "*SPEED-Mk.II*". The *SPEED-Mk.II* apparatus consists of a cubic-type high-pressure vessel, a 1500 ton hydraulic press, and an energy dispersive X-ray diffraction system (Katsura et al. 2003b). The specimen assembly used in the present experiment is schematically illustrated in Fig. 1. The octahedral pressure medium comprised Cr_2O_3-doped MgO. A cylindrical Re-furnace inside a $LaCrO_3$-sleeve thermal insulator was used as a heater. The powdered sample was put into the Re-furnace, which was used as a sample chamber. Experimental details are described elsewhere (Ono et al. 2000). Temperatures were measured using a W3%Re/W25%Re thermocouple, the junction of which was placed on the outside of the sample chamber. No correction was made for the effect of pressure

on the thermocouple emf. Occasional temperature fluctuations around the set point were typically less than five degrees.

We used a starting material made of a fine powder of silica (SiO_2) + zirconia (ZrO2). The powdered sample was mixed with powdered platinum (Pt). Pt is a pressure standard, and also acts as a dilutant to reduce grain growth within samples at high temperature.

X-ray diffraction was conducted by the energy dispersive method using a white X-ray up to 150 keV, and a Ge solid-state detector in a transmitting geometry. The Bragg angle was fixed at 5.6 or 6.0 degrees to cover the main diffraction peaks of the sample and Pt. Typical exposure times were about 5-20 minutes, producing data of sufficient quality to identify the phase and to evaluate the unit cell parameters. The X-ray diffraction profile of the powdered mixture of the sample and Pt was acquired at a position close to the hot junction of the thermocouple. Pressure values were determined from the unit cell volume of Pt measured under each experimental condition, using the Pt equation of state (EOS) of Holmes et al. (1989) with the electronic thermal pressure correction of Tsuchiya and Kawamura (2002).

Results

First, pressure was applied to the sample by compressing it to the desired oil pressure. Next, the sample was heated slowly until it reached the desired temperature for a given oil pressure. After reaching the desired temperature, we made *in situ* measurements using the synchrotron X-ray for 5-70 minutes. Determination of the stable phase at each condition was carried out by observing the X-ray diffraction patterns emitted from the sample. After the identification of the stable phase, the sample was quenched by cutting off the electric power supply, resulting in a temperature drop to $<200\ ^{o}C$ in 2-5 s.

In the first experiment, z01, the sample was compressed to a load of about 12 GPa, and then heated. Below 800 K, broad peaks from the sample were observed because of the accumulated differential stress during the compression and the small grain size of the sample. When the temperature reached about 900 K, the sample started to transform to reidite. Finally, the temperature reached 1700 K and was kept stable for 70 minutes, and reidite was observed to remain. Typical diffraction patterns are reproduced in Fig. 2. In addition to the diffraction peaks of the $ZrSiO_4$ phases and Pt, there are several intense Pt fluorescence lines. However, there are sufficient diffraction lines that are free from interference to make it

possible to identify the $ZrSiO_4$ phase. Reidite was observed to remain on cooling to 300 K at constant oil pressure. In order to observe the transition from two oxides to zircon, the starting pressure for measurement was set to about 7 GPa in the second experiment, z02. Only the two oxides were present before the temperature was increased. The transition to zircon was observed at 1300 K. This procedure was repeated to investigate the phase boundary between zircon and reidite, and X-ray diffraction patterns of $ZrSiO_4$ polymorphs were collected at seven pressure and temperature conditions. Experimental results are summarized in Table 1.

The results of our determinations of the zircon and reidite stability fields are shown in Fig. 3. The transition boundary in Fig. 3 is represented by a linear equation

$$P\ (GPa) = 8.5(3) + 0.0017(14) \times (T - 1200)\ (K)$$

The uncertainty in the slope, dP/dT, is rather large because the range of experimental temperatures was narrow.

Discussion

Fig. 4 compares the experimental results of the $ZrSiO_4$ polymorph phases in this study with those reported by previous studies. The boundary found in this study is generally consistent with the large-volume press experiments using the heated method (Reid and Ringwood 1969; Tange and Takahashi 2002), and with the boundary estimated by Ono et al. (2004), who used the laser-heated diamond anvil cell method combined with synchrotron X-rays. However, the boundary in this study disagrees with those determined by room-temperature compression (Knittle and Williams 1993; van Westrenen et al 2004) and shock compression studies (Kusaba et al 1985). These studies indicated much higher transition pressures than that indicated by our results, and there is also a large discrepancy among them. The pressure discrepancy between this study and room-temperature compression experiments (Knittle and Williams 1993; van Westrenen et al 2004) indicates that the high-temperature heating played a fundamental role in overcoming kinetic effects of the phase transition from zircon to reidite. In the case of the shock experiments (Kusaba et al 1985), the duration at high-pressure and high-temperature was much shorter than that of the static compression experiment. It is generally accepted that the shock experiments is not a suitable

method for the determination of the phase boundary. Therefore, it seems that previous shock experiments were not able to determine the appropriate phase boundary between zircon and reidite.

In the case of dating rocks, U-Pb dating of zircon is useful for investigations of crustal and metamorphic environments. To obtain meaningful ages using this method, it is important that the U and Pb in the zircon remain in a closed system. However, our study indicates that zircon transforms to reidite under upper mantle conditions, and zircon may, therefore, no longer remain a closed system for U and Pb. Zircon can also occur in metamorphic rocks. Recently, ultrahigh-pressure metamorphic rocks have been reported. These rocks were subducted to mantle depths and returned to the surface. An occurrence of microdiamonds in the ultrahigh-pressure metamorphic rocks indicates that these rocks subducted into at least 120 km depth corresponding to 4 GPa which is a lower pressure boundary of diamond stability field (Sobolev and Shatsky 1990; Zhang et al. 1997). The maximum subducted depth of the ultrahigh-pressure metamorphic rocks is still unknown. As there is a possibility that the phase transition of zircon occurs in the upper mantle, zircon dating should be used with caution in investigations of ultrahigh-pressure metamorphic rocks.

Although reidite is not stable at ambient pressures, it was discovered in impact ejecta, most likely related to the Chesapeake Bay impact structure, recovered from Deep Sea Drilling Project-Ocean Drilling Program sites on the upper continental slope off New Jersey (Glass and Liu 2001). This occurrence of reidite implies that the shock event, which formed the reidite, produced high pressure conditions. According to our results and those of a previous study (Tange and Takahashi 2002), the stability field of reidite is from 8 to 20 GPa, with slight variations depending on the temperature of the shock event. Therefore, the presence of reidite indicates that the peak pressure of the shock event was higher than 8 GPa. Glass and Liu (2001) estimated that reidite formed at pressures between 20 and 90 GPa. However, our study indicates that reidite can crystallize at pressures lower than that estimated by Glass and Liu (2001). In the case of the impact ejecta, the reidite formation process remains unclear. There are two possible mechanisms for its formation. One is that reidite was transformed by a solid-state transition directly from the pre-existing zircon. Although this formation mechanism is similar to previous shock compression studies, these experimental results are useful to understand the formation of natural reidite. The second is that reidite crystallized from a shock-induced melt. This mechanism is quite different from that in previous shock compression studies. It is difficult to estimate the

pressure-temperature history of the shock event from only the $ZrSiO_4$ polymorph phase diagram because complex processes occur during shock events. In order to understand the formation mechanism, further investigations of the textures of the reidite and the host rock are needed.

Acknowledgments

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Table 1

Experimental conditions and results.

Run	P (GPa)	T (K)	t (min)	Products
z01	13.4(3)	1700	70	Reidite
z02	5.9(3)	1300	5	Zircon
z03	5.2(4)	1500	5	Zircon
z04	8.4(3)	1300	30	Zircon
z05	8.7(1)	1200	40	Reidite
z06	9.3(2)	1400	10	Reidite
z07	8.1(3)	1100	30	Zircon
z08	9.8(3)	1600	10	Reidite
z09	8.8(5)	1900	17	Zircon

Temperature fluctuations around the set point were within five degrees except for z09. A temperature uncertainty of z09 was 50 degrees. Errors in pressure are based on the standard deviations of lattice parameters calculated from different diffraction lines of Pt.

Figure captions

Fig. 1.

Schematic illustration of the cell assembly.

(1) Cr-doped MgO, (2) MgO rod, (3) thermocouple of W3%Re/W25%Re, (4) $LaCrO_3$ sleeve thermal insulator, (5) cylindrical Re-furnace, (6) Al_2O_3 rods, (7) sample.

Fig. 2.

Examples of x-ray diffraction profiles.

Upper, reidite at 9.3 GPa and 1400 K; Lower, zircon at 8.4 GPa and 1300 K. Abbreviations of peaks are as follows: Z, zircon; R, reidite; P, Pt; E, emissions from Pt.

Fig. 3.

Experimental results and a phase boundary determined by *in situ* observation.

Solid squares and circles represent conditions where zircon and reidite were stable, respectively.

Solid line is the inferred phase boundary between zircon and reidite.

Fig. 4.

Phase diagram for $ZrSiO_4$.

Abbreviations are as follows: a, zircon-reidite (this study); b, zircon-reidite (Ono et al 2003); c, decomposition of reidite (Tange and Takahashi 2003); d, decomposition of reidite (Liu 1979); e, zircon-reidite (van Westrenen et al 2003); f, zircon-reidite (Knittle and Williams 1993) g, zircon-reidite (Kusaba et al 1985); solid circle, reidite (Reid and Ringwood 1969).

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Fig. 1

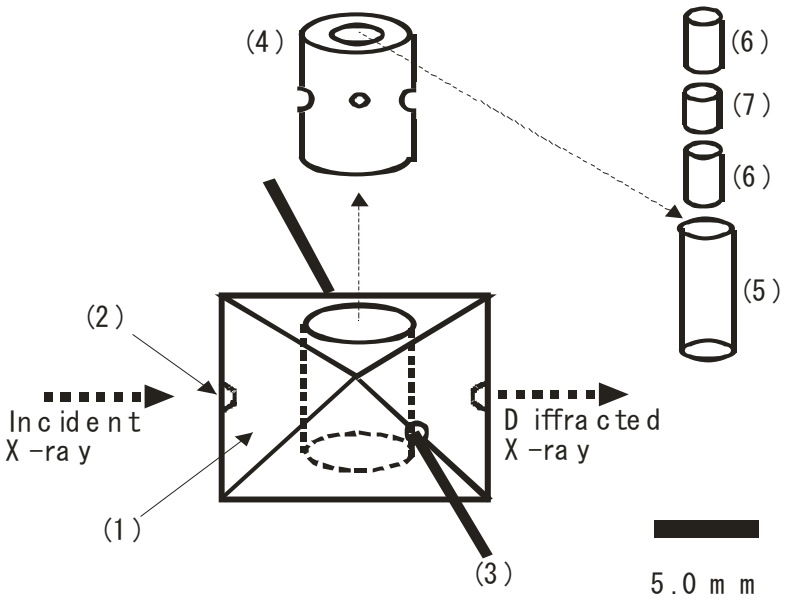

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Fig. 2

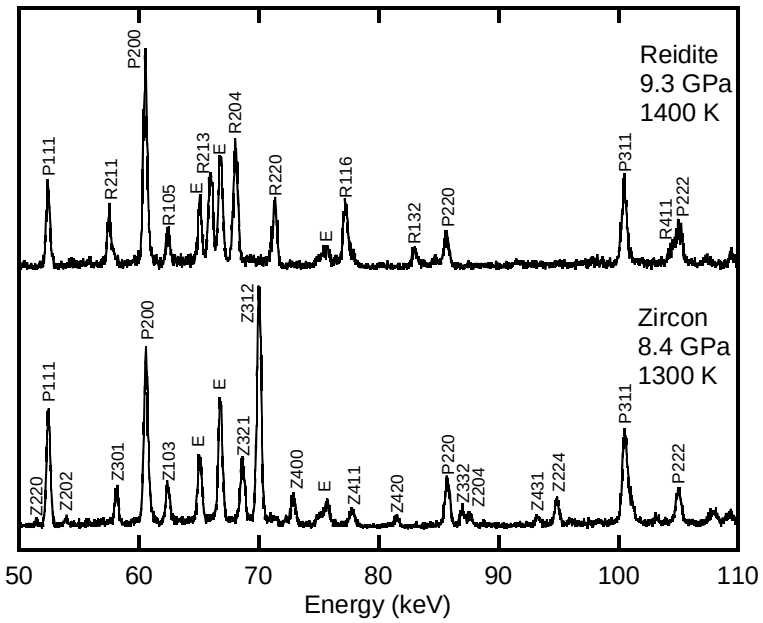

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Fig. 3

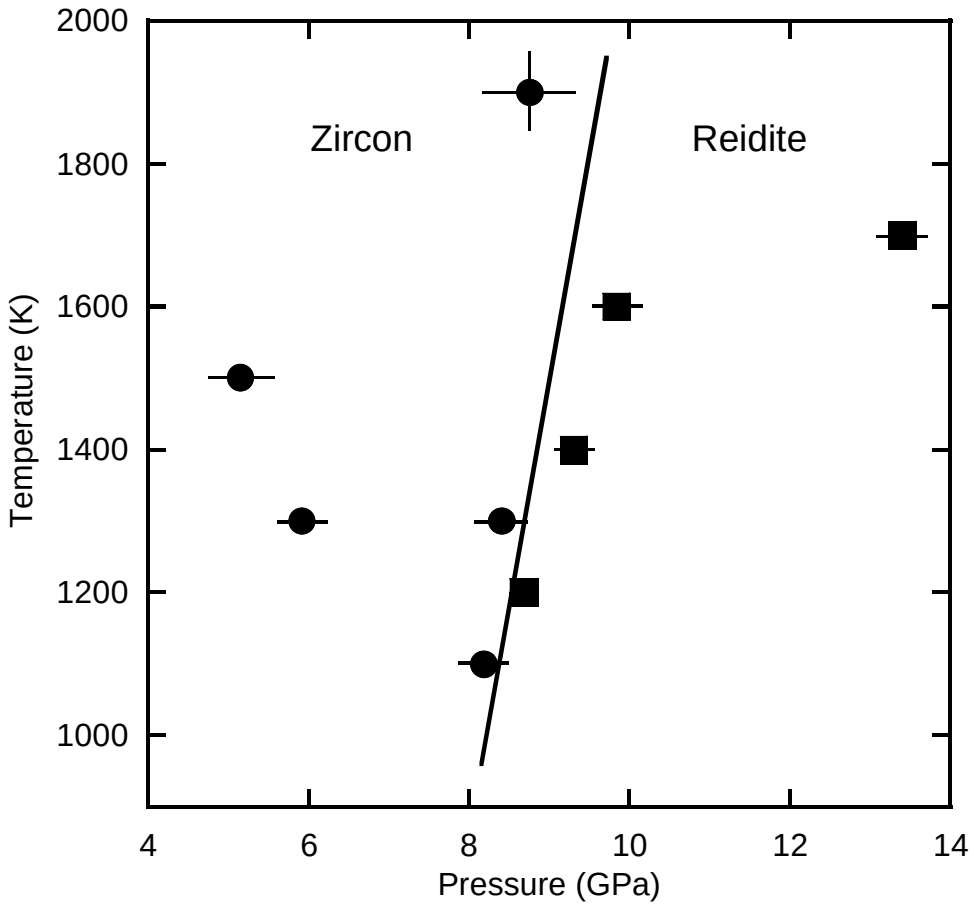

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Fig. 4