

High-PT study of solid solutions in the system $\text{ZrO}_2\text{-TiO}_2$: The stability of srilankite

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Abstract: The $\text{ZrO}_2\text{-TiO}_2$ phase diagram was studied with synthesis experiments between 1200°C and 1650°C, 1 atm and 28 kbar, investigating the effect of pressure on the compositions of rutile [TiO_2], zirconia [ZrO_2], and zirconium titanate [$(\text{Zr,Ti})_2\text{O}_4$] solid solutions. All three phases become more Ti-rich with increasing pressure, which is in good agreement with the smaller ionic radius of Ti^{4+} compared to Zr^{4+} , and consistent with the observed unit-cell volume of $(\text{Zr,Ti})_2\text{O}_4$. The range of zirconium titanate solid solution, which is limited to $X_{\text{Ti}} < 0.58$ at room pressure, was extended to $X_{\text{Ti}} = 0.68$ at 28 kbar and 1500°C. Thus the compounds $(\text{Zr,Ti})_2\text{O}_4$ [also referred to ZrTiO_4 when $X_{\text{Ti}} = 0.5$] and ZrTi_2O_6 (srilankite), which were previously regarded as the respective high- and low-temperature forms of zirconium-titanate, are both stable at high temperatures ($< 1200^\circ\text{C}$), and are part of the same solid solution that is continuous with pressure.

Srilankite ($X_{\text{Ti}} = 0.67$) formed at 1440°C and 28 kbar in equilibrium with rutile. This is the first synthesis of the phase at high pressures under equilibrium conditions. The stability of srilankite at high pressures and temperatures in our experiments contrasts with earlier studies that proposed a hydrothermal origin for the mineral, with an upper stability limit of 900°C. Our results, however, are consistent with the natural occurrence of srilankite in high-grade rocks such as eclogites, granulites, lamprophyres and chromitites. Our experiments show that the stability of zirconium titanate is also strongly dependent on oxygen fugacity.

Key-words: srilankite, $(\text{Zr,Ti})_2\text{O}_4$, ZrTiO_4 , solid solution, phase diagram, high-pressure study.

Introduction

The binary system $\text{ZrO}_2\text{-TiO}_2$ has received much attention in the past because it hosts a variety of phases of industrial interest, such as the polymorphs of zirconia [ZrO_2], titania [TiO_2] and zirconium-titanate [$(\text{Zr,Ti})_2\text{O}_4$ with $X_{\text{Ti}} \approx 0.5$], and their respective solid-solutions. For example, the different types of zirconia are known to form ceramics of extreme toughness, resistance to temperature and corrosion, and oxygen conductivity (Somiya *et al.*, 1988). Titania, in the form of rutile, is used as pigment, abrasive material, and dielectric ceramic. Zirconium-titanate is employed as a temperature-stable dielectric material for ceramic capacitors (Wolfram & Göbel, 1981; Azough *et al.*, 1996; Wang *et al.*, 1997), and more recently became important as a stable oscillator at microwave frequencies, used in satellite communication such as cell phones and GPS. The industrial use of $(\text{Zr,Ti})_2\text{O}_4$ motivated numerous studies of its structure, stability, and physical properties.

The $\text{ZrO}_2\text{-TiO}_2$ system is also of relevance for geologists interested in the composition and stability fields of accessory minerals such as baddeleyite (monoclinic ZrO_2), rutile (tetragonal TiO_2), srilankite (ZrTi_2O_6), as well as calzirtite ($\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$) and zirconolite ($\text{CaZrTi}_2\text{O}_7$). Only recently have petrologists started to decipher the stability of zirconium-bearing minerals as a potential tool for the reconstruction of petrogenetic conditions (Bingen *et al.*, 2001; Degeling *et al.*, 2001; Ferry *et al.*, 2002).

Despite the abundance of room pressure experiments in the classical ceramic system $\text{ZrO}_2\text{-TiO}_2$, experiments at elevated pressures are scarce, which prompted this study. Moreover, many previous studies focussed on the synthesis of certain $\text{ZrO}_2\text{-TiO}_2$ compounds regardless of whether or not thermodynamic equilibrium was reached in the experiments, thus rendering these data less useful for the study of phase equilibria in natural rocks. By providing data on the simple $\text{ZrO}_2\text{-TiO}_2$ binary at various pressures, this study represents a starting point for future work aimed at more complicated chemical systems that more closely approach natural conditions.

Although the $\text{ZrO}_2\text{-TiO}_2$ phase diagram is well characterised at room pressure above 1200°C (Coughanour *et al.*, 1954; Brown & Duwez, 1954; Noguchi & Mizuno, 1968; Ono, 1972; Shevchenko, 1980), slow reaction rates below 1200°C make equilibrium experiments using the oxides impossible (McHale & Roth, 1986). That is why many alternative low-temperature synthesis methods were explored for Zr-Ti ceramics, such as aqueous and sol-gel processes (Bianco *et al.*, 1998) and ball-milling (Kong *et al.*, 2002), all of which were prone to result in the formation of metastable phases, and thus cannot be used for

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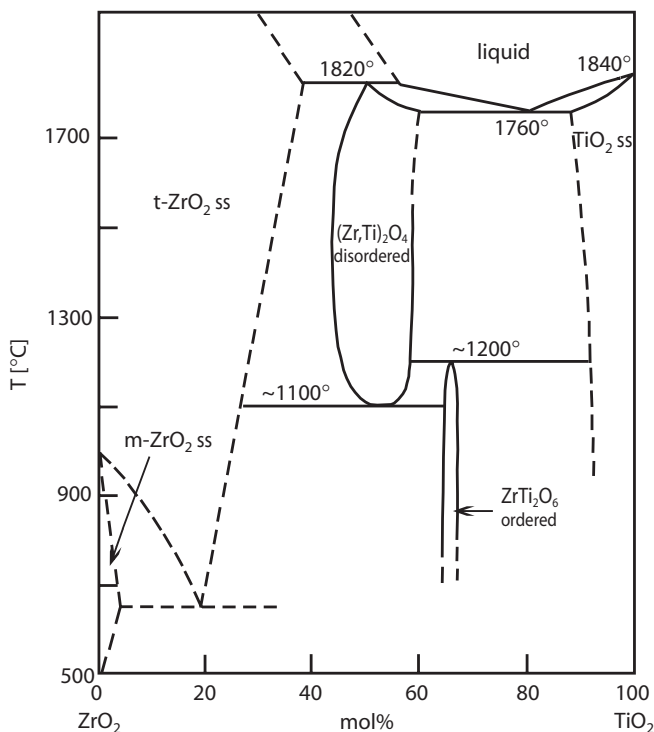


Fig. 1. ZrO₂-TiO₂ phase diagram based on McHale & Roth (1986). Dashed lines are inferred. ss = solid solution, t = tetragonal, m = monoclinic. 'Disordered' and 'ordered' refer to distribution of Zr and Ti in crystal structure, see text.

phase equilibrium studies. Experimental data collected at near-equilibrium conditions are essentially lacking below 1200°C, which is unfortunate given that most geological and some ceramic manufacturing processes occur at these temperatures. For example, the petrogenetic conditions of the formation of the mineral srilankite [ZrTi₂O₆] are still object of discussion, as this phase does not occur in the room pressure ZrO₂-TiO₂ phase diagram as we know it.

The most recent experimental ZrO₂-TiO₂ phase diagram by McHale & Roth (1986) suggests that disordered (Zr,Ti)₂O₄ is stable above 1100°C (Fig. 1), with a maximum compositional range of about $0.41 < X_{\text{Ti}} < 0.53$ at 1700°C (Noguchi & Mizuno, 1968). This high-temperature phase crystallizes in the orthorhombic α -PbO₂ structure (Blasse, 1966; Newnham, 1967), space group *Pbcn*, and is characterised by the random distribution of Zr and Ti atoms on the octahedral sites. Below 1200°C, McHale & Roth (1986) proposed that an ordered and more Ti-rich phase, ZrTi₂O₆ ($X_{\text{Ti}} = 0.67$), is stable (Fig. 1) based on the results of low-T annealing experiments of disordered (Zr,Ti)₂O₄ with $X_{\text{Ti}} = 0.5$. Ordering of their sample was indicated by the formation of superstructure reflections indicative of a fersmite-type structure AB₂O₆, with a tripled *a*-dimension compared to the disordered polymorph. The change in composition during the ordering process from $X_{\text{Ti}} = 0.5$ to $X_{\text{Ti}} = 0.67$ was inferred by McHale & Roth (1986) from the structure type AB₂O₆ as well as small amounts of exsolved ZrO₂ in the sample. However, the ordered compounds exact composition was not determined directly. Its uncertainty was highlighted by

the finding that also Zr₅Ti₇O₂₄ ($X_{\text{Ti}} = 0.58$) crystallizes in the fersmite structure, without being of exact AB₂O₆ stoichiometry (Bordet *et al.*, 1986). It is important to note that although the mineral srilankite has the same composition as the low-T compound suggested by McHale & Roth (1986), natural srilankite is not ordered, but disordered like the high-temperature polymorph of (Zr,Ti)₂O₄ (Willgallis & Hartl, 1983). Thus, no conclusions should be drawn from the stability of ordered ZrTi₂O₆ in Fig. 1 regarding the stability of srilankite.

Srilankite was first discovered in pebbles from a gemstone mine in Sri Lanka, where it is associated with zirconolite, baddeleyite, geikielite, spinel, and perovskite (Willgallis *et al.*, 1983). Subsequent synthesis experiments, where ultra-fine powder precipitates were annealed at room pressure as well as hydrothermal conditions ($P < 150$ MPa), lead the authors to propose a hydrothermal origin of srilankite, with a maximum stability temperature at 900°C (Willgallis *et al.*, 1987; Buhl & Willgallis, 1989). Both natural and synthetic srilankite were reported to have the orthorhombic α -PbO₂ structure with space group *Pbcn*, and are thus isostructural to the disordered high-temperature polymorph of (Zr,Ti)₂O₄. It is likely that the disordered ZrTi₂O₆ crystallized metastably in the low-T experiments of Willgallis *et al.* (1987) and Buhl & Willgallis (1989), as reported from a similar low-T study by McHale & Roth (1986). More recently, srilankite was found in rocks that suggest a more high-grade origin, such as eclogites (Wang *et al.*, 1999) and granulites (Bingen *et al.*, 2001), where it is clearly part of the metamorphic assemblage, and was also reported from chromitite (Merkle, 1991) and lamprophyre (Kostrovitskiy *et al.*, 1995).

Experimental methods

Starting materials were prepared from the oxides ZrO₂ (SPEX) and TiO₂ (Degussa), which were dried at 1100°C for 1 hour, mixed in various proportions, and ground by hand in an agate mortar. Between 20 to 40 mg of mix was used per experiment, and sealed in 2 mm-diameter platinum [Pt] or silver-palladium [Ag₇₅Pd₂₅] capsules.

In view of previous problems with metastabilities, we decided to use fluxes to aid the equilibration of experimental runs at lower temperature: copper oxide [CuO] (Merck) and an ammonium carbonate mixture [NH₄HCO₃ plus NH₂COONH₄] (UNIVAR) (Troitzsch *et al.*, submitted). Copper oxide forms a melt at about 900°C in the presence of ZrO₂ and TiO₂ (Gadalla & White, 1966; Lu *et al.*, 2001), thus acting as a transport medium in high-temperature experiments, facilitating diffusion of the reactants in the sample at room as well as elevated pressure. It turned out that during the experiment most of the Cu slowly alloyed with the precious metal of the surrounding capsule, so that the actual run product was virtually Cu-free apart from small, isolated melt-pockets. In contrast, ammonium carbonate, a highly volatile compound at room conditions ('smelling salt'), can only be used in high-pressure experiments, where the confining pressure exceeds the internal gas-pressure of the sample, trapping the ammonium

Table 1. Run conditions and results of direct and reversal experiments.

Sample	Starting mix [X _{Ti}]	Flux ₁	P [kbar]	T [°C]	t [h]	Run products ²
<i>Direct</i>						
ATMU98	0.60	C	0.001	1200	142	(Z) + ZT _{52.0} + R _{93.0}
ATM73	0.40	-	0.001	1200	86	Z _{13.4} + (ZT _{50.3}) + R _{92.7}
ATM73	0.60	-	0.001	1200	86	Z _{13.5} + (ZT _{52.0}) + R _{92.9}
ATMRSES	0.40	-	0.001	1300	24	Z _{15.0} + ZT _{47.8}
ATMU100	0.80	C	0.001	1300	20	ZT _{54.0} + R _{91.6}
ATM70	0.20	-	0.001	1400	25	Z _{15.5} + ZT _{46.2}
ATM70	0.40	-	0.001	1400	25	Z _{15.8} + ZT _{45.9}
ATM70	0.60	-	0.001	1400	25	ZT _{55.2} + R _{90.0}
ATM70	0.80	-	0.001	1400	25	ZT _{54.6} + R _{90.1}
ATM72	0.20	-	0.001	1600	31	Z _{17.9} + ZT _{42.8}
ATM72	0.60	-	0.001	1600	31	ZT _{57.5} + R _{86.6}
ATM72	0.80	-	0.001	1600	31	ZT _{57.9} + R _{86.7}
ATM75	0.40	-	0.001	1650	1	Z _{19.4} + ZT _{42.3}
ATM75	0.60	-	0.001	1650	1	ZT _{57.6} + R _{86.15}
G-594	0.70	N	15	1300	27	(Z _{18.0}) + ZT _{58.5} + R _{93.5}
G-595 ³	0.70	N	15	1300	24	Z _{19.1} + R _{92.7}
G-596 ³	ZT _{55.0} ⁴	-	15	1300	24	Z _{20.5} + R _{91.7}
G-575	0.60	N	20	1250	70	(Z _{21.9}) + ZT _{60.0} + R _{94.7}
G-576	0.60	N	20	1275	120	(Z) + ZT _{59.2-60.6} + R _{93.7}
G-582	0.60	N	20	1275	144	Z _{20.5} + ZT _{59.0-60.0} + R _{93.3}
G-583	0.40	-	20	1300	24	Z _{20.0} + ZT _{58.6} + (R)
G-583	0.60	-	20	1300	24	(Z _{19.9}) + ZT _{59.9} + R _{94.1}
G-568	0.80	N	20	1300	24	(Z _{20.3}) + ZT _{58.7-60.7} + R _{94.0}
G-479	0.60	-	20	1500	3	(Z _{22.3}) + ZT _{56.8-63.9} + R _{92.2}
G-498	0.67	-	28	1440	7	ZT _{66.8} + R _{91.9}
G-490	0.67	-	28	1500	4	Z _{26.9} + ZT _{63.5-67.8} + R _{92.98}
<i>Reversals</i>						
ATMU104	ATM72/20	-	0.001	1300	120	Z _{14.4} + ZT _{46.7}
ATMU105	ATM72/60	-	0.001	1300	48	ZT _{56.74} + R _{91.2}
¹ C: copper oxide, N: ammonium carbonate						
² Run products are solid solutions of zirconia [Z], disordered (Zr,Ti) ₂ O ₄ [ZT], and rutile [R]. Phases that occur in trace amounts are bracketed. Subscripts show composition of the phases [mol% TiO ₂] determined with SEM. Standard deviation for all analyses is less than 1 mol% for each sample, except when compositional ranges are given (e.g. ZT _{58.7-60.7}) based on maximum/minimum values.						
³ samples equilibrated without Fe ₂ O ₃ -buffer, which were blue, contained Ti ³⁺ , and were not used for phase diagrams						
⁴ synthesised from the oxides at 1500°C, 1 atm, 6 h						

carbonate as a fluid. This flux did not react with the capsule material, but escaped the sample upon opening of the capsule without leaving a residue. The use of sintering additives such as ZnO or CuO to lower the melting point is a common procedure in zirconium titanate synthesis, as is the addition of compounds such as Y₂O₃ to speed up the ordering process during cooling (e.g. Azough *et al.*, 1996).

Efficient cooling of the capsules with a water-soaked tissue sleeve during welding was essential to prevent the heating of the flux and its escape as gas. About 10 wt.% of either of the fluxes was added to the starting mix of low-T experiments. While CuO was ground together with the mix to assure thorough wetting of all grains with the melt, ammonium carbonate was added straight into the bottom of the capsule, as it penetrates the entire sample easily as a fluid at high temperature. Experiments carried out with and without each flux at otherwise identical PT-conditions indicate that the fluxes do not alter the phase assemblages or compositions, but greatly speed up the equilibration process (ATMU98 and ATM73, G-568 and G-583, Table 1).

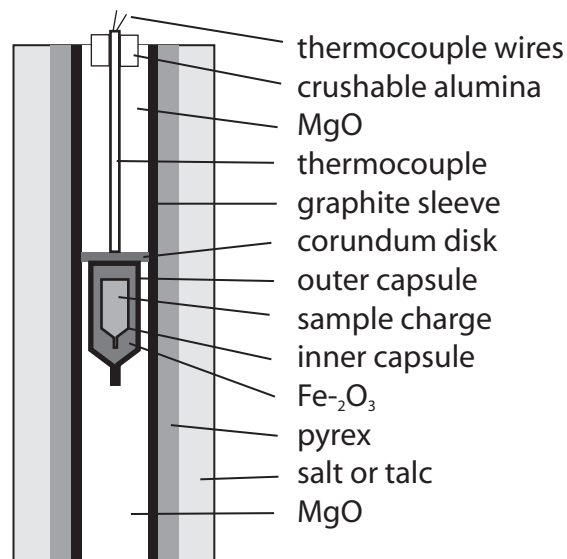


Fig. 2. High-pressure sample assemblage.

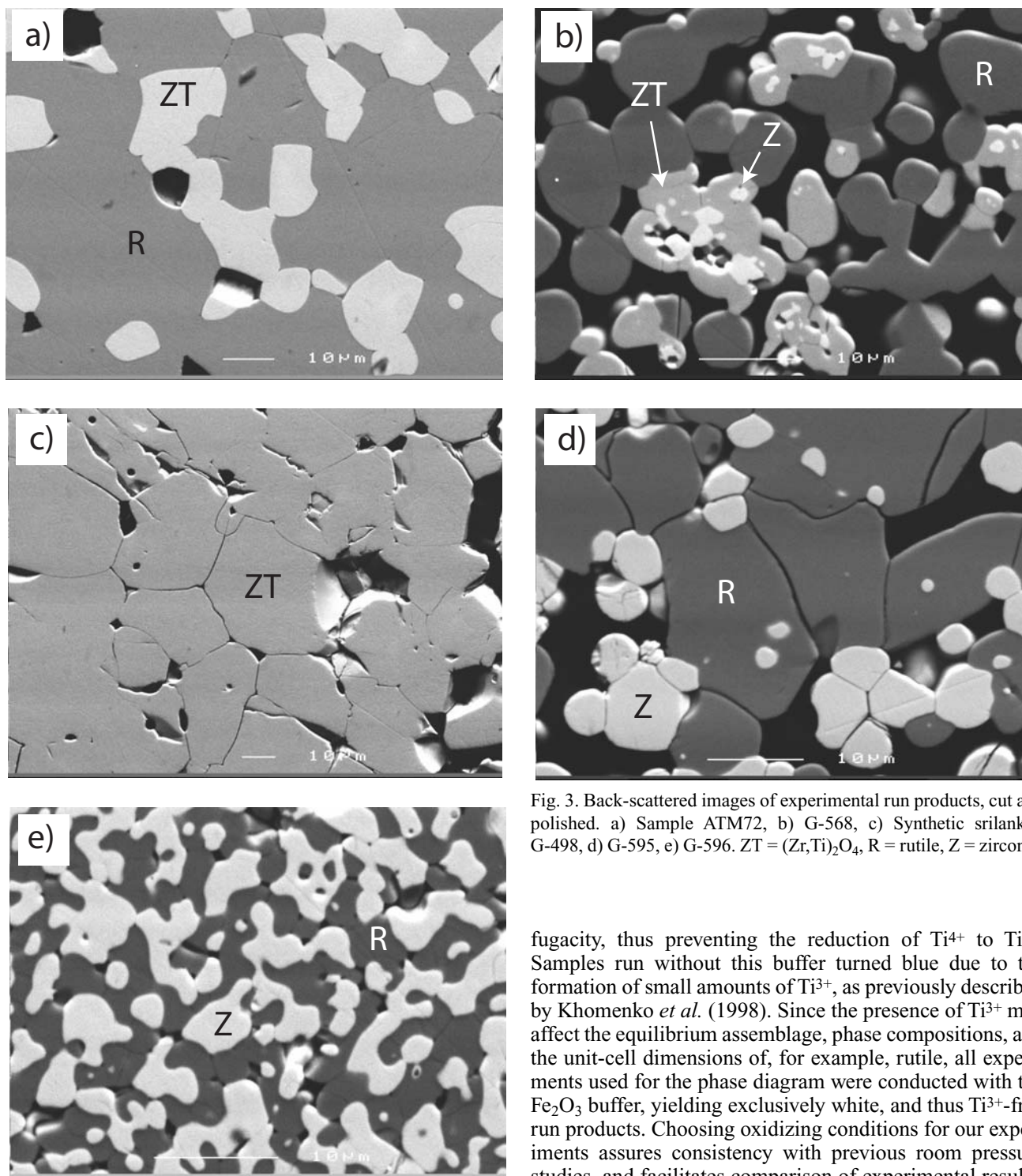


Fig. 3. Back-scattered images of experimental run products, cut and polished. a) Sample ATM72, b) G-568, c) Synthetic srilankite G-498, d) G-595, e) G-596. ZT = $(\text{Zr,Ti})_2\text{O}_4$, R = rutile, Z = zirconia.

Room pressure experiments were carried out in a standard bench-top muffle oven ($< 1100^\circ\text{C}$) and a vertical-tube furnace ($< 1700^\circ\text{C}$), whereas those at elevated pressures were conducted with the piston-cylinder apparatus at the Geology Department, Australian National University. The sample assemblage is shown in Fig. 2. The sample capsules for high-pressure runs were surrounded by a second Pt or $\text{Ag}_{75}\text{Pd}_{25}$ capsule of 3 mm diameter together with Fe_2O_3 powder. The presence of Fe_2O_3 ensures a high oxygen

fugacity, thus preventing the reduction of Ti^{4+} to Ti^{3+} . Samples run without this buffer turned blue due to the formation of small amounts of Ti^{3+} , as previously described by Khomenko *et al.* (1998). Since the presence of Ti^{3+} may affect the equilibrium assemblage, phase compositions, and the unit-cell dimensions of, for example, rutile, all experiments used for the phase diagram were conducted with the Fe_2O_3 buffer, yielding exclusively white, and thus Ti^{3+} -free run products. Choosing oxidizing conditions for our experiments assures consistency with previous room pressure studies, and facilitates comparison of experimental results. The double capsule was surrounded by an assemblage of MgO, a graphite tube, and placed into a talc or salt sleeve, with or without a layer of pyrex. The temperature was monitored by a platinum-platinum/rhodium ($\text{Pt}_{90}\text{Rh}_{10}$) thermocouple, and was regulated automatically. Run times of piston-cylinder experiments at very high temperatures were limited to a few hours because of the fast reduction of the Fe_2O_3 -buffer material, thus not always allowing for complete equilibration. Samples that were only locally equilibrated, but at oxidizing conditions, were preferred to

those that reached equilibrium across the entire sample, but were blue, and thus reduced. Individual run conditions and starting mix compositions are summarized in Table 1.

For phase identification, all run products were analysed with a Siemens D501 diffractometer, equipped with a curved graphite monochromator, a scintillation detector, using CuK α radiation. The samples were placed on a quartz-low-background holder, and scanned between 5 and 90° 2-theta, at a step-width of 0.02° and scan speed of 0.5° per minute. Unit-cell dimensions of synthetic (Zr,Ti)₂O₄ solid solution were determined with the Rietveld method using the program RIETAN-2000 (Izumi & Ikeda, 2000). However, the polyphase nature of most of the experimental run products of this study prevents a thorough crystal structure study. Quantitative analyses were obtained with a JEOL JSM-6400 scanning electron microscope with attached Si(Li) detector, Link ISIS EDS, at 15 kV and 1 nA. Analyses were calculated using the ZAF correction. Synthetic, homogeneous zirconolite was used as standard for Zr and Ti.

Results and discussion

Experimental results and run conditions of direct and reversal experiments are listed in Table 1. Most samples, especially high-temperature experiments, produced well-equilibrated assemblages (Fig. 3a) with uniform phase compositions throughout the entire sample (*e.g.*, ATM72 with mixes $X_{\text{Ti}} = 0.60$ and 0.80, Table 1). Other samples contained relic phases that were easily identified, based on reaction textures (Fig. 3b, large pore-space of this sample due to presence of flux). Even in those samples equilibrium was probably approached on the local scale, as suggested for example by the reproducibility of the (Zr,Ti)₂O₄ composition in well and poorly equilibrated samples ATMU98 and ATM73/60, respectively. Relic grains of zirconia sometimes contained cores of pure ZrO₂ that were deliberately avoided during microanalytical determination of the equilibrium composition of ZrO₂ solid solution.

Table 1 shows what we interpreted to represent the equilibrium compositions of the phases, based on both textural evidence and reproducibility of analyses across each sample. These composition data were then used to construct the ZrO₂-TiO₂ phase diagram at room pressure, 15 kbar, 20 kbar and 28 kbar (Fig. 4).

In order to test whether the phase boundaries in Fig. 4 are reliable and approach equilibrium conditions, reversal experiments were conducted at 1300°C using samples ATM72/20 and ATM72/60. Having previously been annealed at 1600°C, 1 atm, these samples contained very Ti-rich zirconia and very Zr-rich rutile respectively (Table 1). In the reversal runs these samples were re-equilibrated at 1300°C. Figure 5a is an enlarged section of Fig. 4, whereby the lines show the composition of zirconia in equilibrium with (Zr,Ti)₂O₄ as determined in the direct experiments (filled circles). Open circles depict the composition of zirconia grains analysed after the sample was re-annealed at 1300°C, showing that the composition of zirconia adjusted from $X_{\text{Ti}} = 0.18$ to lower Ti-contents,

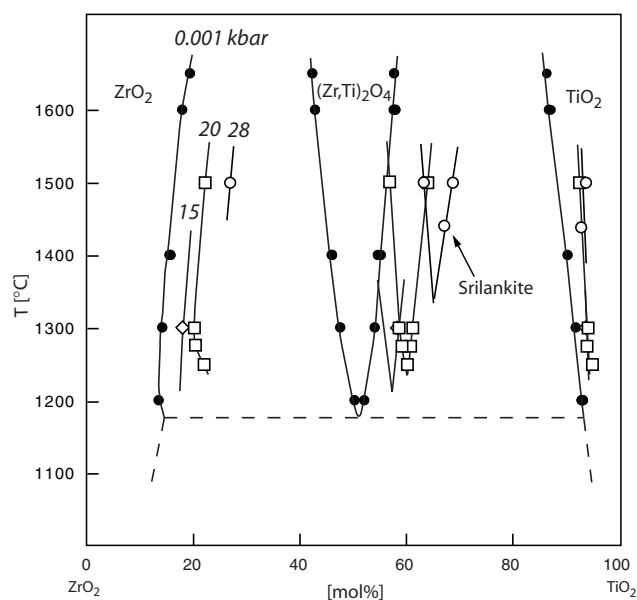


Fig. 4. Effect of pressure and temperature on phase boundaries in the ZrO₂-TiO₂ phase diagram. No distinction was made between tetragonal and monoclinic zirconia, as this would require *in-situ* structure analysis due to the non-quenchable tetragonal phase.

clustering close to the equilibrium boundary established in our direct experiments. Thus the phase boundary was bracketed from both sides to within 1 mol% by direct and reversal experiments. The same is demonstrated for rutile (Fig. 5c). Also, the composition of the intermediate phase (Zr,Ti)₂O₄ re-adjusted to the new equilibrium conditions in accordance with the phase boundaries (Fig. 5b). The approach of equilibrium in our experiments is also suggested with the gradual change of all phase compositions with temperature without much scatter (Fig. 4).

(Zr,Ti)₂O₄ was disordered in all experiments, as indicated by the absence of superstructure reflections from the XRD patterns. Disorder of (Zr,Ti)₂O₄ was also indicated by its largest unit-cell dimension *b*, which always exceeded 5.45 Å (Table 2), thus contrasting ordered (Zr,Ti)₂O₄ that has a significantly shorter cell-edge (McHale & Roth, 1983). The exclusively disordered state of (Zr,Ti)₂O₄ in our experiments agrees well with the phase diagram by McHale & Roth (1996), who suggested that disordered (Zr,Ti)₂O₄ is stable above 1100°C, whereas the ordered phase is restricted to temperatures below 1200°C (Fig. 1). The structure of zirconia is not discussed in this paper, because the non-quenchable monoclinic-tetragonal phase transition at elevated temperatures would require *in-situ* structure investigations during the experiments. It is likely, however, that all samples equilibrated in the tetragonal stability field of ZrO₂ (Fig. 1).

Based on the data in Table 1, the ZrO₂-TiO₂ phase diagram was constructed at 1 atm, 15 kbar, 20 kbar and 28 kbar (Fig. 4). The room pressure data confirm previous studies in that solid solutions of zirconia, rutile and disordered (Zr,Ti)₂O₄ are stable. At room pressure, the extent of solid solution of the phases increases with temperature to a maximum range of $X_{\text{Ti}} < 0.19$ [ZrO₂], 0.42-0.58

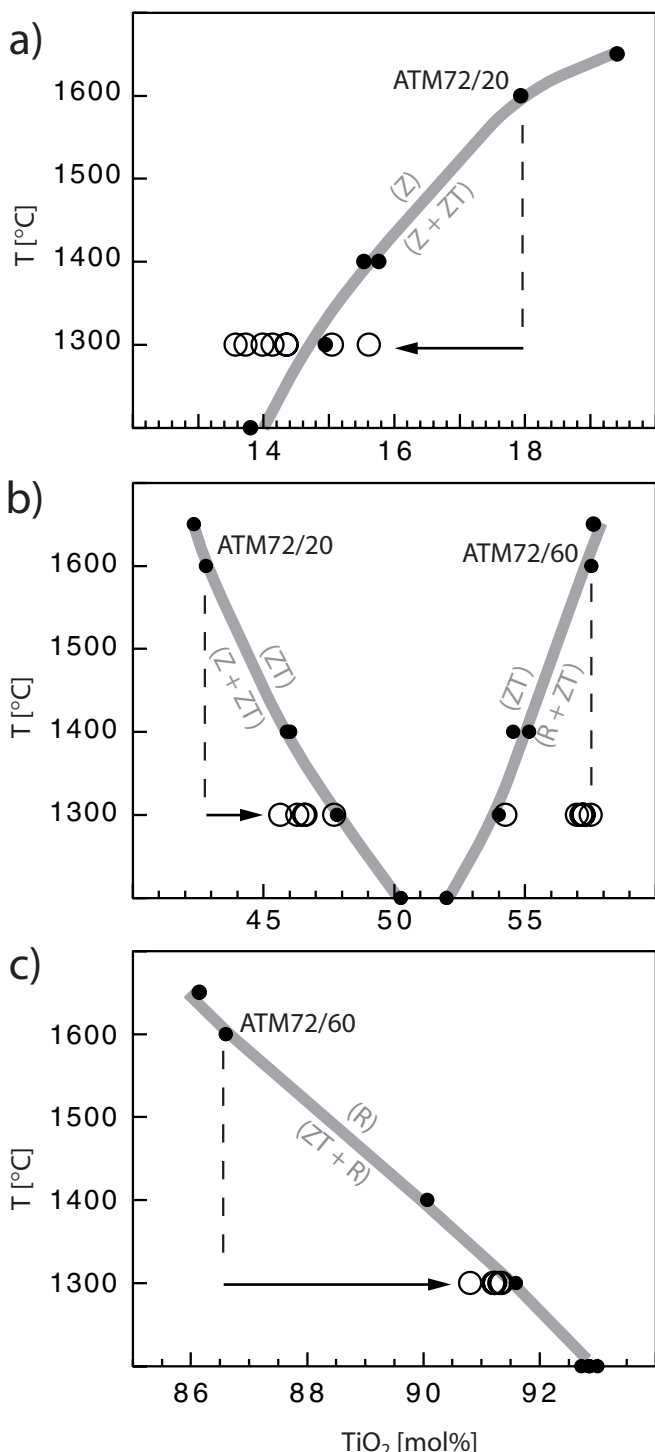


Fig. 5. Reversal experiments (open circles) superimposed on enlarged sections of Fig. 4. Re-equilibration at 1300°C of previous high-temperature samples ATM72/20 and ATM72/60 demonstrates that the phase compositions of zirconia (a), $(\text{Zr,Ti})_2\text{O}_4$ (b), and rutile (c) are reproducible and reversible. Individual analysis points of the reversal runs (open circles) approach the previously determined phase boundaries (filled circles and interpolation). Abbreviations denoting the phase fields as in Fig. 3.

$[(\text{Zr,Ti})_2\text{O}_4]$, and $X_{\text{Ti}} > 0.86$ [TiO_2]. With increasing pressure all phases become more Ti-rich, which is consistent

Table 2. Unit cell-dimensions of $(\text{Zr,Ti})_2\text{O}_4$ with compositions ranging from $X_{\text{Ti}} = 0.423$ to 0.668. Standard deviation is 0.0010 Å for a , b and c , and 0.01 for $X_{\text{Ti}} = X_{\text{Ti}}/[X_{\text{Zr}}+X_{\text{Ti}}]$.

Sample	X_{Ti}	a [Å]	b [Å]	c [Å]
ATM75 0.40	0.423	4.8525	5.4631	5.0466
ATM70 0.40	0.459	4.8317	5.4654	5.0406
ATM70 0.20	0.462	4.8323	5.4654	5.0411
ATMRSRS 0.40	0.478	4.8229	5.4515	5.0370
ATMU98	0.520	4.7902	5.4808	5.0283
ATMU100	0.540	4.7819	5.4919	5.0271
ATM70 0.80	0.546	4.7777	5.4892	5.0228
ATM70 0.60	0.552	4.7778	5.4900	5.0254
ATM72 0.60	0.575	4.7600	5.4971	5.0172
ATM75 0.60	0.576	4.7612	5.5012	5.0187
ATM72 0.80	0.579	4.7596	5.4979	5.0170
G-498	0.668	4.7110	5.4940	4.9960

with the smaller ionic radius of Ti^{4+} (0.605 Å) compared to Zr^{4+} (0.72 Å) (Shannon & Prewitt, 1969). At 28 kbar, ZrO_2 extends to $X_{\text{Ti}} = 0.27$, and $(\text{Zr,Ti})_2\text{O}_4$ ranges from $X_{\text{Ti}} = 0.64$ to 0.68.

Figure 6 and Table 2 show the unit-cell dimensions of $(\text{Zr,Ti})_2\text{O}_4$ with different Ti-contents, as determined with powder X-ray diffraction and Rietveld analysis from our run products. Samples containing $(\text{Zr,Ti})_2\text{O}_4$ of inhomogeneous composition due to poor equilibration were excluded from this data set. The decrease of the unit-cell volume with increasing Ti-content is consistent with the formation of the most Ti-rich $(\text{Zr,Ti})_2\text{O}_4$ in the experiments conducted at the highest pressures. A detailed crystal structure study of the disordered $(\text{Zr,Ti})_2\text{O}_4$ solid solution based on samples with less contaminant phases is in preparation.

Srilankite, *i.e.* $(\text{Zr,Ti})_2\text{O}_4$ with 67 mol% TiO_2 , was synthesised at 1440°C and 28 kbar (Fig. 4), forming homogeneous, large grains (Fig. 3c) that coexist with small amounts of rutile. The unit-cell dimensions of this synthetic compound are comparable to those of natural srilankite, and previously reported synthetic compounds formed at hydrothermal conditions (Table 3, Fig. 5).

This is the first time that the equivalent of srilankite was synthesised at high pressures. Moreover, we believe that the high-temperature, high-pressure synthesis of srilankite of this study represents the formation of srilankite at thermodynamic equilibrium, as indicated by the reversibility of the $(\text{Zr,Ti})_2\text{O}_4$ composition in our experiments.

Since the extent of solid solution in $(\text{Zr,Ti})_2\text{O}_4$ at room pressure was limited to $X_{\text{Ti}} = 0.41$ -0.53 (Noguchi & Mizuno, 1968), earlier studies treated srilankite as a separate phase from the $(\text{Zr,Ti})_2\text{O}_4$ solid solution series. This distinction was supported by the suggested hydrothermal origin of srilankite, as opposed to the high-temperature stability of disordered $(\text{Zr,Ti})_2\text{O}_4$. In contrast to this, our experiments demonstrate that the solid solution of disordered $(\text{Zr,Ti})_2\text{O}_4$ is continuous with pressure between at least $X_{\text{Ti}} = 0.42$ and 0.68 (Table 1), and thus includes srilankite. The formation of srilankite composition in our experiments requires very high pressures and temperatures (Fig. 3), rather than a hydrothermal environment. We agree with McHale & Roth (1986) and Xu *et al.* (2000) that the

crystallization of disordered (Zr,Ti)₂O₄ from a co-precipitated powder at low temperatures, such as in the experiments of Willgallis *et al.* (1987) and Buhl & Willgallis (1989), is likely to represent the formation of a metastable phase. These latter experiments should therefore not be used to derive petrogenetic conditions for geological processes at least for higher-grade rocks, which are more likely to approach equilibrium conditions.

Our experiments suggest that the composition of srilankite may vary with pressure and temperature of formation, and that there does not seem to be a reason why it should be limited to the composition X_{Ti} = 0.667. This is in agreement with natural srilankite compositions which range from at least X_{Ti} = 0.63 to 0.71 (Kostrovitskiy *et al.*, 1995), and indicates that the fairly exact ZrTi₂O₆ stoichiometry reported by Willgallis *et al.* (1983) and Wang *et al.* (1999) represents an end-member of a solid solution, but is not necessarily representative of all srilankite found in nature.

The formation of srilankite at high pressures, as indicated by our experiments, is in general agreement with the reports of srilankite as part of granulite-facies and eclogite-facies mineral assemblages by Bingen *et al.* (2001) and Wang *et al.* (1999), respectively. However, note that our experiments only quantify the relations between a strictly binary composition, pressure and temperature. There are many other factors in a natural environment that may affect the stability and crystal structure of srilankite, such as other elements that could form solid solution in srilankite, or fluid pressures, all of which need to be understood before the stability of srilankite can be predicted in natural environments. For example, the presence of tin is known to expand the stability field of disordered (Zr,Ti)₂O₄ by inhibiting the ordering process (McHale & Roth, 1983). Also, small amounts of iron are common in natural srilankite, but its effect on the stability of the phase yet unknown.

Moreover, our experiments demonstrate that also the oxygen fugacity affects the stability of (Zr,Ti)₂O₄, and that therefore the phase relationships and compositions determined in a fully oxidised system (Fig. 1 and 3) do not necessarily apply to every type of geological setting. Three samples (G-594, 595, 596) equilibrated at 1300°C and 15 kbar resulted in different phase assemblages depending on whether or not they were surrounded by the oxygen buffer (Table 1). While (Zr,Ti)₂O₄ is the dominant phase in the buffered experiment G-594, it is absent from the unbuffered sample G-595, which is composed of rutile and zirconia (Fig. 2d). The instability of (Zr,Ti)₂O₄ at these

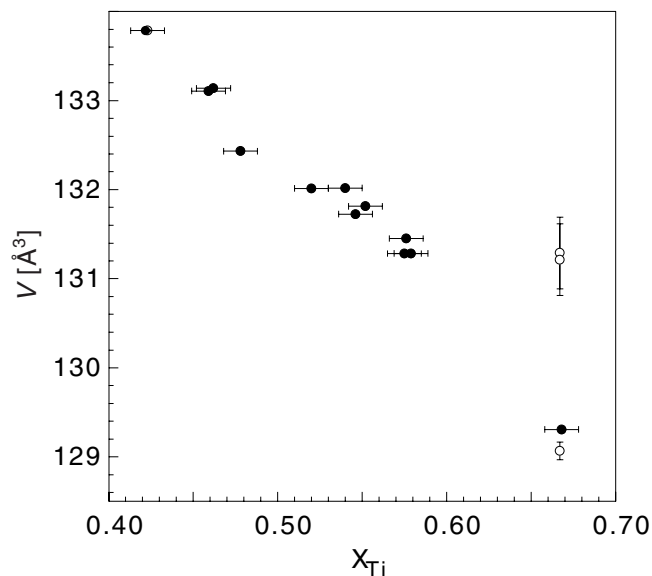


Fig. 6. Unit-cell volume of synthetic (Zr,Ti)₂O₄ solid solution (filled circles) based on this study (Table 2), compared to that of previously reported natural and synthetic srilankite (open circles) from Table 3.

more reduced conditions was confirmed with a second experiment, annealing previously synthesised (Zr,Ti)₂O₄ [X_{Ti} = 0.55] without oxygen buffer. In the more reduced environment the compound decomposed entirely to a fine-grained intergrowth of rutile and zirconia (Fig. 2e), with compositions comparable to those of G-595 (Table 1). The fact that natural srilankite has been found in association with armalcolite (Kostrovitskiy *et al.*, 1992), a mineral stable at extremely reduced conditions, seems to contradict our experiments, and demonstrates that a thorough quantitative investigation into the oxygen fugacity – (Zr,Ti)₂O₄ stability is required to fully understand the stability of srilankite.

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Table 3. Unit-cell dimensions of ZrTi₂O₆ (Srilankite).

	a [Å]	b [Å]	c [Å]	Refs.
Natural	4.706(5)	5.553(5)	5.024(4)	1
	4.708(5)	5.553(5)	5.019(5)	2
Synthetic	4.711(1)	5.494(1)	4.996(1)	<i>this study</i>
	4.701(1)	5.501(2)	4.991(1)	3
	4.706	5.514	4.9928	4

Refs.: 1 Willgallis & Hartl (1983), 2 Willgallis *et al.* (1983), 3 Buhl & Willgallis (1989), 4 Willgallis *et al.* (1987)

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