The effect of radiation damage on local structure in the crystalline fraction of ZrSiO₄: Investigating the ²⁹Si NMR response to pressure in zircon and reidite

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ABSTRACT

Periodic density functional theory (DFT) was used to calculate the structure of zircon ($ZrSiO_4$) and reidite (scheelite polymorph of $ZrSiO_4$) at pressures from 0-41 GPa. Subsequently, the ^{29}Si nuclear magnetic resonance (NMR) chemical shifts at each pressure were determined using the GIPAW method. The results show that in both zircon and reidite the chemical shifts become more negative with increasing pressure. The chemical shift of reidite is predicted by calculation to be –91.8 ppm and measured as –91.1 ppm. The results are used to interpret the previously observed systematic decrease in ^{29}Si NMR chemical shifts (increasingly negative) in the crystalline fraction of radiation-damaged zircon with increasing α-dose. The original hypothesis that strain induced by the compression of the crystal by internal regions of damaged, amorphized material at high pressure was the origin of the shifts was disproved. An alternative source of internal pressure in the radiation-damaged crystals linked to "'stuffing" of the lattice with interstitial O or He atoms is proposed.

INTRODUCTION

The safe disposal of nuclear waste in a durable insoluble matrix is a major scientific challenge. One of the key issues, especially for the actinide elements, is how the structure of the material is affected following internal α-decay events. The damage caused by one event and the manner in which damage from many events accumulates are not well understood. These are important because accurate long-term predictions about the durability of the material are required. For this to happen, the structural consequences of radioactive decay need to be known.

Natural zircon ($ZrSiO_4$) often contains several thousand parts per million of uranium or thorium. The radioactive decay of these elements via an α-process over geologic time causes disruption of the crystal structure of the orthosilicate and "metamictization" occurs; part of the crystal structure becomes amorphous. These materials, when well characterized in radiation dose, are very good models for the long-term stability and durability of oxide ceramics proposed as hosts for radioactive waste. In order to investigate the radiation damage process local structural probes that do not depend on the existence of long-range order (crystallinity) are required. Nuclear magnetic resonance is such a probe.

Recently, ^{29}Si (NMR) has been used to investigate local structural changes in radiation damaged (metamict) zircon (Farnan 1999; Farnan and Salje 2001). At the same time, methods have become available whereby NMR chemical shifts may be calculated directly from proposed structures using periodic ab initio techniques (Mauri et al. 1996; Pickard and Mauri 2001;

Balan et al. 2003). ^{29}Si NMR experiments tell us that a systematic change in chemical shift occurs in crystalline zircon as a function of cumulative α-particle dose and this must correspond to a systematic change in local structure. In this paper we attempt to find the origin of these changes by investigating the effect of pressure on the ^{29}Si NMR chemical shift in zircon. This also involves understanding the ^{29}Si NMR chemical shift in the high-pressure polymorph of $ZrSiO_4$. This was recently discovered terrestrially and has acquired the mineral name reidite (Glass et al. 2002).

Figure 1 shows the spectra of two zircon samples with low and intermediate α-dose. The single narrow line at –81.6 ppm in the low dose sample is characteristic of silicon in four-fold co-ordination with O atoms. The –81.6 ppm shift is the most negative reported for Q^0 silicon in a binary silicate containing only four coordinated Si atoms (Stebbins 1995). In the sample with intermediate radiation dose, this resonance line for crystalline Q^0 silicon has been shifted to –83.7 ppm (it is also broadened) and the amorphized areas are represented by the major broad line in the spectrum. It is clear that there is a systematic change in the crystalline fraction as a function of the damage. In a model of damage accumulation in zircon where amorphous islands of damaged material are constrained to have the same density as the surrounding crystalline matrix, it is conceivable that an increasing pressure is exerted on the crystalline matrix by the more damaged regions as their amount increases through further α-decay. Figure 2 shows the variation of the ^{29}Si NMR peak position of Q^0 in zircon as a function of α-dose. The proposition is that the crystalline matrix is constrained to a smaller than equilibrium volume by the damaged regions and the stress induced in the surrounding crystal causes a systematic shift in

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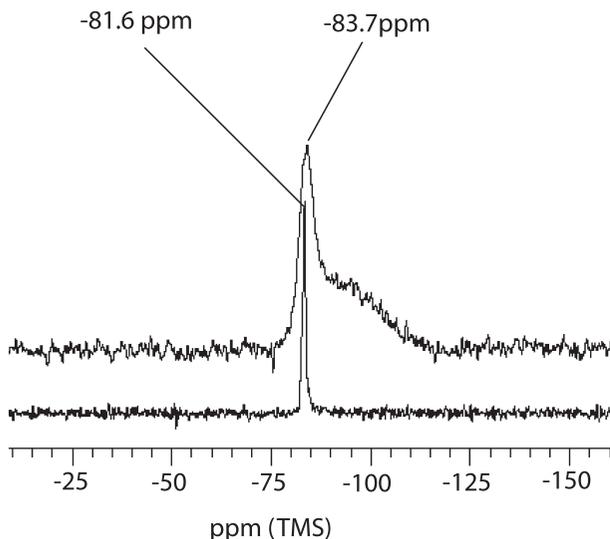
FIGURE 1. ^{29}Si MASNMR spectra of radiation damaged zircons. The lower trace is the spectrum from a zircon that has accumulated 1×10^{18} α-decays/g and the upper 4.2×10^{18} α-decays/g. The broad line in the upper spectrum is due to silicon in amorphized regions. Spectra were acquired at a spinning speed of 5 kHz by collecting several hundred free induction decays following $\pi/12$ pulses with pulse delays of 300 s.
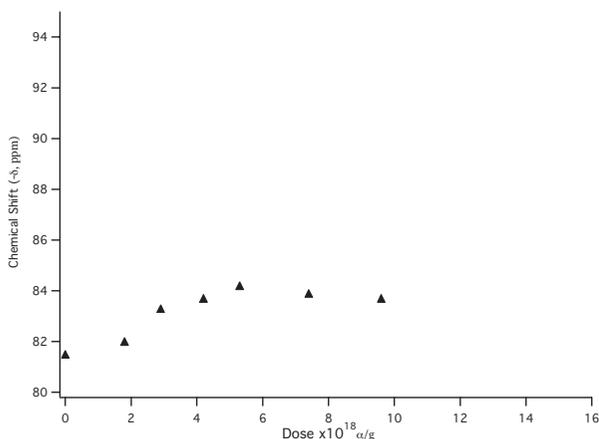
FIGURE 2. Variation of the average ^{29}Si NMR chemical shift of the crystalline fraction in partially metamict zircons as a function of α-dose.

peak position until the percolation point has passed and the stress is released. Whether this is the origin of the systematic shift in peak position can be investigated by calculation of the ^{29}Si NMR chemical shifts in zircon at different pressures.

CALCULATIONS

Structural relaxations were performed using the Density Functional Theory (DFT). Two calculations were performed using either the local density approximation (LDA) or the generalized gradient approximation (GGA). For the GGA calcula-

tion, we used the functional proposed by Perdew, Burke, and Ernzerhof (PBE) (Perdew et al. 1996). Ionic cores were described by norm-conserving pseudo-potentials (Troullier and Martins 1991) in the Kleinman-Bylander form (Kleinman and Bylander 1982). For the Zr pseudo-potential 4s and 4p were treated as valence states with core radii of 1.42 (4s, 4p) and 1.46 a.u. (4d). The Si and O pseudopotentials were constructed with core radii of 2.0 (3s, 3p, 3d) and 1.45 a.u. (2s, 2p), respectively. For the structural relaxation, a 100 Ry cutoff on the wave-functions was required because of the slow convergence of the stress tensor with respect to the size of the plane-waves basis set. The Brillouin zone was sampled according to the Monkhorst-Pack scheme (Monkhorst and Pack 1976) using grids with $2 \times 2 \times 2$ and $3 \times 3 \times 3$ k-points for reidite ($ZrSiO_4$ scheelite phase; Glass et al. 2002) and zircon, respectively.

The NMR parameters were calculated using the GGA and a 70 Ry cutoff on the wave-functions. However, because of the slow convergence of the chemical shift with respect to the Brillouin zone sampling, the size of the grids was increased to $4 \times 4 \times 2$ and $4 \times 4 \times 4$ k-points for reidite and zircon, respectively. The NMR ^{29}Si chemical shifts were obtained by calculating the shielding of the ^{29}Si nuclei relative to the electronic current induced by the external magnetic field. This current was calculated by using the GIPAW approach, which allows to reconstruct the all-electron magnetic response from the pseudo-wave-functions (Pickard and Mauri 2001). Relative values of the chemical shifts can therefore be obtained from our pseudo-potential approach with the accuracy of a fully converged all-electron calculation. Absolute values of the theoretical ^{29}Si chemical shifts were referenced using the experimental value measured from zircon at zero pressure (–81.5 ppm). Calculations were performed using the PARATEC code (Pfrommer et al. http://www.nersc.gov/projects/paratec).

Structural parameters were determined for five pressures, ranging between 0 and 41 GPa. The theoretical pressures of the phase transition between zircon and reidite at 0 K are 6.2 and 11.4 GPa at the LDA and GGA levels, respectively. The equilibrium volume and bulk modulus calculated at the LDA level are in good agreement with experimental data (Table 1). Similar agreement was previously obtained from the zircon and reidite structures at the LDA level (Crocombette and Ghaleb 1998). Therefore, we use the structures obtained with the LDA in the next part of the paper. However, we note that the calculated bulk modulus of reidite is significantly lower than that determined by Scott et al. (Scott et al. 2002). Cell parameters and internal coordinates of the O atom obtained for both phases are reported in Table 2. For zircon, the internal coordinates are in excellent agreement with experiment, whereas only a relative agreement is obtained for reidite [$u = 0.28$, $v = 0.14$, $w = 0.07$; (Kusaba et al. 1986)]. This could be related to the experimental uncertainties caused by the high degree of residual strain in the shock-produced reidite sample (Kusaba et al. 1986). The SiO distance at zero pressure is much larger in reidite than in zircon (Fig. 3). In comparison, the average ZrO distance is similar in the two structures. However, the distortion of the ZrO_8 polyhedron increases with pressure in zircon, whereas the opposite behavior is observed in reidite.

TABLE 1. Equilibrium volume at zero pressure and bulk modulus of reidite and zircon

	V_0 (Å³)			K_0 (GPa)			dK/dP		
	LDA	GGA	exp.	LDA	GGA	exp.	LDA	GGA	exp.
reidite	229.8	243.3	235.8*	254	212	301‡	5.9	6.7	4.1‡
zircon	256.1	270.4	260.8†	228	196	227†	6.3	6.8	6.5†

* Kusaba et al. 1986.
† Hazen and Finger 1979.
‡ Scott et al. 2002.

TABLE 2. Structural parameters (LDA level) and ²⁹Si chemical shift in reidite and zircon

	P (GPa)	δ (ppm)	a (Å)	c (Å)	V (Å³)	u	v	w	d(SiO) (Å)	d(ZrO)$_1$ (Å)	d(ZrO)$_2$ (Å)
reidite	0.69	−91.8	4.701	10.371	229.2	0.258	0.157	0.078	1.64	2.24	2.13
	10.78	−92.8	4.653	10.215	221.1	0.257	0.158	0.080	1.62	2.20	2.11
	20.93	−93.6	4.610	10.088	214.4	0.257	0.159	0.081	1.61	2.17	2.10
	30.88	−94.1	4.571	9.980	208.6	0.256	0.160	0.082	1.60	2.14	2.08
	40.61	−94.5	4.536	9.886	203.4	0.255	0.161	0.082	1.59	2.12	2.06
zircon	0.53	−81.6	6.567	5.926	255.5	0.066	0.00	0.195	1.61	2.25	2.12
	10.68	−82.6	6.471	5.868	245.7	0.065	0.00	0.196	1.59	2.23	2.08
	20.85	−83.0	6.392	5.816	237.6	0.064	0.00	0.196	1.58	2.22	2.05
	30.78	−83.1	6.327	5.765	230.7	0.063	0.00	0.197	1.57	2.20	2.02
	40.44	−82.9	6.269	5.720	224.7	0.062	0.00	0.197	1.56	2.18	2.00
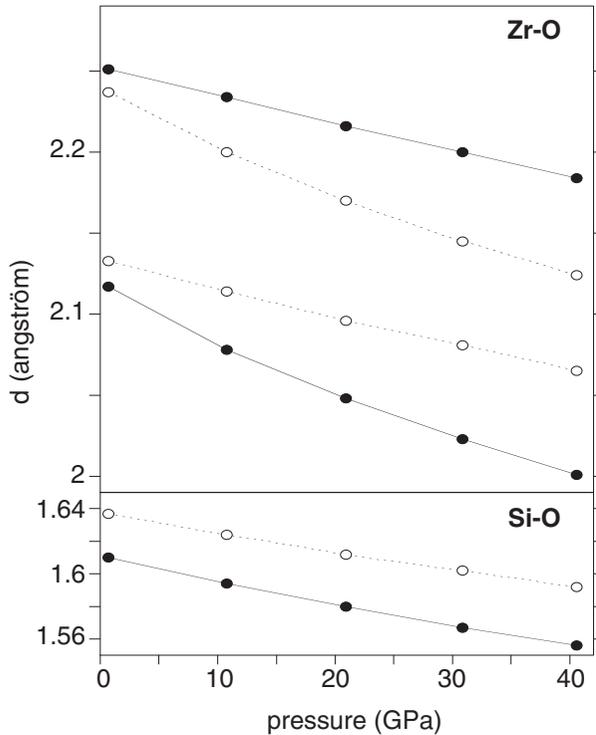
FIGURE 3. Variation of cation-O atom bond-lengths in the zircon and reidite structures as a function of pressure. Filled circles are for zircon, open circles are for reidite.

FIGURE 4. Variation of the theoretical ²⁹Si NMR chemical shifts (circles) in zircon and reidite as a function of pressure. Experimental chemical shifts measured at room pressure are reported (squares). Filled symbols are for zircon, open symbols are reidite.

RESULTS: CALCULATION OF NMR PARAMETERS

The ²⁹Si chemical shifts were calculated for zircon at pressures from 0 to 41 GPa using the structures determined from the DFT calculations. The results are reported in Table 2. There is a monotonic decrease in the chemical shift (becomes more negative) with increasing pressure as shown in Figure 4. The magnitude of the change from zero pressure to 20 GPa, where the effect saturates, is ~1.5 ppm. The ²⁹Si chemical shifts for the high pressure form of ZrSiO₄ (reidite) are also shown in Figure 4; these show a similar trend with increasing pressure but are substantially shifted from zircon even at zero pressure. This shift is 10 ppm more negative than any binary orthosilicate containing only four-coordinated silicon previously reported in the literature (Stebbins 1995). The result of this calculation is verified by the previously unpublished ²⁹Si NMR data of Fiske. In this experimental work, the ²⁹Si NMR spectrum of a single crystal of zircon was recorded both before and after a shock experiment using the light gas gun at Lawrence Livermore National Laboratory. Figure 5 shows the spectra of the shocked and unshocked crystals. The peak pressure in the

shock experiment was 52 GPa (the zircon-reidite transformation pressure at 298 K is 23 GPa, Scott et al. 2002) and the resonance is clearly at a much higher shift than in zircon. In fact, the calculated shift of –91.8 ppm is in good agreement with the experimental shift of –91.1 ± 0.25 ppm.

DISCUSSION

Calculated chemical shifts and relaxed structures for high-pressure zircon and reidite give us an insight into the structural origin of the experimentally observed shifts. Both zircon and reidite are orthosilicates, containing only isolated SiO_4 tetrahedra. Using the structural information in Table 2, the effect of bond-distance around the O atom on Si chemical shifts in both structures at zero pressure can be examined. The average O-Zr distances in both structures are effectively the same, differing by only 10^{-3} Å. The Si-O distance in reidite is 2.7×10^{-2} Å longer than in zircon even though its density is higher. Thus, the –9.5 ppm experimental difference in chemical shift between zircon and reidite can be explained in terms of the increase in Si-O distance. An increasing Si-O distance results in a more negative chemical shift at a rate of 3.5 ppm per picometre. As we examine the effect of pressure on structure and chemical shift the more rapid decrease of Zr-O distances with pressure results in an overall more negative chemical shift even as the Si-O bonds shorten. There are two competing effects: a shortening of the Si-O distance makes the chemical shift more positive, whereas a decreasing Zr-O distance makes the chemical shift more negative. This results in the weak curvature of the chemical shift vs. pressure behavior for both zircon and reidite shown in Figure 4. Following these ideas the data for zircon and reidite at zero pressure and above can be fitted to an empirical equation of the form (see Fig. 6):

$$\delta = 13.02 - 340.80\, d_{Si-O} + 207.59[(d_{O-Zr1} + d_{OZr2}) / 2] \quad (1)$$
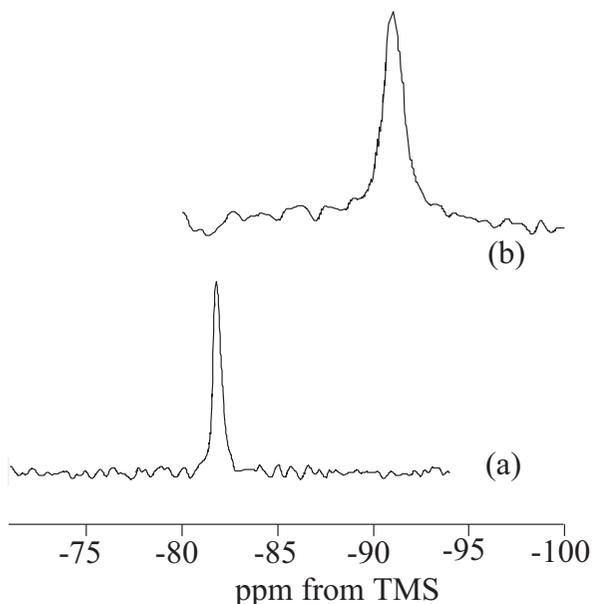
Using the equation above, the chemical shift difference between reidite and zircon will be $\delta = -340.80(1.637 - 1.610) = -9.2$ ppm.

The ^{29}Si chemical shift observed in reidite is exceptionally negative for an orthosilicate. This strong negative shift is caused by the Si-O distance increase related to the phase transition from the zircon structure to the scheelite structure. The mineral scheelite ($CaWO_4$) transforms at high pressure to a hexagonal close-packed arrangement of O atoms with octahedral coordination for both cations (Errandonea et al. 2002). Thus there is a tendency for this type of structure to take up a close-packed arrangement of O atoms with increasing pressure. As a matter of fact, the Si-O and Zr-O bond lengths tend to be slightly more similar in reidite than in zircon and the O atom arrangement moves more towards close-packed (Scott et al. 2002); whereas the Si and Zr coordination numbers remain the same at four and eight, respectively. The trend to equalize the cation-O atom bond lengths (although some way from this situation) could thus be responsible for the greater shielding (more negative chemical shift) of the Si nucleus observed in the NMR spectra.

We can use the analysis of the local structural changes occurring in high-pressure zircon and reidite to understand the evolution of chemical shifts in radiation-damaged zircon. It is clear that the internal stress generated by the swelling of damaged regions is not the origin of the shifts shown in Figure 2. Firstly, pressures up to 40 GPa could not generate such shifts and, secondly, the structure would transform to a denser, scheelite polymorph (reidite) at 23 GPa where the decreased shift is only –1.4 ppm. However, the local structural response observed through changes in ^{29}Si chemical shift is in the same sense as increasing pressure. Calculations of ^{29}Si chemical shifts in zircon at negative pressures, consistent with the increased

FIGURE 5. ^{29}Si MASNMR spectra of (a) zircon (–81.5 ppm) before shock experiment (b) reidite (–91.1 ppm) obtained after shock experiment performed with a peak pressure of 52 GPa.
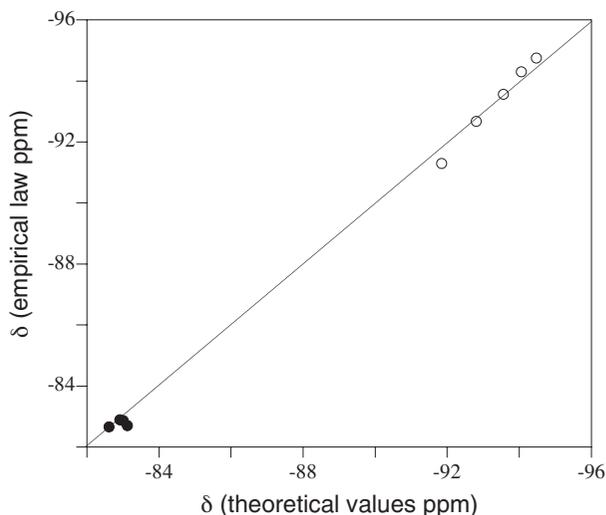
FIGURE 6. ^{29}Si NMR chemical shifts of zircon (filled circles) and reidite (open circles) structures calculated using the empirical equation ($\delta = 13.02 - 340.80\, d_{Si-O} + 207.59[(d_{O-Zr1} + d_{OZr2})/2]$, d in angstroms) as a function of the theoretical ^{29}Si NMR chemical shifts calculated with the GIPAW method. The line represents a perfect agreement between the two calculations.

lattice parameters determined by X-ray diffraction (Rios et al. 2000), produce shifts in the opposite direction (more positive). Two, apparently contradictory, experimental facts have to be reconciled. Macroscopically, the "X-ray density" of the crystalline phase in partially metamict zircon is known to decrease (Holland and Gottfried 1955). The lattice parameters increase but locally (as measured by NMR) the structure responds as if under pressure. Following the empirical correlation obtained for zircon and reidite, the increase of the shielding observed for the ^{29}Si nucleus in damaged zircon could be explained by a lengthening of the Si-O bond and shortening of Zr-O bonds. In that case, the effects would be additive and produce a more negative shift than that obtained by applying an external pressure to the structure. An increase of the Si-O bond lengths is consistent with the softening of the Si-O stretching frequency of the damaged crystalline phase observed using Raman spectroscopy (Zhang et al. 2000). However, the simultaneous lengthening of the Si-O bonds and shortening of the Zr-O bonds imply that locally the structure differs from that obtained by simply compressing or swelling the zircon structure. It is well understood that the crystalline regions in partially metamict zircons contain a large amount of defects, either in rapidly recrystallized regions surrounding the amorphous cores or along the alpha-particle tracks. One explanation could be that the lattice is being "stuffed"; extra atoms are being inserted that cause the long-range measure (X-ray) to see expansion, while locally, the length of the softer bonds decreases as atoms push into the structure. There are two candidates for this interstitial atom: O or He. The case for O atoms would be that amorphization of the zircon structure produces polymerized or connected SiO_4 tetrahedra in the amorphous phase (Farnan and Salje 2001). Isolated SiO_4 tetrahedra have four O atoms per unit cell and connected tetrahedra have fewer, therefore, given the stoichiometry of the original crystalline phase, a large number of O atoms remain unaccounted for in the amorphous plus crystalline structure. It is conceivable that these are trapped interstitially in the crystalline zircon in defect arrangements such as the O-O "dumbell" proposed by Crocombette (Crocombette 1999). However, exactly how local charge balance is maintained in the amorphous phase is not clear. The He atoms formed by recombination of the α-particles produced by radioactive decay could also become trapped in the zircon structure contributing to the lattice expansion and the distortion of the bonds locally. Helium incorporation has recently been proposed to occur in just this way in radiation-damaged monazites (Seydoux-Guillaume et al. 2002) causing a 1% expansion of the lattice. The local structural changes due to accumulated radiation damage derived from these calculations show that the NMR results are not accounted for by pure swelling of the zircon lattice as indicated by longer range X-ray diffraction measurements nor by a stress imposed by surrounding amorphous areas. We suggest a "stuffing" mechanism based on interstitial oxygen or helium, although other point defect mechanisms cannot be ruled out.

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