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Pressure-Induced Coordination Change of Ti in Silicate Glass: a XANES Study

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Abstract. The effect of pressure on titanium coordination in glasses, with composition $K_2TiSi_4O_{11}$, quenched isobarically from liquids equilibrated at high pressure (5, 10, 15, 20, 25, 30 kbar respectively) and $T = 1600°$ C has been investigated by X-ray absorption spectroscopy (XAS). The XANES spectra collected at the Ti *K*-edge clearly show a variation with pressure that is related to changes in the geometrical environment around the Ti atoms. By comparison with spectra of standard materials, the XANES spectra of the glasses suggest a relatively low average coordination number (near 5) in samples quenched at low pressure and a higher coordination number (near 6) in samples quenched from the highest pressure. The combination of XANES data with density and compressibility measurements supports the idea that a mixture of 6- and lower coordinated (4- and/ or 5-coordinated) Ti geometries are present in the 1 bar glass, and an increasing proportion of 6-coordinated Ti occurs in the glasses synthesized at progressively higher pressures.

Introduction

The influence of cationic coordination on the properties of silicate melts has been widely discussed in the literature (Bottinga et al. 1982; Bottinga 1985; Rigden et al. 1984; Stolper and Ahrens 1987). Perhaps the most direct consequence imaginable is the effect of cationic coordination on melt density (Waff 1975). A variable coordination number can influence the contribution of a melt component to the melt density through the different volumes corresponding to the coordination states. Additionally, the existence of a homogeneous equilibrium, dependent on temperature and pressure, between two coordination states of a cation, can drastically influence the values of thermal expansivity and compressibility of the melt. For these reasons and due to the importance of predicting melt densities at high pressures (e.g. Stolper et al. 1981), the pressure dependence of the coordination of cations in silicate melts has been the subject of several investigations. The TiO_2 component in silicate melts has been demonstrated to exhibit a partial molar volume and compressibility that is dependent on composition (Johnson and Carmichael 1987; Lange and Carmichael 1990; Dingwell 1992). Also, the investigation of silicate glasses, quenched from liquid at 1 atm pressure, suggests that the average coordination number of Ti in silicate melts may be composition-dependent (Dingwell et al. 1984). Thus it is appropriate to investigate the dependence of the structural role of Ti on pressure of synthesis or density. We have chosen a melt with an apparent low average coordination number of Ti at 1 atm (Dingwell et al. 1994) to test whether compression will induce a significant increase in the average coordination number of Ti.

X-ray absorption spectroscopy (XAS) is a well known technique (Brown et al. 1988) that provides element-specific structural data even at very low concentration of the selected element and regardless of the crystalline or amorphous nature of the sample (Calas and Petiau 1973; Kohn et al. 1990; Galoisy and Calas 1993). XANES spectra (X-ray Absorption Near Edge Structure) are recorded through an energy range from the pre-edge to about 70 eV beyond the edge. This region is dominated by multiple scattering effects between the absorber and its near neighbours and has been shown to be suited to yielding information on the coordination and local geometry around the selected absorbing atom (Davoli and Paris 1990). XANES spectra can also give information about the oxidation state of the absorber since different oxidation states produce a shift of the absorption edge (chemical shift) (Brown et al. 1988).

In this work, XANES spectra have been collected on a set of glass samples with the same chemical composition, that have been quenched from different pressures. The observed differences in these XANES spectra are compared with the results of density measurements obtained on the same samples.

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Materials and Methods

The 1 atm preparation and analysis of the $K_2TiSi_4O_{11}$ glass starting material has been described in Dingwell et al. (1994). For the purposes of the present investigation bubble- and crystal-free cylinders (4.8 mm diameter) of this glass were drilled from the 1 atm fusion products and cut to lengths of 10 mm. These cylinders were loaded into Pt capsules (5 mm dia.) and sealed by welding. The sealed capsules were surrounded by Al_2O_3 powder and packed into talc-pyrex-graphite cylindrical assemblies for a 1/2″ piston cylinder apparatus. The high pressure syntheses were performed at 1600° C and pressures of 5, 10, 15, 20, 25 and 30 kbar respectively. Pressure has been calibrated against the polymorphic transitions in $CaGeO_3$ and Mg_2GeO_4 (Ross et al. 1986; Ross and Navrotsky 1987). A pressure correction of $-18(2)\%$ of nominal pressure for piston-in-conditions was obtained.

The samples were held at the high temperature, high pressure condition for 1–2 hours and then quenched isobarically in a few seconds from the run temperature to a few hundred degrees by switching off power to the electrical heating and pumping during the quench. The quenching rate is thus on the order of 50–100° C/sec. This quenching rate is more rapid than that experienced by the 1 atm sample, but the difference in cooling rate (perhaps 1 log unit) should not lead to significant changes in the fictive temperature of the glasses. Estimation of the activation energy of structural relaxation in these melts indicates that a maximum shift of 30° C is expected between the different cooling rates. The effect of pressure on the glass transition for these samples is unknown. We cannot exclude that a significant variation in spectra results from the effect of pressure on the glass transition or fictive temperature of the quenched glasses. However, preliminary determinations of the temperature dependence of the pre-edge peak intensity, determined *in-situ* (Seifert et al. 1994) indicate that only minor variations (1–2%) can be expected to result from shifts in fictive temperature.

The assumption of thermal equilibration of our samples at the time-temperature-pressure conditions of the experimental dwell time is reasonable as the viscosities of these melts at such temperatures are quite low. The extent of relaxation of the melt density to lower temperatures and/or pressures during the quench is not known but some backreaction is probable. Thus we have measured the glass densities in order to quantify the density dependence of the spectra of these glasses.

X-ray absorption spectroscopy measurements have been carried out at the PULS X-rays line of the Frascati synchrotron ADONE (Italy). The XAS spectra have been collected in transmission mode using a Si (111) channel-cut crystal as monochromator and keeping the sample chamber in high vacuum. The samples were prepared by grinding glass fragments in a agate mortar and then smearing the powder on a kapton tape taking care of the thickness and homogeneity of the sample to obtain a good signal-to-noise ratio. To ensure the reproducibility of our measurements and for checking for the oxidation state of the samples, energy calibration has been performed using a standard Ti metal foil (EXAFS Materials, 4966.0 eV). The XANES spectra have been collected in an energy range of 100 eV to 70 eV after the absorption edge with an energy step of 0.2 eV. The energy resolution is 1 eV. After subtraction of the background with a linear function, all the XANES spectra have been normalized at high energy (5027 eV) to avoid the influence of multiple scattering effects. Peak energy position and intensity have been evaluated by a curve-fitting procedure, using Lorentzian curves. The spectra first derivative has been calculated to determine the energy position of the absorption edge to check for possible chemical shifts and to verify the oxidation state of the samples.

Several XRD structurally-characterized crystalline materials have been used as reference compounds, including synthetic rutile, anatase, narsarsukite and a natural titanite; literature data have been used for comparison and to investigate the relationship between spectral features and Ti coordination. All the standards have been chosen to be representative of the widest range of different coordination numbers and polyhedral geometries of oxygen-coordinated tetravalent titanium compounds. The collected data are reported in our companion paper (Dingwell et al. 1994: Table 2) and have been used to attempt a quantitative determination of the coordination numbers in the glasses using the pre-edge peak intensity.

Results

XANES Data

The XANES region is particularly sensitive to the local environment around the photoabsorber and thus, in principle, provides information concerning the average overall shape of the site, i.e. type of coordination polyhedron, presence of distortion, symmetry of the site (Brown et al. 1988). For transition elements, and in particular for titanium due to its electronic structure, the analysis of XANES spectra is particularly useful because the pre-edge resonance shows dramatic changes in intensity with changes in polyhedral geometry around the absorber (Waychunas 1987). The intensity variation of the pre-edge peak (labelled P in Fig. 1 and in the following) is related to the electronic transition $1s$–$3d$, that is forbidden in centrosymmetrical sites (e.g. regular octahedron) but partially allowed in non-centrosymmetrical polyhedra (e.g. tetrahedron: Waychunas 1987). Different polyhedral geometries produce a different overlapping of the orbital wave-functions and intermediate intensity of the pre-edge peak P (e.g. distorted octahedron, trigonal bipyramid, tetragonal pyramid: Paris et al. 1994), and it is therefore a good indicator of the prevalent geometry in the material under investigation.

The XANES spectrum of the uncompressed $K_2TiSi_4O_{11}$ glass is shown in Fig. 1 (curve R). It shows an intense pre-edge peak at 4971.6 eV (peak P), followed by a shoulder at about 4978 eV (A) and two asymmetric maxima in the region of the absorption edge, respectively at 4986.3 eV (B) and 4997.6 eV (C) (Table 1). Given the

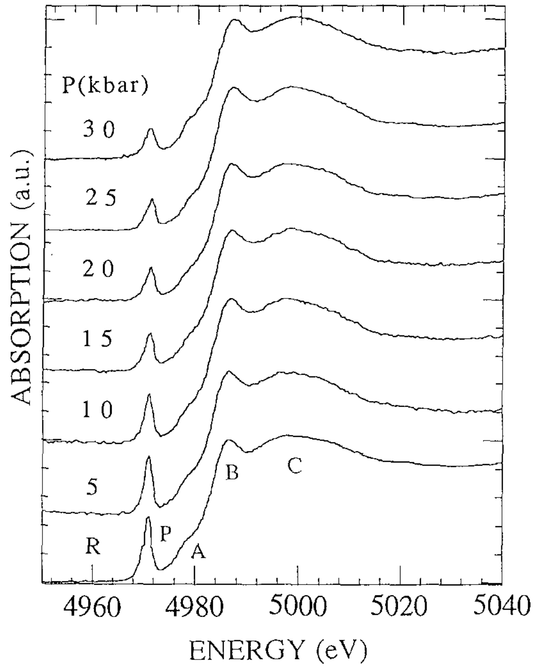

Fig. 1. Ti K-XANES spectra of $K_2TiSi_4O_{11}$ glasses quenched from different pressures. The main resonances are shown and labelled according to the text (P pre-edge peak, A, B, C). The intensity of peak P decreases strongly with the increasing pressures, suggesting an increase of the titanium average coordination number with pressure

sensitivity of the peak P to changes in coordination geometry of the target atom this peak can in principle give an indication of coordination number when calibrated with standards of known Ti coordination. A very intense pre-edge peak (72–88%) has been found to be characteristic of tetrahedrally-coordinated Ti (e.g. Ba_2TiO_4: Yarker et al. 1985) whereas it has intermediate intensity (55–62%) in compounds with 5-fold Ti (e.g. $Sr_2TiSi_2O_8$: Behrens et al. 1990) (Dingwell et al. 1994). In compounds with octahedrally-coordinated titanium the pre-edge peak is even less intense and varying in a range of intensity values between 6% (benitoite, regular octahedron: Fischer 1969) and 38% (narsarsukite, distorted octahedron: Peacor and Buerger 1962), depending on site symmetry and degree of polyhedral distorsion (Waychunas 1987; Dingwell et al. 1994; Paris et al. 1994). From the comparison with the standards, the glass at room pressure, whose pre-edge peak intensity (IP) is 58%, indicates an average coordination number (CN) close to 5, in good agreement with previous studies on similar glass compositions (Dingwell et al. 1994; Yarker et al. 1986).

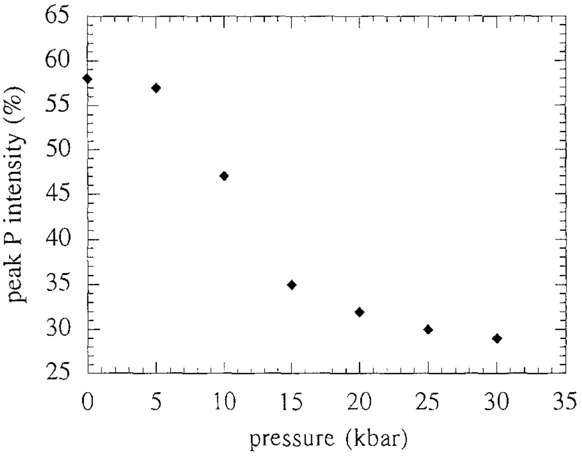

Fig. 2. Non-linear variation of pre-edge peak P intensity (IP) with pressure up to 30 kbar. The IP values (expressed in %) are normalized to high energy. A major decrease of the IP values occurs between 5 and 20 kbar, with little change above 25 kbar

Figure 1 shows the variation of the XANES spectra with pressure, up to 30 kbar. XANES resonances energy positions and intensities, evaluated by curve fitting, are reported in Table 1. Minor variations affect the resonances B and C at increasing pressures, whereas the spectra exhibit a strong decrease of the pre-edge peak P intensity (IP) with pressure, passing from 58% at room pressure to 29% at 30 kbar. The IP variation with pressure is clearly non-linear (Fig. 2) and it is very small up to 5 kbar, becomes very steep between 5 and 20 kbar, and flattens out at higher pressure. From comparison with reference compounds, the decrease in peak P intensity in these glasses is consistent with an increase in the average coordination number with increasing pressure. In fact, the peak P intensities at the highest pressures are comparable with those characteristic of 6-fold coordinated standards. Support to this interpretation comes also from the developments of the theoretical XANES modelling (e.g. Natoli et al. 1990) and the modelling of titanium polyhedral geometry by multiple scattering calculations. These calculations, using clusters of a few oxygen atoms around titanium to simulate the Ti local

Table 1. Characteristics of XANES resonances, calculated average coordination numbers and density data for the set of glasses at different pressures

P(kbar)	EP(eV)	IP	CN	EB(eV)	EC(eV)	D(g/cm^3)
0.001	4970.9	58	4.8	4986.3	4997.6	2.538 ± 0.002
5	4971.0	57	4.8	4986.6	4999.2	2.553 ± 0.001
10	4971.0	47	5.2	4986.2	4997.9	2.592 ± 0.002
15	4971.1	35	5.6	4987.0	4997.9	2.477 ± 0.001
20	4971.1	32	5.7	4986.6	4998.3	2.722 ± 0.007
25	4971.1	30	5.8	4986.9	4998.1	2.802 ± 0.03
30	4970.9	29	5.8	4987.0	4998.8	2.820 ± 0.05

EP peak P energy position; IP peak P normalized intensity; CN calculated average coordination number, using the equation given in the text; EB peak B energy position; EC peak C energy position; D measured density environment in a glass, permit discrimination of the contributions to the total spectrum coming from different geometrical environments and demonstrate the presence of more than one geometry in the glass structure (Paris et al. 1994).

In an attempt to further quantify the average coordination number using the observed variations in the pre-edge, data for all the titanium standards reported from the literature have been plotted versus coordination number (Dingwell et al. 1994). The regression line calculated as $\mathrm{IP} = -28.57\ \mathrm{CN} + 194.9$, where CN is the coordination number and IP is the normalized intensity of peak P ($R = 0.95$), has been used for obtaining average coordination numbers for the samples quenched from high pressures. The use of this approximation is supported by comparison with glasses whose CN has been independently determined and found to be in good agreement with our calculated values (Dingwell et al. 1994; Yarker et al. 1986). The application of a relationship obtained on crystalline compounds to glasses, appears perhaps suspect at first, but becomes less so when one considers that the resonance we are considering (peak P) is mostly due to interactions with the first coordination shell and it is therefore not affected by long-range order structural effects like other XANES resonances. A similar trend of the variation of CN with IP is also shown by theoretical spectra of Ti and O clusters reproducing different geometries (Paris et al. 1994). Applying therefore the above equation to our glasses we obtain coordination numbers varying from 4.8 (for the room pressure sample) to a value of 5.8 for the highest pressure samples (Table 1). Figure 4 shows the range of calculated average coordination numbers at the different pressures for the present samples. The calculated values support the idea of a lower average coordination number, close to 5, for the room pressure sample and a coordination number close to 6 for the high pressure samples, in full agreement with the more qualitative observation made by simple comparison with standard materials.

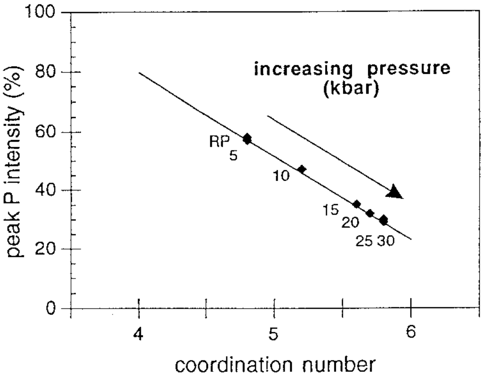

Fig. 3. Range of variation of average coordination numbers, as calculated from the equation of Dingwell et al. (1994), increasing from 4.8 for the room pressure glass to 5.8 for the highest pressure glass (30 kbar)

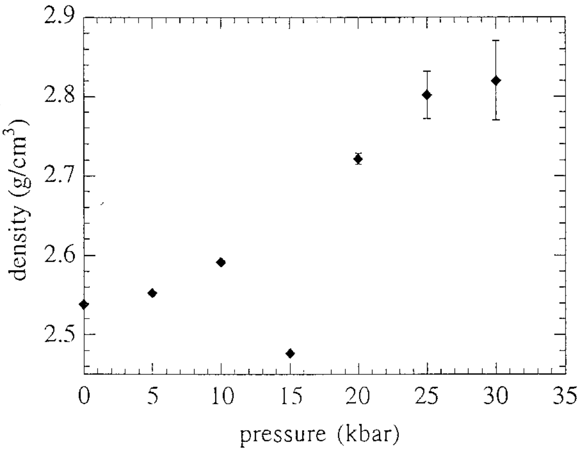

Fig. 4. Variation of measured glass density with synthesis pressure. The density increases also non-linearly, suggesting a rigid structural response at low pressure followed by a dramatic change between 5 and 25 kbar. (The 15 kbar sample disintegrated during the quench such that no suitably large fragments remained for accurate density determination.)

Another observation regarding the pre-edge region of our spectra concerns the peak P full-width at half-maximum values (FWHM) which increase with pressure from 2.0 to 2.8 eV. In crystalline compounds, as well as in glasses, narrower peaks have been found to be related to tetrahedrally coordinated Ti (e.g. $\mathrm{Ba_2TiO_4}$ 1.5 eV: Greegor et al. 1983) whereas larger FWHM values can been related either to the presence of a mixture of 4- and 6-coordinated Ti (e.g. diopside, 3.5–3.8 eV: Quartieri et al. 1993), or to a prevalent 6-coordinated distorted titanium environment whose pre-edges generally have larger FWHM (e.g. kaersutite, 2.7 eV: Lopez et al. 1993). However, in silicate glasses, in the case of a mixture of 4- and 6-coordinated Ti (Greegor et al. 1983) the spectra also show a strong increase of peak C (as well as P) with increasing of the tetrahedral component whereas this effect does not occur in the case of octahedral environments, as confirmed by MS calculations (Paris et al. 1994). The observation of these combined effects is therefore useful to discriminate between the two possibilities. The FWHM of 2.0 eV reported for the 5-coordinated Ti in glass by Yarker et al. (1986) is in agreement with the FWHM value for our room pressure spectrum and supports our interpretation of an average CN of 4.8. The increase of FWHM values in our set of spectra suggests therefore an increase of the octahedral component with pressure. The higher FWHM values are consistent with a distorted 6-coordinated environment (Lopez et al. 1993), although the presence of minor amounts of other geometries cannot be ruled out. The detailed analysis made by Waychunas (1987) on a suite of octahedrally-coordinated Ti crystalline compounds also shows the pre-edge peak to be composed of different lines which appear to be symmetry dependent. The limited number of Ti compounds with geometries other than octahedral does not allow similar arguments to be applied to them.

The energy position of the absorption edge gives an indication of the oxidation state of the material under investigation, if energy calibration is done using reference materials (Brown et al. 1988). However it has been shown that there is a large uncertainty in the determination of Ti oxidation state, due to the small shift in energy observed between Ti^{3+} and Ti^{4+} (about 2 eV) and also due to the "structure" effect that influences the resonance energies (Waychunas 1987). In this study, a Ti metal foil (4966.4 eV) has been used for energy calibration. First derivatives of both the first inflection point of the spectrum and the inflection point on the edge ramp have been taken into consideration and the values scatter around 4970.1 ± 0.1 and 4977.2 ± 0.5 respectively. If the pre-edge peak P energy position is considered as the most reliable measure of oxidation state (Waychunas, 1987) the samples show an energy shift of 4.5–4.7 eV (Table 1) relative to Ti metal. These values are consistent with the presence of tetravalent titanium but it is interesting to observe that they are much higher than those found for crystalline compounds with both tetrahedral (3.5 eV, Ba_2TiO_4: Yarker et al. 1986) and octahedral coordination (2.0–3.5 eV: Waychunas 1987; Lopez et al. 1993). Instead, they are consistent with the values found for glasses (3.8–4.6 eV: Greegor et al. 1983; 4.8 eV; Yarker et al. 1986), suggesting not only a bond-length effect but also a structure-dependence of the pre-edge feature energy position, as already observed between crystalline silicates and oxides (Waychunas 1987). For the purpose of our work however, it is important to note that no pressure-induced changes in the oxidation state were detected in our samples. However, given the large uncertainty of the method at this energy, up to 10% Ti^{3+}/Ti_{tot} could be present but not detected (Waychunas 1987). On the other hand, absence of anomalous colour of the glasses is a good indications that the presence of even small amounts of Ti^{3+} can be excluded.

Density Data

The measured density data for the set of studied glasses synthesized at different pressures are reported in Table 1. Figure 4 shows that the density increases slightly at low pressure then more steeply between 10 and 25 kbar and then less steeply again at the highest pressures. This behaviour suggests that the Ti environment reacts rigidly at low pressures (<10 kbar), followed by a larger change in the structure between 10 and 25 kbar and minor variation at higher pressures (>25 kbar). This general variation of density versus pressure is consistent with the notion of a homogeneous equilibrium between the various coordination states of Ti which goes to completion at $P > 25$ kbar. It is worthwhile to note that the pattern of density variation with pressure (Fig. 4) is very similar to that of the pre-edge peak intensity (Fig. 2), suggesting a close correlation between density and Ti structural environment for these glasses.

Discussion and Conclusions

The effect of pressure on the coordination state of cations of geological interest and their analogues has been studied with a variety of methods. In general the conclusion has been reached that either there is little or no coordination change, or it is unquenchable to room pressure. For example, for SiO_2 glasses it is has been shown that an increase in pressure up to 30 kbar produces no changes of the Si – O bond-length of the network-forming tetrahedra but produces instead a decrease of the intertetrahedral angles (Seifert et al. 1983; Davoli et al. 1992). Highly sensitive NMR investigations have identified the presence of several percent of more highly coordinated Si from pressures much higher than those accessed in this work (Stebbins and McMillan 1989; Xue et al. 1989). Only one report of a pressure induced coordination change of Al exists to date, that of Ohtani et al. (1985). An early investigation of Fe, Ga and Ge in silicate glasses quenched from pressures up to 30 kbar (Fleet et al. 1984) indicated no evidence for quenchable coordination shifts of those three cations. That study utilized X-ray absorption data for Ga and both XANES and EXAFS revealed no evidence for a coordination shift for synthesis pressures up to 25 kbar. More recent *in-situ* studies of coordination have illustrated a pressure-induced coordination shift of Ge at much higher pressures than those investigated here (Durben and Wolf, 1991). For GeO_2 glasses, *in-situ* high-pressure XAS studies have shown a transition from 4-fold to 6-fold coordination at ~70 kbar and it has been found to be similar to that occurring in crystalline GeO_2 (i.e. from quartz-like phase to rutile-like phase) (Itié et al. 1989). Recently, Keppler and Rubie (1993) have pointed out that pressure produce changes of coordination for Ni and Co in doped albite glasses quenched from 100 kbar and 2900° C. Using crystalfield spectroscopy they found that Co and Ni, which seemed to be respectively tetrahedral and in a mixture of very distorted octahedral and tetrahedral sites at room pressure (cf. Galoisy and Calas 1993) become octahedral at high pressure.

Previously, no information was available on the influence of pressure on titanium-bearing silicate glasses. The predominance of a distorted octahedral environment around Ti atoms at the higher pressures, was determined mainly by comparison with mineral standards XANES data and also confirmed by a preliminary EXAFS analysis which yields an average bond length of 1.95(0.02) for the sample treated at 30 kbar. The pressure dependence of Ti coordination inferred in the present study is qualitatively different from all of the above cases. Our results show a large shift in average coordination number of Ti over a moderate range of pressure relevant to the petrogenesis of magmas in the crust and mantle.

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