

Phase changes and amorphization of zeolites at high pressures: The case of scolecite and mesolite

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ABSTRACT

Pressure-induced amorphous-phase transitions (amorphization) have been observed in framework silicates like quartz and feldspars. A similar crystalline to highly disordered solid phase transition is reported in this study for two zeolites, scolecite and mesolite. Pressure-induced amorphization is demonstrated using in situ X-ray diffraction and Raman spectroscopy. Before complete amorphization, progressive structural changes are observed below 10 GPa. The transition from the crystal to the amorphous phase is irreversible, and the pressure-quenched samples exhibit Raman spectra that bear strong resemblance to aluminosilicate glasses obtained by quenching a liquid. In some cases, however, decompression from 15 GPa of fully amorphized samples is accompanied by a rim recrystallization of the sample and preservation of an amorphous phase with a structure different from that quenched in other experiments. Shear stresses seem to have important control of the transformation occurring during the decompression of the samples.

INTRODUCTION AND PREVIOUS WORKS

Zeolites are very common minerals at the Earth's surface and are often found as late-stage crystallization or alteration products within cavities in basaltic rocks. Much of the interest in zeolites comes from their industrial applications as catalysts and selective sorbers. These properties are related to the typical structure of zeolites, which consists of an aluminosilicate framework with cavities and channels of various sizes that are occupied by cations and extra molecules. Their structural properties have been extensively reviewed in numerous articles or monographs (e.g., Gottardi and Villa 1985). The stability, the phase changes, and the dehydration of zeolites during heating at room pressure have been the subject of numerous experimental studies. However, there exist only a few studies on the effect of pressure at room temperature on the structure of zeolites (Velde and Besson 1981; Belitsky et al. 1992).

Since the discovery of a static pressure-induced amorphous-phase transition (amorphization) in hexagonal (Ih) H₂O ice (Mishima et al. 1984), the phenomenon has been observed to occur for a range of crystal structures and chemistries, in particular in framework silicates like SiO₂ (quartz and coesite) (Hemley 1987; Hemley et al. 1988) and feldspars (Williams and Jeanloz 1989; Daniel et al., unpublished data). The nature of the low-temperature amorphization process has been the subject of numerous theoretical (Tse and Klug 1992, 1993; Lam and Okamoto 1994) and experimental investigations, using a range of experimental probes sensitive to different length scales:

in situ X-ray diffraction and Raman, IR, and Brillouin spectroscopies, and high-resolution transmission electron microscopy of recovered samples. Previous studies of quartz-related materials (SiO₂, GeO₂, AlPO₄) have shown that the details of the amorphization process are sensitive to the state of stress undergone by the samples (hydrostatic vs. nonhydrostatic loading), and the nature of the recovered samples depends on the maximum pressure reached (Wolf et al. 1992; Kingma et al. 1993a, 1993b; Gillet et al. 1995).

Belitsky et al. (1992) showed that zeolites of the natrolite group undergo numerous phase changes upon compression at room temperature, and they briefly mentioned that amorphization might occur at pressures in excess of 8 GPa. The purpose of the present study is to investigate the pressure-induced amorphization of zeolites of the natrolite type (scolecite and mesolite) by means of in situ X-ray diffraction and Raman spectroscopy at high pressures.

SAMPLES AND EXPERIMENTAL TECHNIQUES

The zeolites studied are of the natrolite type. The scolecite and mesolite samples were kindly provided by P. Bariat (Collection de Minéralogie, Université de Paris VI). They have been characterized by X-ray diffraction, electron microprobe, and Raman spectroscopy. Their chemical compositions are very close to those of the scolecite end-member Ca₈Al₁₆Si₂₄O₈₀·24H₂O and the mesolite end-member Na₁₆Ca₁₆Al₄₈Si₇₂O₂₄₀·64H₂O.

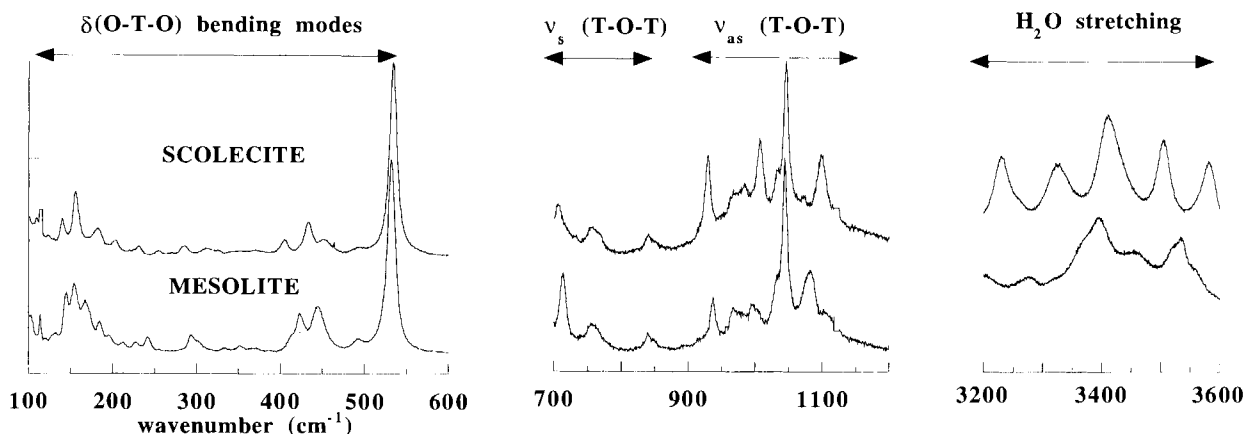


FIGURE 1. Room-temperature spectra of scolecite and mesolite and mode assignment.

All the experiments were performed in a diamond-anvil cell equipped with low-fluorescence diamonds. Previous studies at high pressures (Belitsky et al. 1992) have shown that for natrolite-type zeolites, fluids used as pressure-transmitting media, depending on their nature, may or may not enter in the channels of the crystals during compression. To avoid such problems we used soft plastic solids such as KBr as pressure-transmitting media. It must be kept in mind that these media provide only quasi-hydrostatic pressures. Shear stresses due to pressure gradients are thus present. The samples (fragments chipped from single crystals, with sizes ranging from 50 to 150 μm long and initial thicknesses between 20 and 50 μm) were loaded into 200 μm holes drilled in preindented stainless-steel gaskets. The pressure gradient was measured by recording fluorescence spectra from ruby grains at several points within the cell, and pressure differences within the cell never exceeded 1–2 GPa at 20 GPa in the quasi-hydrostatic experiments. Care was taken to ensure that the sample never bridged the diamond anvils. This was achieved by embedding the sample between two layers of KBr powder prior to compression. Unpolarized Raman spectra were obtained with an XY Dilor Raman spectrometer equipped with a charge-coupled-device detector. Gratings of 1800 grooves per mm were used, and the spectra were collected in a backscattering geometry through a long-working-distance Mitutoyo microscope objective. Raman scattering was excited with the 514.5 or 488 nm lines of an argon ion laser. Pressure was measured using the ruby-fluorescence technique.

X-ray diffraction experiments were conducted in an energy-dispersive mode at the DCI storage ring (LURE, Orsay-France). A polychromatic X-ray beam was collimated to a $50 \times 50 \mu\text{m}$ sized spot on the pressurized powder sample. The diffracted beam was collected between 5 and 50 keV by a Canberra planar germanium detector. Silicon oil (dimethyl-polysiloxane, ref 47V1000 from Prolabo) was used as pressure-transmitting medium. Even if this oil remains liquid up to 15 GPa, bridging of the powder

with the diamonds can generate deviatoric stresses by enhancing grain-to-grain contact during compression.

RAMAN AND X-RAY DATA AT HIGH PRESSURES

The Raman spectra of the two zeolites at ambient conditions are shown in Figure 1. According to previous Raman spectroscopic investigations (Dutta and Del Barco 1985; Dutta et al. 1988; Bärtsch et al. 1994), the following features and mode assignments can be outlined for both zeolites. The modes between 900 and 1100 cm^{-1} are assigned to antisymmetric T-O-T (T = Si or Al) stretching vibrations. Symmetric T-O-T stretching vibrations are located between 700 and 850 cm^{-1} . The modes below 550 cm^{-1} are assigned to various $\delta(\text{O-T-O})$ bending and rotational modes. The intense mode near 530 cm^{-1} is clearly attributed to the O atom's motion in the plane perpendicular to the T-O-T bond (Dutta et al. 1988). Vibrations of the H_2O molecules are observed by the O-H stretching motions in the 3200–3600 cm^{-1} region of the spectra.

Upon compression at room temperature, scolecite undergoes a series of modifications visible on the Raman spectra. Figure 2a shows a series of in situ Raman spectra recorded in succession at increasing pressures. Between room pressure and 1.8 GPa no significant changes in the Raman spectra are observed. Between 2 and 4 GPa slight changes (band broadening and peak disappearance) are detected in the 100–350 cm^{-1} region. Despite these minor changes the intense Raman bands of the starting crystal (e.g., 533 cm^{-1}) are well resolved up to 6 GPa and shifted toward higher wavenumbers. Between 6 and 8 GPa several more significant changes are observed. First of all, there is a strong decrease in the total intensity of the Raman signal. Above 6 GPa new broad bands appear. During pressure increase from 0.1 MPa to 4 GPa there is a strong increase in the frequency of the main 533 cm^{-1} mode (5.6 $\text{cm}^{-1}/\text{GPa}$) and only a very slight increase in the band width (Fig. 3). Above 4 GPa and up to 9 GPa there is a strong increase in the line width and a strong decrease in the frequency shift (Fig. 3). In the 900–1100

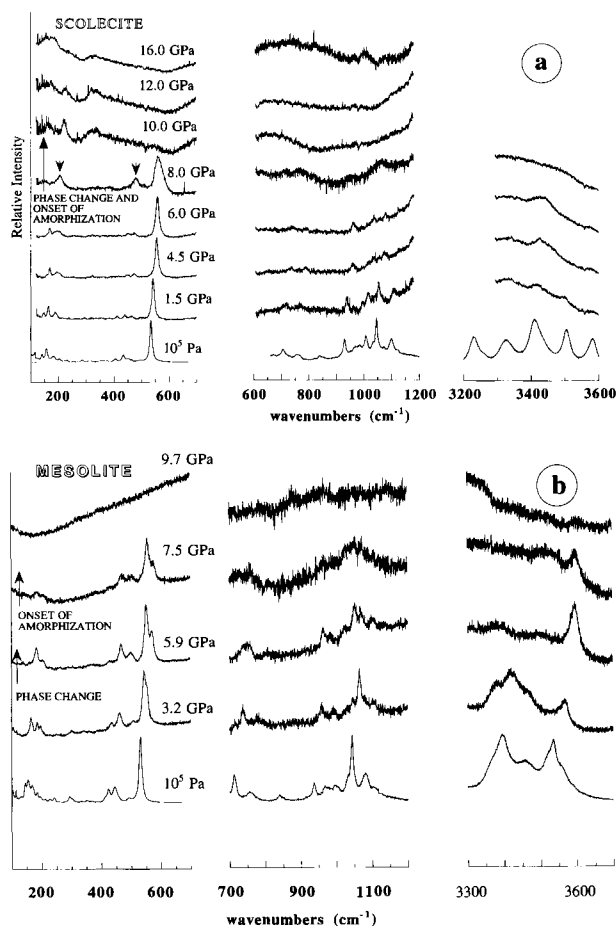


FIGURE 2. Typical spectra of scolecite (a) and mesolite (b) obtained during compression.

and 3200–3600 cm^{-1} regions, the discrete bands are replaced by broad bands. Above 9 GPa most of the sharp modes have disappeared, even the most intense 533 cm^{-1} mode. Spectra of samples decompressed from peak pressures of 16 GPa show only broad features similar to those of aluminosilicate glasses produced by thermal quenching (Fig. 4).

Mesolite exhibits similar changes (Fig. 2b). Up to 3 GPa the Raman spectra are quite similar to those of the starting crystal. Above 3 and up to 7.5 GPa the appearance of new bands and the splitting of the intense 530 cm^{-1} mode are observed. Important changes in the number and intensity of bands in the 3200–3600 cm^{-1} region are also observed. Above 8 GPa all the sharp modes have disappeared, only broad features are preserved, and a strong background fluorescence is observed. As in the case of scolecite, the spectra of samples decompressed from pressures in excess of 11 GPa exhibit broad bands typical of an amorphous phase (Fig. 4).

Figure 5 shows a series of X-ray spectra of scolecite recorded between room pressure and 11 GPa. From 0.1

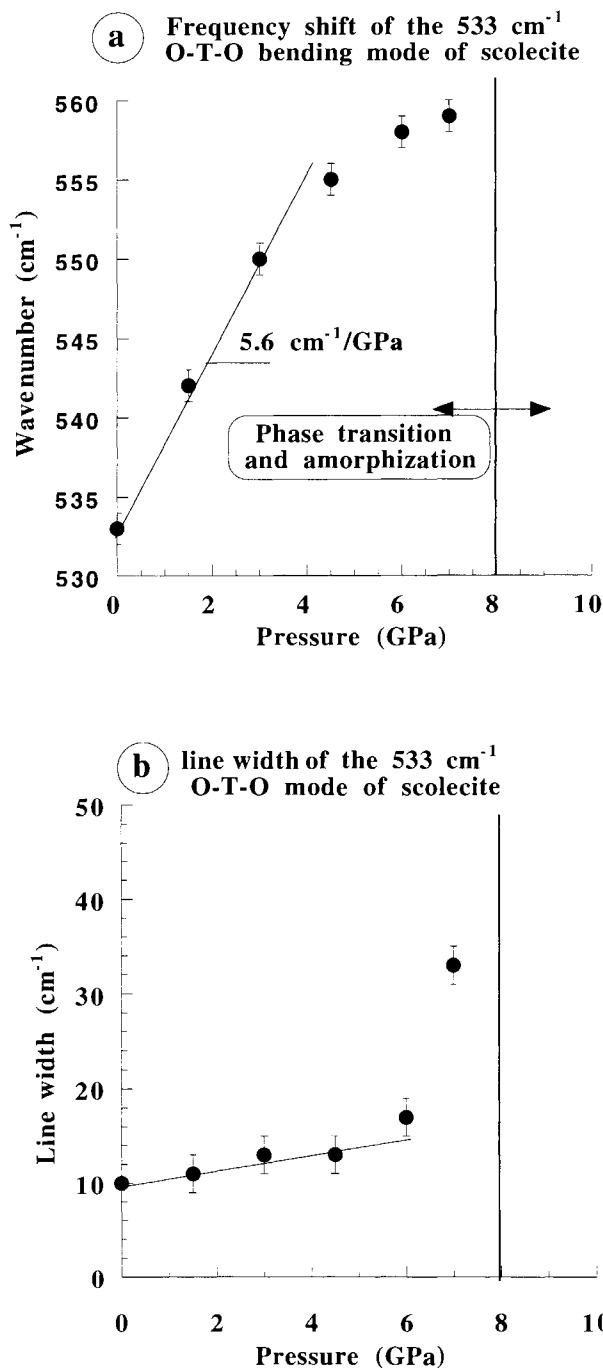


FIGURE 3. (a) Pressure-induced shift of the most intense Raman band of scolecite (room-pressure wavenumber at 533 cm^{-1}). This mode corresponds to O-T-O bending motion. (b) Bandwidth evolution of the same mode with increasing pressure.

MPa to 5 GPa the X-ray patterns show only minor changes, which can be related to those observed in the Raman spectra. Changes in the peak intensities are related to the development of preferred orientations in the

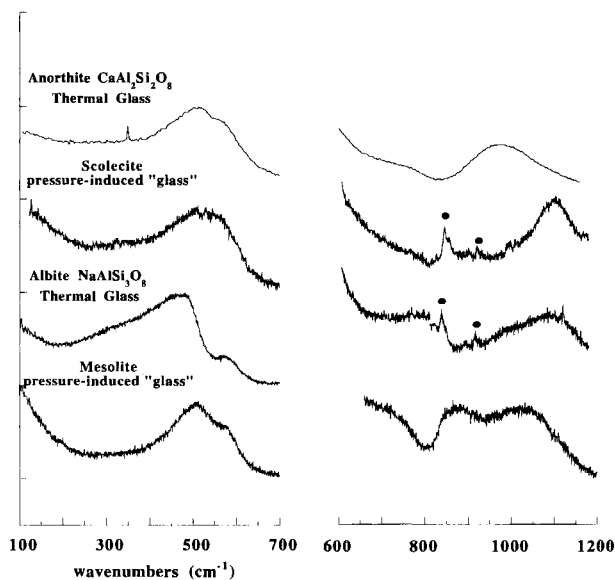


FIGURE 4. Raman spectra of pressure-induced disordered zeolites compared with thermal aluminosilicate glasses of anorthite and albite compositions (Daniel et al. 1995). The peaks near 850 cm^{-1} in the scolecite and albite glasses are due to coating of the microscope objective of the micro-Raman spectrometer.

compressed powder. The intense peak near 21 keV corresponding to a (441) plane is observed up to 6 GPa. Above 6 GPa this intense peak becomes weaker and broader. Other diffraction peaks also appear above 6 GPa. Above 9 GPa only a broad feature characteristic of amorphous material is observed. The X-ray spectrum of the decompressed sample is similar to the one recorded at 11 GPa.

PRESSURE-INDUCED STRUCTURAL CHANGES AND AMORPHIZATION

The Raman and X-ray data indicate that scolecite undergoes a series of structural transformations between 0.1 MPa and 9 GPa. Between 0 and 4 GPa there are only minor changes in the Raman and X-ray diffraction data, which may be due to a polymorphic phase transition. Between 6 and 8 GPa major continuous changes are observed preceding a crystal to amorphous phase transition occurring above 8 GPa. The band broadening in both X-ray and Raman spectra indicates that a progressive and important disordering precedes the transition to the (highly disordered?) amorphous state.

In well-ordered minerals, like the present starting products prior to compression, the typical line width of the Raman bands is on the order of 10 cm^{-1} . In disordered crystals or in crystals heated close to their melting point, band widths of $30\text{--}40\text{ cm}^{-1}$ are commonly observed and are similar to those observed just before the onset of pressure-induced amorphization. The strong band broadening of the 530 cm^{-1} mode observed just before the dis-

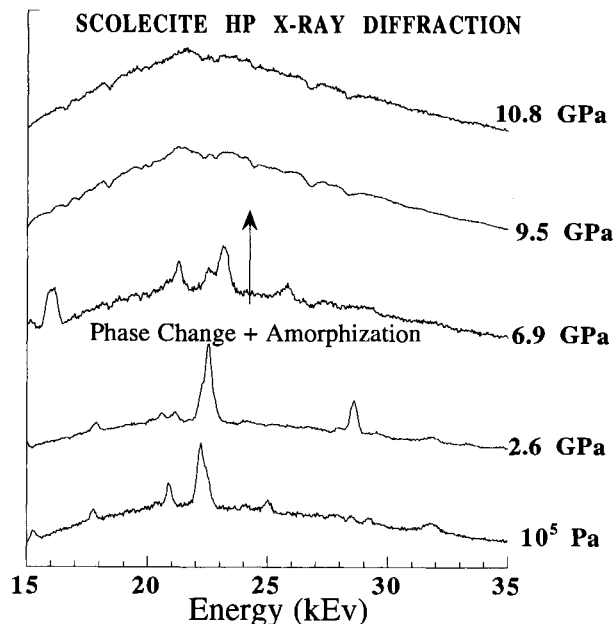


FIGURE 5. X-ray diffraction pattern of scolecite at different pressures. Between room pressure and 1.8 GPa slight modifications are related to a first pressure-induced, crystal-crystal phase transition less evident than those occurring at higher pressures.

appearance of the crystal Raman signal (Fig. 3) may be indicative of an increased spread of T-O-T angles caused by disruption and collapse of the four-membered rings. The Raman-active modes lying between 850 and 1100 cm^{-1} attributed to antisymmetric T-O-T (T = Si or Al) stretching vibrations also exhibit strong broadening just before amorphization (Fig. 2). This phenomenon is also indicative of progressive disruption of the four-membered ring structure. This progressive disruption of a crystal during pressurization was discussed by Wolf et al. (1992).

The evolution of the frequency and the line width of the T-O-T-bending Raman-active modes provides insights on the mechanism responsible for the observed amorphization. Dutta et al. (1988) showed that in zeolites there is a linear relationship between the mean T-O-T bond angle in the four-membered TO_4 rings and the frequency of the intense Raman-active mode near 500 cm^{-1} : the mode frequency (ν) increases with decreasing T-O-T angle (α), $\partial\nu/\partial\alpha = 5\text{--}6\text{ cm}^{-1}/^\circ$. This mode is related to a deformation of the T-O-T angle. Its pressure dependence may thus be indicative of the bond-angle decrease during compression up to the amorphization. The mean T-O-T angle in scolecite at room pressure is about 137° . If the frequency-angle relationship is valid, then at the onset of amorphization the T-O-T angle decreased to 130° . Most of this bond-angle change occurs between 0.1 MPa and 4 GPa. Similar T-O-T bond-angle changes have also been observed in SiO_2 and GeO_2 quartz prior to amorphization (Hazen et al. 1989; Madon et al. 1991).

The behavior of scolecite upon compression shares common aspects with the structural evolution of α -SiO₂ and α -GeO₂ quartz structures (Wolf et al. 1992; Kingma et al. 1993a, 1993b; Richet and Gillet, in preparation). It is now well established that the α -quartz phases of SiO₂ and GeO₂ gradually transform to an amorphous state upon static compression at room temperature. For SiO₂ it has been established that a crystal-crystal phase transition precedes, or perhaps accompanies, the amorphization process. For GeO₂ and SiO₂ it has been shown that at the onset of amorphization there is a strong peak broadening and a sudden drop in Raman-mode intensities. Similar observations have been made for feldspars like anorthite (Daniel et al., unpublished data) and clathrasils (Tse et al. 1994). All these features are observed in the present study.

In mesolite there is a splitting of the intense 530 cm⁻¹ mode upon compression (Fig. 2b). This splitting may indicate subtle changes in the puckering of the four-membered rings (Mihailova et al. 1994). As in the case of scolecite there is also a band broadening in both the 500 and 1000 cm⁻¹ regions just before the onset of amorphization, which is marked by the disappearance of the discrete Raman bands.

The present results indicate that the volume changes of zeolites during compression prior to pressure-induced amorphization are essentially achieved by closure of the T-O-T angles to 130°. Further closure of these angles cannot occur probably because of repulsion between O and Si atoms. Zeolites accommodate further compression by a disordering process leading ultimately to an amorphous solid.

From a thermodynamic perspective several comments can be made. The amorphous zeolites are in highly metastable states because they are probably compressed well outside their stability fields. Thus, the transition from the crystal to the amorphous phase is probably driven by large volume changes. In the case of quartz this has been clearly established because the equation of state of the crystalline form and that of the glass are known to very high pressures. It appears that quartz becomes less dense than SiO₂ glass at pressures close to those reported for the onset of amorphization. Such data are unfortunately missing for zeolites and their equivalent glasses. Some estimates of the volume changes driving the crystal to amorphous phase transition could be obtained if the thermodynamically stable phase assemblage for the zeolites (oxide + silicate + H₂O) was known in the pressure range of pressure-induced amorphization. To our knowledge, no high-pressure, high-temperature experimental data on the stability of the two studied zeolites exist in the pressure range explored in the present study.

STRUCTURE OF PRESSURE-QUENCHED PHASES

The Raman spectra of pressure-quenched products are presented in Figure 4. They consist of broad bands (400–800 and 900–1300 cm⁻¹). Thermal glasses produced by the quenching of melts of similar compositions cannot be

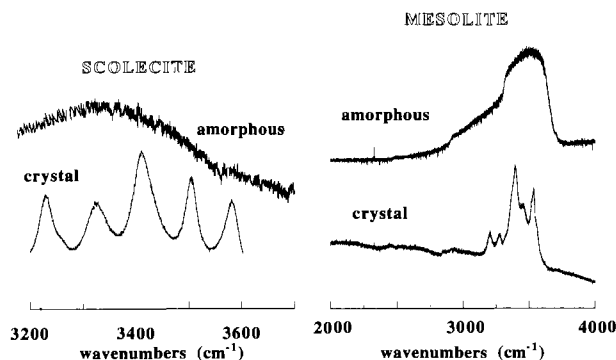


FIGURE 6. Raman spectra in the OH stretching region in the starting crystals and in the pressure-induced disordered solids decompressed from 11 GPa.

obtained. However, the present spectra share common features with those of temperature-quenched aluminosilicate glasses obtained from other dry-chemical compositions (Fig. 4). These common features indicate that for zeolites the structures of pressure-quenched products are broadly similar to the archetypal amorphous solids represented by thermal glasses. Such similarities between amorphous phases produced by pressurization and phases produced by quenching a high-temperature melt have already been observed in SiO₂ (Hemley 1987).

The spectra of pressure-quenched products are sensitive to chemical compositions, as also observed in thermal glasses (e.g., McMillan et al. 1982). The spectral differences may represent various subtle differences in (1) the Al and Si tetrahedral arrangement, (2) changes in the number of Al-O-Al linkages, or (3) changes in the number of tetrahedra in (Al,Si)-containing rings (McMillan et al. 1982; Matson et al. 1983; Kubicki and Sykes 1993; Daniel et al. 1995). Alternatively, these spectral changes may also represent pressure-induced coordination changes of Al-Si quenched upon decompression.

The spectral region between 3000 and 3600 cm⁻¹ (corresponding to the vibration of the H₂O molecules) shows only broad bands (Fig. 6). This is also indicative of a highly disordered solid. The position of the H₂O molecule is no longer controlled by a regular arrangement of the channels and cages that exist in the crystalline starting product. IR spectroscopy measurements could provide further insights into the structural evolution of the H₂O molecules. Strong compression of the zeolites could perhaps lead to the local formation of high-pressure clusters of ice VI or VII, the high-pressure forms of ice I (normal ice) in the channels of the structures. At the moment no sign of such a phenomenon has been observed. Moreover, no sign of dehydration of the zeolites has been observed during compression.

In some scolecite experiments the decompression history is quite complex. After compression to peak pressures in excess of 10 GPa, at which the sample was fully amorphous, it was observed (optically and by Raman

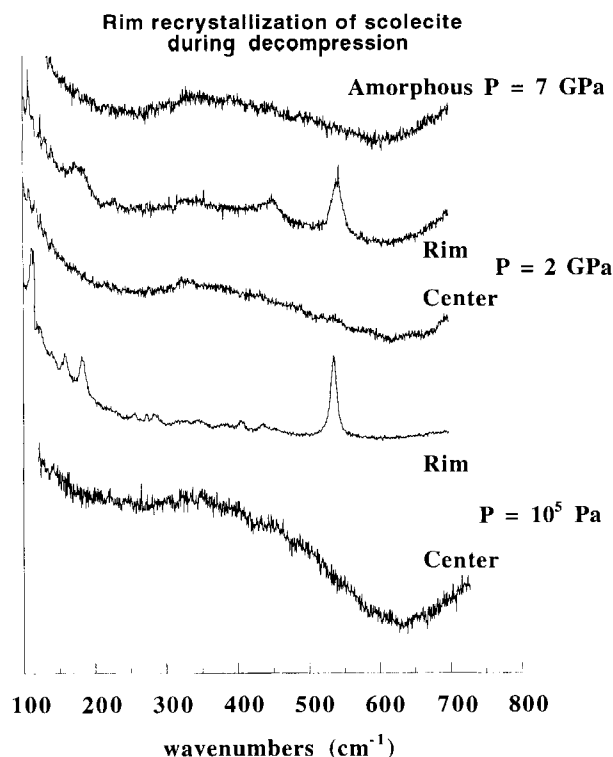


FIGURE 7. Rim recrystallization of the disordered scolecite upon decompression. Above 10 GPa and down to 7 GPa the sample was fully amorphous, as demonstrated by Raman spectra recorded on different places in the sample. Below 7 GPa the Raman spectra of the rim have characteristic peaks of scolecite, whereas the interior of the sample has spectra characteristic of an amorphous material. The spectra of the amorphous material is different from the amorphous solid quenched in experiments in which no recrystallization was observed.

spectroscopy) that during progressive decompression the amorphous samples develop a crystalline rim of back-transformed material, but the interiors of the grains remain in the high-pressure amorphous or highly disordered phase (Fig. 7). On recovery, the interiors consist of amorphous material coexisting with scolecite. In this case the spectra of the quenched amorphous phase are different from those observed in the other experiments (compare Fig. 4 and Fig. 7). They are similar to the high-pressure spectra and may thus represent the quenched product of a high-pressure amorphous material with a structure different from that of samples quenched in experiments in which no recrystallization was observed. In the experiments in which no recrystallization was observed, the amorphous phase may have undergone some structural changes upon decompression. However, the spectroscopic evidence for an actual transition or for structural differences between the two amorphous phases is very poor, and further work is needed to elucidate this complexity. The rim recrystallization is probably induced at the sample surface by shear stresses due to the quasi-

hydrostatic pressure transmitting medium (KBr) or to slight bridging of the sample with the diamonds. Similar effects have also been observed in α -AlPO₄ during compression in solid pressure-transmitting media (Gillet et al. 1995). Tensile cracks were also observed to form during decompression and may have been caused by relaxation of internal tensile stresses during decompression, which could have been induced by elastic mismatch between amorphous and crystalline domains. In conclusion, it appears that the decompression history is extremely sensitive to the nonhydrostaticity of the pressure-transmitting medium. Shear stresses may promote structural changes in the amorphous phases and partial recrystallization of the samples upon decompression.

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REFERENCES CITED

- Bärtsch, M., Bornhauser, P., Calzaferri, G., and Imhof, R. (1994) H₂Si₄O₁₂: A model for the vibrational structure of zeolite-A. *Journal of Physical Chemistry*, 98, 2817–2831.
- Belitsky, I.A., Fursenko, B.A., Gabuda, S.P., Kholdeev, O.V., and Seryotkin, Y.V. (1992) Structural transformations in natrolite and edingtonite. *Physics and Chemistry of Minerals*, 18, 497–505.
- Daniel, I., Gillet, P., McMillan, P.F., and Poe, B.T. (1995) In-situ high-temperature Raman spectroscopic studies of aluminosilicate liquids. *Physics and Chemistry of Minerals*, 22, 74–86.
- Dutta, P.K., and Del Barco, B. (1985) Raman spectroscopic studies of zeolite framework: Hydrated zeolite A and the influence of cations. *Journal of Physical Chemistry*, 89, 1861–1865.
- Dutta, P.K., Shieh, D.C., and Puri, M. (1988) Correlation of framework Raman bands of zeolites with structure. *Zeolites*, 8, 306–309.
- Gillet, Ph., Badro, J., Varel, B., and McMillan, P.F. (1995) High pressure behavior in α -AlPO₄: Amorphization and the "Memory Glass" effect revisited. *Physical Review B*, 51, 11262–11269.
- Gottardi, H., and Villa, J.M. (1985) *Natural zeolites*, 409 p. Springer-Verlag, Berlin.
- Hazen, R.M., Finger, L.W., Hemley, R.J., and Mao, H.K. (1989) High-pressure crystal chemistry and amorphisation of α -quartz. *Solid State Communication*, 72, 507–511.
- Hemley, R.J. (1987) Pressure dependence of Raman spectra of SiO₂ polymorphs: α quartz, coesite and stishovite. In M.H. Manghni and Y. Syono, Eds., *High-pressure research in mineral physics*, p. 347–360. Terra Scientific, Tokyo.
- Hemley, R.J., Jephcoat, A.P., Mao, H.K., Ming, L.C., and Manghni, M.H. (1988) Pressure-induced amorphization of crystalline silica. *Nature*, 334, 52–54.
- Kingma, K.J., Meade, C., Hemley, R.J., Mao, H.K., and Veblen, D.R. (1993a) Microstructural observations of α -quartz amorphization. *Science*, 259, 666–669.
- Kingma, K.J., Hemley, R.J., Mao, H.K., and Veblen, D.R. (1993b) New high-pressure transformation in α -quartz. *Physical Review Letters*, 25, 3927–3930.
- Kubicki, J.D., and Sykes, D. (1993) Molecular orbital calculations of vibrations in three-membered aluminosilicates rings. *Physics and Chemistry of Minerals*, 19, 381–391.
- Lam, N.Q., and Okamoto, P.R. (1994) A unified approach to solid-state amorphization and melting. *Material Research Bulletin*, 19, 41–46.
- Madon, M., Gillet, Ph., Julien, C., and Price, G.D. (1991) A vibrational study of phase transitions among the GeO₂ polymorphs. *Physics and Chemistry of Minerals*, 18, 7–18.

- Matson, D.W., Sharma, S.K., and Philpotts, J.A. (1983) The structure of high-silica alkali silicate glasses: A raman spectroscopic investigation. *Journal of Non-Crystalline Solids*, 58, 323–352.
- McMillan, P.F., Piriou, B., and Navrotsky, A. (1982) A Raman spectroscopic study of glasses along the joins silica-calcium aluminate, silica-sodium aluminate, and silica-potassium aluminate. *Geochimica and Cosmochimica Acta*, 46, 2021–2037.
- Mihailova, B., Zotov, N., Marinov, M., Nikolov, J., and Konstantinov, L. (1994) Vibrational spectra of rings in silicate glasses. *Journal of Non-Crystalline Solids*, 168, 265–274.
- Mishima, O., Calvert, L.D., and Whalley, E. (1984) "Melting ice I" at 77 K and 10 kbar: A new method for making amorphous solids. *Nature*, 310, 393–394.
- Tse, J.S., and Klug, D.D. (1992) Structural memory in pressure-amorphized AlPO_4 . *Science*, 255, 1559–1561.
- (1993) Anisotropy in the structure of pressure-induced disordered solids. *Physical Review Letters*, 70, 174–177.
- Tse, J.S., Klug, D.D., Ripmeester, J.A., Desgreniers, S., and Lagarec, K. (1994) The role of non-deformable units in pressure-induced reversible amorphization of clathrasils. *Nature*, 369, 724–727.
- Velde, B., and Besson, J.M. (1981) Raman spectra of analcime under pressure. *Physics and Chemistry of Minerals*, 7, 96–99.
- Williams, Q., and Jeanloz, R. (1989) Static amorphization of anorthite at 300 K and comparison with diaplectic glass. *Nature*, 338, 413–415.
- Wolf, G.H., Wang, S.A., Herbst, C.A., Durben, D.J., Oliver, W.F., Kang, Z.C., and Halvorson, K. (1992) Pressure-induced collapse of the tetrahedral framework of crystalline and amorphous GeO_2 . In Y. Syono and M.H. Manghnani, Eds., *High pressure research in minerals physics: Applications to earth and planetary sciences*, p. 503–517. Terrapub AGU, Washington, DC.

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