

Compressibility and pressure-induced amorphization of guest-free melanophlogite: An in-situ synchrotron X-ray diffraction study

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ABSTRACT

Melanophlogite, a clathrasil, possesses a framework of corner-linked silica tetrahedra forming framework cavities that can enclose small guest molecules. Synchrotron X-ray diffraction experiments of the guest-free melanophlogite have been conducted at pressures up to 12 GPa and temperatures up to 1473 K. Upon compression at room temperature, melanophlogite gradually lost its crystallinity and became completely X-ray amorphous at ~8 GPa. The amorphization process was similar to those of denser silica polymorphs, but it reached completion at a much lower pressure (e.g., quartz becomes X-ray amorphous at ~30 GPa). The decreased amorphization pressure of melanophlogite may be attributed to its lower framework density and the ease of bending of its Si-O-Si linkages, thereby accelerating the collapse of the structure under high pressure. Determination of cell volumes of melanophlogite prior to its amorphization yielded a room-temperature bulk modulus of 26.3 ± 1.7 GPa, which is consistent with the relatively large compressibilities reported for the structurally similar zeolites. When heated at ~8 GPa, the amorphous phase started to crystallize at 873 K into coesite, the stable silica phase at these pressure and temperature conditions. Thus the occurrence of pressure-induced amorphization in melanophlogite appears to result from the kinetic hindrance to its transformation to the thermodynamically stable coesite.

Keywords: Melanophlogite, clathrasil, pressure-induced amorphization, compressibility, synchrotron X-ray diffraction

INTRODUCTION

Melanophlogite, $46\text{SiO}_2 \cdot 6\text{M}^{14} \cdot 2\text{M}^{12}$ ($\text{M}^{14} = \text{CO}_2, \text{N}_2$; $\text{M}^{12} = \text{CH}_4, \text{N}_2$), belongs to a family of silicas called “clathrasils” that possess a framework of corner-linked $[\text{SiO}_4]$ tetrahedra surrounding isolated pores and cages (Liebau 1983). Because their openings are small, these cavities can encage certain sizes of polyatomic ions and/or molecules (such as CH_4, N_2 , and CO_2 gas molecules in melanophlogite) that cannot diffuse through the crystal. Though rare in nature, melanophlogite is of considerable interest due to its ability to store up to 8 wt% (~15 mol%) volatile molecules (Skinner and Appleman 1963). Thus melanophlogite, which has been successfully synthesized in the laboratory (Gies et al. 1982), may potentially serve as a host for greenhouse gases and radon.

Melanophlogite is also interesting from the viewpoint of crystal chemistry. At ambient condition, melanophlogite is tetragonal with space group $P4_2/nbc$ (Nakagawa et al. 2001). On heating, however, it transforms displacively to the cubic phase ($Pm\bar{3}n$), which is isostructural with hydrate clathrate sI, at 338 K (Gies 1983). Upon further heating, the cubic framework expands, as do the openings of its cavities. As a result, the trapped gases can be completely released above 873 K (Liu et al. 1997). On cooling to room temperature, the framework contracts but maintains its

integrity (though its symmetry probably changes), resulting in the so-called “guest-free melanophlogite.” This phase is essentially a polymorph of silica, but has a much larger molar volume (or lower framework density) than common silica phases (such as quartz and tridymite). Since crystalline silica is one of the most comprehensively studied systems for its various applications (Heaney et al. 1994), investigating this microporous silica phase and comparing it with other, denser polymorphs will provide important insights into the effects that structure can exert on physical properties, including compressibility and pressure-induced amorphization, which are the topics of this study.

High-pressure behavior of silica has been an active research area not only for its geophysical significance but also for its materials applications (Hemley et al. 1994). One of the most distinctive properties of the silica system is its richness in polymorphism as a function of pressure, temperature, and synthesis conditions; the reported silica phases include low-pressure polymorphs such as quartz, cristobalite and pure-silica zeolites, and high-pressure polymorphs, including coesite and stishovite. Upon compression, the structures of these phases (except stishovite whose framework is composed of $[\text{SiO}_6]$ octahedra) decrease in volume via the following mechanisms with increasing pressure: (1) a rigid rotation of $[\text{SiO}_4]$ tetrahedra, reflected by decreases in the intertetrahedral Si-O-Si angles; (2) a distortion of tetrahedra due to changes in the O-Si-O angles; and (3) a decrease in the Si-O bond lengths (Jorgensen 1978; Hemley et al. 1994; Ovsyuk

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and Goryainov 1999). The pressure ranges in which these three compression mechanisms operate may, however, overlap with each other and vary from polymorph to polymorph, largely depending on the framework topology and density. At some point during compression, at least some of the crystalline silica polymorphs gradually lose their long-range order and eventually become fully amorphous, a phenomenon known as “pressure-induced amorphization” (Sharma and Sikka 1996; Richet and Gillet 1997). This amorphization process may be reversible or irreversible, depending on the structure of the original crystalline phase and the maximum pressure applied.

Unlike the conventional route of synthesizing a glass, which is fast quenching of a melt or liquid from sufficiently high temperatures to room temperature, pressure-induced amorphization occurs within the crystalline solid without going through the intermediate melt or liquid state. Though mechanistically peculiar, this phenomenon has been found to occur in various materials including silicates, phosphates, tungstates, hydroxides, and pure elements (Sharma and Sikka 1996; Richet and Gillet 1997) since its first discovery in hexagonal ice (Mishima et al. 1984). However, the underlying mechanisms remain largely speculative, and several hypotheses—including thermodynamic melting, mechanical instability, and kinetic hindrance to a phase transition—have been proposed to interpret this unusual behavior (Sharma and Sikka 1996). In addition, the local structure of the pressure-induced amorphous phase may be intrinsically different from that of its thermally induced counterpart, which still needs further study.

One of the means to help unravel the structural mechanisms for pressure-induced amorphization is to study an isostructural or isochemical series of compounds to determine their systematics in compressibility and amorphization. Owing to its richness in polymorphism, crystalline silica provides an ideal system for systematically investigating the effects of framework topology/density on high-pressure properties. Quartz is the first silica phase that was found to become amorphous when subjected to high pressures. Hemley (1987) and Hemley et al. (1988) first discovered the progressive amorphization of α -quartz in the pressure range 25–30 GPa using Raman spectroscopy and synchrotron X-ray diffraction (XRD). Subsequent studies by theoretical calculations and by other experimental techniques (especially transmission electron microscopy; Kingma et al. 1993) confirmed the “quartz-glass” transformation and attributed it to the elastic instability of quartz under high pressure with a thermodynamic driving force due to the higher density of the amorphous phase (see Hemley et al. 1994 and references therein). In addition to quartz, Hemley et al. (1988) also examined the high-pressure behavior of coesite, a high-pressure stable phase of silica. Although coesite exhibits a similar crystalline-to-amorphous transition as α -quartz, its amorphization appears to occur at higher pressures (e.g., ~35 GPa, at which pressure the amorphization completes, compared with ~30 GPa for quartz). A later molecular simulation study of β -cristobalite, a silica polymorph with a relatively open framework, shows that it becomes fully amorphous at 15 GPa, much lower than the amorphization pressures of quartz and coesite (Zhang and Ong 1993). Since coesite is denser and β -cristobalite is less

dense than α -quartz, these observations imply that a positive correlation may exist between the amorphization pressure and framework density (i.e., the denser the structure the higher the amorphization pressure). In fact, several zeolite phases—microporous framework aluminosilicates containing relatively large cages and tunnels—were found to undergo amorphization at much lower pressures (e.g., 4.1 GPa for hydrated zeolite Na-A) (Gillet et al. 1996; Rutter et al. 2001; Comodi et al. 2001; Colligan et al. 2004). However, because most of these phases (except pure-silica zeolite Y) are compositionally different from silica, which may have significant effects on the amorphization process, direct comparison between the high-pressure behavior of aluminosilicate zeolite and of crystalline silica is complicated by factors other than framework density. In this regard, like the purely siliceous zeolite Y (Colligan et al. 2004), guest-free melanophlogite is ideal since it has a comparable framework density (or larger molar volume) to zeolite yet is compositionally pure silica. Thus high-pressure studies of these microporous silica polymorphs will extend the range of molar volumes for silica phases and better define the framework density-amorphization pressure relation.

Hence, our motivation of this work is twofold: (1) to assess the strength of the melanophlogite framework for gas storage applications; and (2) to better define the systematics in compressibility and amorphization of crystalline silica by providing data for a distinct, more porous phase. Using in situ energy-dispersive synchrotron XRD, we have examined the compressional and amorphization behavior of guest-free melanophlogite at pressures up to 12 GPa and temperatures up to 1473 K. The isothermal bulk modulus at room temperature has been determined and compared with those of other silica polymorphs. The pressure-induced amorphization behavior of the silica phases is discussed in terms of framework density (or molar volume).

EXPERIMENTAL METHODS

We used a melanophlogite from Livorno, Italy (Natural History Museum, London, specimen no. BM1973-116) that was heat-treated for six hours at 1223 K in a muffle furnace to remove all guest molecules. It is the same sample as that used by Liu et al. (1997) in their ^{29}Si NMR studies and by Navrotsky et al. (2003) in their thermochemical measurements. The absence of guest molecules in the sample was confirmed by infrared spectroscopy, which showed no bands corresponding to C = O, C-H, and O-H in CO_2 , hydrocarbon and water molecules (Liu et al. 1997). Prior to the high-pressure, high-temperature synchrotron experiments (see below), the sample had been checked using laboratory XRD and confirmed to be pure single-phase. Powder XRD was conducted with a Scintag Pad-V diffractometer using $\text{CuK}\alpha$ radiation. Sample powders were mounted in a front-loading, shallow-cavity zero-background quartz holder, and data were collected from 5° to 120° 2θ in step scan mode using steps of 0.02° with a counting time of 10 s/step.

Two sets of energy-dispersive synchrotron XRD experiments were performed using white X-ray radiation from the superconducting wiggler magnet at beamline X17B2 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, and from the bending magnet at beamline 13-BM-D of the Advanced Photon Source (APS), Argonne National Laboratory. The incident X-ray beam was collimated to dimensions of $100 \times 200 \mu\text{m}$, and the diffracted beams were collected with a solid Ge detector at fixed angles of 2θ 6.219° and 6.436° for the NSLS and APS experiments, respectively. In the NSLS measurements, the cell assembly used is similar to the DIA-type cells described by Weidner et al. (1992). A mixture of amorphous boron and epoxy resin was utilized as the pressure-transmitting medium, and amorphous carbon as the furnace material. The powdered samples of melanophlogite and NaCl, which served as a pressure marker, were packed as separate layers, into a cylindrical container of boron nitride, 1 mm in diameter and 2 mm in length. For the APS experiments, the cell assembly used is of the so-called

“T-cup” type with boron-epoxy octahedron as the pressure medium (Vaughan et al. 1998). Since this set of experiments was designed for room-temperature compression only, no heating unit was used, and the melanophlogite and NaCl powders were directly loaded into a cylindrical hole of the boron-epoxy octahedron, 1 mm in diameter and in length.

Pressure was calculated from Decker’s equation of state for NaCl (Decker 1971) using the lattice parameter determined from the XRD pattern of NaCl at each experimental condition. Four diffraction peaks of NaCl, (200), (220), (222), and (420), were used for determination of its lattice parameter. The uncertainties in the pressure measurements are mainly due to statistical variation in the positions of diffraction peaks and are between 0.1–0.2 GPa in the pressure range of this study. (The uncertainties of the lower pressures are smaller.) Temperature was registered with a W/Re24%–W/Re6% thermocouple positioned at the center of the furnace and in direct contact with the melanophlogite and NaCl layers. XRD patterns were obtained for both the melanophlogite and NaCl powders in close proximity to the thermocouple junction; errors in measured temperatures were estimated to be <10 K. No correction was applied for the effect of pressure on the thermocouple EMF.

The high-pressure, high-temperature experiments at NSLS were carried out according to the following procedure. The sample was first compressed at room temperature to 0.50, 1.38, 3.62, 5.88, and 8.03 GPa, and then while at 8.03 GPa, it was heated to 1473 K in steps of 200 K, followed by rapid quenching to room temperature and decompression to ambient conditions. Collection of XRD patterns started at ~1 min after reaching each pressure/temperature point during compression and heating as well as after both quenching and decompression. In the APS experiments, the sample was compressed to 0.58, 1.31, 2.41, 3.01, 3.72, 4.86, 6.00, 7.27, 8.24, 10.37, and 11.87 GPa, followed by decompression to room pressure. XRD data collection started at ~1 min after reaching each pressure and after decompression.

RESULTS AND DISCUSSION

Ambient structure

Guest-bearing melanophlogite has a tetragonal structure (space group $P4_1/nbc$) with $a = 26.818(2)$ Å and $c = 13.365(1)$ Å (Nakagawa et al. 2001). Upon heating, however, it becomes cubic at 338 K [space group $Pm\bar{3}n$; $a = 13.436(3)$ Å at 473 K] (Gies 1983) (Fig. 1). This high-temperature phase is isostructural with hydrate clathrate sI and contains two types of cages, denoted by $[5^{12}]$ (pentagonal dodecahedron) and $[5^{12}6^2]$ (tetrakaidecahedron). (In n^m notation, n is the number of edges per face and m the number of faces.) The tetragonal-to-cubic transition at 338 K is reversible and displacive in nature, involving only twisting of the framework by rotation of $[\text{SiO}_4]$ tetrahedra. As reflected by the relationship between their unit-cell parameters, the low-temperature structure is the $(2 \times 2 \times 1)$ superstructure of the high-temperature cubic cell.

Despite the detailed structural studies of guest-bearing melanophlogite, the structure for its guest-free counterpart has not been determined [though a ^{29}Si NMR study shows evidence for symmetry lower than cubic (Liu et al. 1997)]. Nevertheless, based on the likelihood of structural similarity between the guest-bearing and guest-free melanophlogite, we analyzed our laboratory XRD data of the guest-free sample by the Rietveld method [with the GSAS program (Larson and Von Dreele 2000)] using the guest-bearing tetragonal structure (with the gas molecules omitted) as the starting structure model. The refinements proceeded smoothly and gave a reasonably good fit between the observed and calculated profiles ($\chi^2 = 2.4$; $R_{\text{wp}} = 16.2\%$; $R_p = 12.3\%$). The obtained unit-cell parameters were: $a = 26.682(2)$ Å, $c = 13.382(1)$ Å, and $V = 9528(2)$ Å³. (A separate profile-fitting using the Le Bail method yielded almost the same values.) The cell volume is ~0.9% smaller than that of the guest-bearing

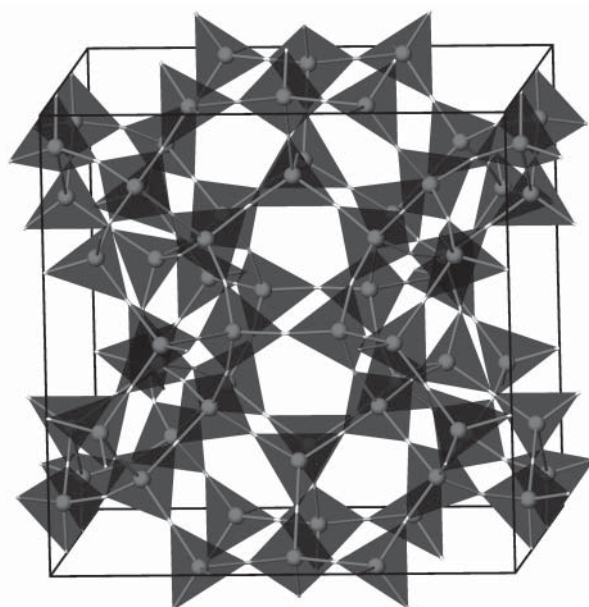


FIGURE 1. Crystal structure of high-temperature melanophlogite (space group $Pm\bar{3}n$). Tetrahedra represent $[\text{SiO}_4]$ units with Si, represented by a sphere, at the center. Lines denote the cubic unit cell.

counterpart [$V = 9612(1)$ Å³], implying that the gas molecules somewhat hold open silica framework. However, because the structure is fairly complex (38 atoms within the asymmetric unit cell) and because of the relatively low resolution of our laboratory XRD data, no attempts were made to determine the atomic positions and atomic displacement parameters. Detailed structural studies would probably need monochromatic synchrotron XRD or single-crystal diffraction measurements, which are beyond the scope of this work.

Pressure-induced amorphization

Selected synchrotron XRD patterns from the APS experiments are shown in Figure 2. Since this set of experiments was designed for room-temperature compression only and the cell assembly was entirely made of amorphous boron-epoxy, all the diffraction peaks in Figure 2 are from the melanophlogite sample. At ambient conditions, the peaks were sharp and distinct, and their positions were in good agreement with those obtained from our laboratory XRD pattern. However, when pressure was increased to 0.58 GPa, all the peaks broadened and lost their intensities. Further increase in pressure resulted in progressive peak broadening and intensity reduction, and at 8.24 GPa the diffraction peaks were replaced by a broad background characteristic of an amorphous state (referred hereafter as “glass hump”). On continuous compression to 11.87 GPa, no significant changes were observed in the diffraction profile, and thus the phase remained amorphous. After decompression to ambient conditions, the “glass hump” was still present, suggesting an irreversible nature of the pressure-induced amorphization. However, the position of the “glass hump” for the recovered sample appeared to move to the lower energy value (larger d -spacing) relative to that for the phase under compression. This behavior

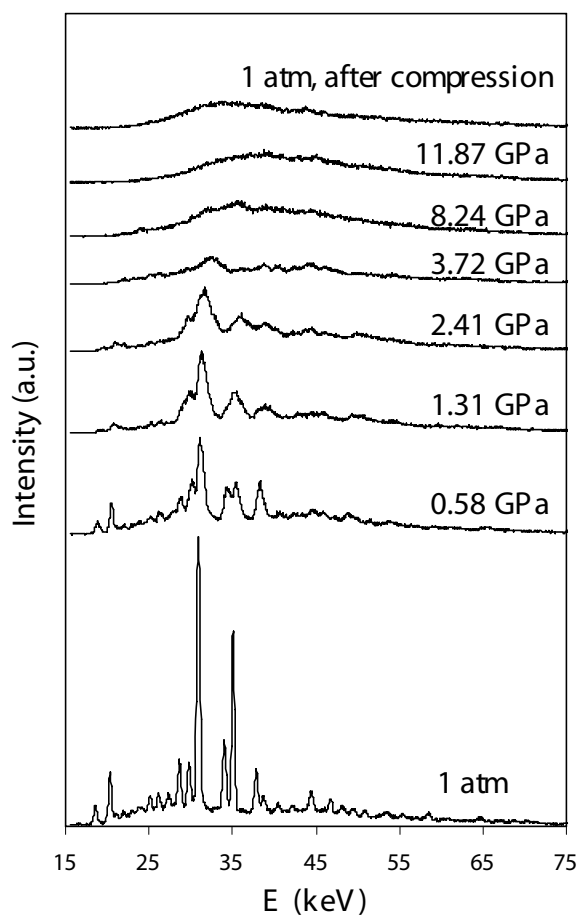


FIGURE 2. Selected XRD patterns of guest-free melanophlogite under compression at 300 K.

suggests possible relaxation of the glass structure upon release of pressure or reflects existence of polyamorphs—amorphous phases of the same composition but different densities—in this system (Navrotsky 2003; Greaves et al. 2003).

It should be mentioned that no liquid or gas pressure medium was used in our cell assembly, so the pressure state did not represent hydrostatic conditions. As demonstrated in previous studies, non-hydrostatic conditions may enhance pressure-induced amorphization (e.g., Hemley 1987). Thus the pressures reported here may be lower bounds for both the onset and complete amorphization for guest-free melanophlogite. Nevertheless, it is interesting to compare the amorphization pressure of this phase with those of other silica polymorphs. Figure 3 plots the pressures of complete amorphization as a function of ambient molar volume (V_0). With increasing V_0 or decreasing framework density, the amorphization pressure decreases. This behavior is understandable: the more porous the framework, the more easily it may collapse under high pressure. As described above, the melanophlogite framework contains the relatively large $[5^{12}]$ and $[5^{12}6^2]$ cages. On compression, rigid $[\text{SiO}_4]$ tetrahedra are expected to tilt toward these cages via bending of the intertetrahedral Si-O-Si angles; eventually, the Si-O-Si linkages become too strained, resulting in framework collapse and amorphization. Since there

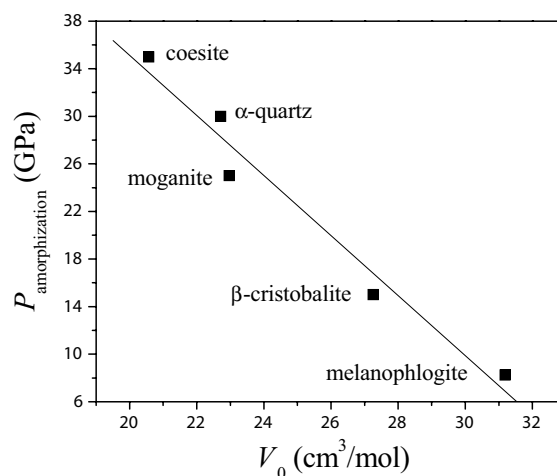


FIGURE 3. The pressures of complete amorphization for silica polymorphs plotted as a function of ambient molar volume. The line, which is the best fit to the data, is used as a guide. Sources of the data: coesite and α -quartz = Hemley et al. (1988); moganite = Léger et al. (2001); β -cristobalite = Zhang and Ong (1993); melanophlogite = this study.

are fewer bonding linkages per unit volume associated with atoms surrounding the larger cavities, which effectively weakens the framework, the amorphization of melanophlogite occurs at lower pressures (Fig. 3). The scatter of the data in Figure 3 may be attributed to several factors. First, the amorphization pressures of these silica polymorphs were obtained using different methods and experimental techniques as well as under different stress conditions (quartz, coesite, and moganite: diamond-anvil XRD; β -cristobalite: molecular dynamics simulation; melanophlogite: large-volume multi-anvil XRD), and thus the associated system errors are different. Second, as shown in the Na zeolites A and Y (Greaves et al. 2003), the values of amorphization pressure may vary with the rate at which pressure is ramped. Third, framework topology in addition to density may play a role in amorphization (i.e., two types of frameworks that have same/similar densities may amorphize at different pressures). Lastly, most materials show a large range of pressures in which crystalline and amorphous phases coexist [e.g., quartz (Kingma et al. 1993)], and thus it is difficult to pinpoint the exact pressure values of the onset and complete amorphization. Nevertheless, the approximately linear relation derived from the available data presented in Figure 3 represents a general relation between the amorphization pressure and molar volume of crystalline silica, and may thus be used for estimation of the $P_{\text{amarphization}}$ values of other polymorphs whose high-pressure behaviors have not been examined (such as tridymite).

Pressure-induced amorphization in some systems has been found to be at least partially reversible (Sharma and Sikka 1996). More specifically, when the pressure is released, the amorphous phase may revert back to its original crystalline state. The occurrence of such reversibility may depend on (1) the maximum pressure applied, (2) the time under compression and after pressure release (A. Likhacheva, personal communication), and (3) whether there exist non-deformable

units in the structure that can serve as driving agents for the amorphous-to-crystalline transformation. Tse et al. (1994) and Tse and Klug (1995) observed a reversible amorphization in dodecasil-3C [$12\text{SiO}_2 \cdot 16\text{M}^{12} \cdot 8\text{M}^{16}$, M = tetrahydrofuran (THF)], also a member of the clathrasil group but isostructural with hydrate clathrate sII. They attributed the reversibility to the so-called “memory effect,” which was induced by the THF guest molecules in the cavities. In other words, upon release of pressure, the enclathrated THF molecules act as the templates and redirect the atoms collapsed around them back into the original positions. Therefore, our observed irreversibility of the amorphization in guest-free melanophlogite might be due to the absence of trapped gas molecules. It is also possible that the maximum pressure applied (11.9 GPa) was so high that the severely deformed framework could not recover. The existence of a threshold pressure, above which the pressure-induced amorphous phase cannot revert back to the original crystalline state, has been found in several systems including anorthite (Daniel et al. 1997) and β -eucryptite (Zhang et al. 2005). To confirm these speculations, however, studies of guest-bearing melanophlogite at different maximum pressures would be needed.

Compressibility

To obtain the bulk modulus (K_0) or compressibility (β_v , where $\beta_v = 1/K_0$) of guest-free melanophlogite, we determined its cell volume as a function of pressure prior to its amorphization using the Le Bail profile-fitting method. Although the melanophlogite structure is tetragonal, its c_p/a_p ratio, where c_p and a_p are the cell parameters in terms of the high-temperature primary cell, is close to unity (≈ 1.003). As a result, the separation of certain pairs of peaks (such as 330 and 303) is rather small, making them difficult to resolve by energy-dispersive XRD. Thus, in our peak fitting, we treated this phase as cubic. This approximation should not have significantly affected the accuracy of the derived cell volumes. Figure 4 shows the obtained cell volumes at pressures up to 3.01 GPa. Although guest-free melanophlogite did not achieve complete amorphization until 8.24 GPa, the diffraction peaks in the pressure range 3.01–8.24 GPa were too broad and weak to derive reliable cell volumes. Fitting the data in Figure 4 to a second-order Birch-Murnaghan equation of state (Birch 1952) using the EOS-FIT program (Angel 2001) gave a refined V_0 of $2397.6(2.6) \text{ \AA}^3$ and a bulk modulus K_0 of $26.3(1.7) \text{ GPa}$. The uncertainties of V_0 and K_0 took into account the errors associated with the cell volumes but not those of the pressures. Because of the limited pressure range that did not allow an accurate constraint on $K'_0 (= \partial K_0 / \partial P)$, we assumed the pressure derivative of bulk modulus to be 4.0. The obtained K_0 value of guest-free melanophlogite is similar to that of the dodecasil-3C clathrasil (22.5 GPa), measured by Brillouin spectroscopy (Freimann and Küppers 1991). This value is also within the reported range of bulk moduli for aluminosilicate zeolites (22.1–61 GPa), which were determined using the diamond-anvil cell XRD with non-penetrating media (Comodi et al. 2001, 2002, 2003; Ferro et al. 2002; Arletti et al. 2003; Gatta et al. 2003, 2004; Fois et al. 2005; Gatta 2005; Gatta and Lee 2006). Though compositionally more complex, zeolite is structurally similar to clathrasil in the sense that they are both comprised of three-dimensional tetrahedral

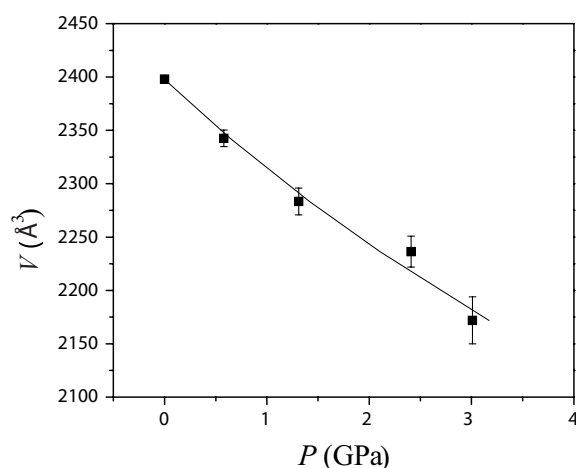


FIGURE 4. Variation of the cell volumes of guest-free melanophlogite as a function of pressure. Curve shows a fit of the Birch-Murnaghan second-order equation of state to the data points.

networks ($[\text{SiO}_4]$ or $[\text{AlO}_4]$) with comparable framework densities. Thus it is conceivable that these two groups of materials may have similar elastic properties including compressibility. Detailed structure refinements of several zeolites at high pressure reveal that zeolite compression is a result of the “soft” behavior of the channels/cages and the more rigid behavior of the tetrahedral framework, which operate via tetrahedral tilting (Comodi et al. 2001, 2002; Gatta et al. 2003, 2004). Clathrasil is expected to exhibit similar structural behavior at high pressure, though the absence of extra-framework cations in clathrasil means lack of the “templates,” which occur in zeolite, in its compression process (Fois et al. 2005).

There has been considerable interest to seek correlations between the compressibilities of materials and their structural parameters such as bond lengths and unit-cell constants. In particular, for various isostructural compounds, bulk modulus appears to correlate with ambient cell volume in an inverse linear fashion (e.g., Anderson and Anderson 1970). However, deviation from the linearity has been found in some systems such as calcite-structure carbonate, which is attributed to differences in cation type, bonding character and other factors (e.g., Zhang and Reeder 1999). Hence, the compressional behavior of materials is controlled by both structure and composition (Hazen and Finger 1982). Although previous studies have mostly focused on the bulk modulus-volume systematics of isostructural series, it is important to determine the effects of structure type on compressibility. Our newly measured bulk modulus for guest-free melanophlogite, together with those for other silica polymorphs, allows us to address this issue for the silica system. Figure 5 plots the bulk moduli of silica polymorphs as a function of ambient molar volume. With increasing V_0 , K_0 decreases drastically from 298 GPa for stishovite to 100.8 GPa for coesite and to 38.7 GPa for α -quartz (moganite has V_0 and K_0 values similar to those of quartz), but then shows relatively small variations for the more open cristobalite, melanophlogite, and silica zeolite Y. The dramatic increase in compressibility (decrease in K_0) from stishovite to coesite is related to the decrease in coordination

number of Si from six to four. In stishovite, edge-shared $[\text{SiO}_6]$ octahedra form infinite chains parallel to the *c*-axis, and each chain is linked to four other chains via corner-sharing, resulting in a more efficiently packed structure than the tetrahedral coesite framework (Sinclair and Ringwood 1978). However, since both coesite and quartz contain 4-coordinated Si, the large difference between their K_0 values must be due to their differences in the topology of linked $[\text{SiO}_4]$ tetrahedra. More specifically, the structure of coesite is composed of four-membered rings of $[\text{SiO}_4]$, whereas that of quartz contains the larger six- and eight-membered rings (Hemley et al. 1994). Because of the larger “free” space associated with its larger rings, the quartz framework is more flexible, when subjected to high pressure, via decreasing the intertetrahedral Si-O-Si bond angles. When the silica framework becomes even more open (quartz \rightarrow cristobalite \rightarrow melanophlogite \rightarrow silica zeolite Y), however, the compressibility is no longer a function of molar volume (Fig. 5). This “saturation” behavior is consistent with the lack of a direct correlation between porosity and compressibility revealed in some zeolites (Gatta et al. 2003), though they are complicated by their differences in composition. Thus, the degree of flexibility of the $[\text{SiO}_4]$ framework (or the bending force constant) remains roughly unchanged when V_0 exceeds a certain threshold. In particular, because guest-free melanophlogite becomes amorphous at relatively low pressures (~ 8 GPa), its contraction prior to the amorphization is likely to be solely due to rigid rotation of $[\text{SiO}_4]$ tetrahedra around its two kinds of cages (pentagonal dodecahedron and tetrakaidecahedron). As demonstrated in quartz, upon compression, the Si-O-Si bond angle decreases from 144° at room pressure to 124.2° at 12.5 GPa (largely due to the $[\text{SiO}_4]$ rotation), above which distortion of $[\text{SiO}_4]$ tetrahedra becomes the dominant mechanism (Hazen et al. 1989; Hemley et al. 1994). It should be pointed out, though, that the degree of bending of the Si-O-Si linkages may depend on the topology of the $[\text{SiO}_4]$ framework (e.g., whether the framework is isotropic

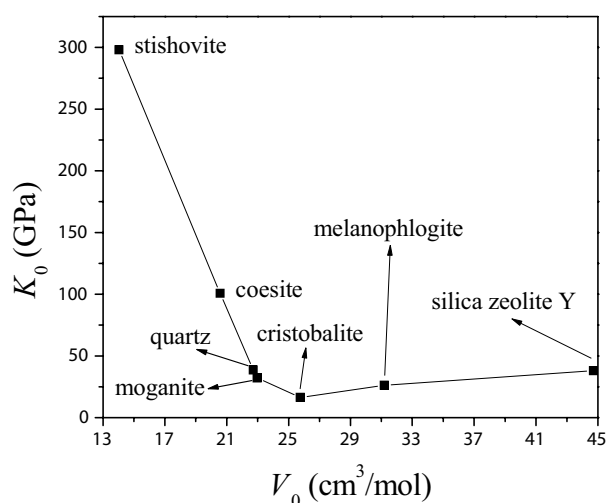


FIGURE 5. Variation of the bulk moduli (K_0) of silica polymorphs with ambient molar volume. Sources of the data: stishovite = Ross et al. (1990); Coesite = Angel et al. (2001); quartz = Hemley et al. (1994); moganite = Léger et al. (2001); cristobalite = Yeganeh-Haeri et al. (1992); melanophlogite = this study; silica zeolite Y = Colligan et al. (2004).

or anisotropic). Correspondingly, porous frameworks that have similar densities (or V_0) may have different degrees of flexibility and thus different bulk moduli. In fact, Gatta et al. (2003) have discovered this behavior in heulandite and scolecite, which have similar framework densities but very different bulk moduli (27.5 ± 0.2 and 54.6 ± 0.33 GPa, respectively). Therefore, the K_0 - V_0 trends shown in Figure 5 may not be universal and, rather, are likely to be system-dependent.

Phase equilibrium at high temperature

Mineral reactions at room temperature tend to be sluggish, so the phases produced during ambient compression frequently represent thermodynamically metastable states. Thus, it has been generally argued that pressure-induced amorphization may be related to kinetic hindrance of phase transformations to thermodynamically stable polymorphs (Richet and Gillet 1997). To determine whether this mechanism applies to guest-free melanophlogite, we heated the amorphous phase at 8.03 GPa up to 1473 K (Fig. 6). With increasing temperature, no significant changes in diffraction pattern were observed until 873 K, at which point diffraction peaks characteristic of coesite started to appear. On further heating to 1323 K, these peaks became much more distinct and stronger, and the broad “amorphous” background disappeared, indicating complete crystallization of the amorphous phase into coesite. Since coesite is the thermodynamically stable phase of silica at these pressure conditions

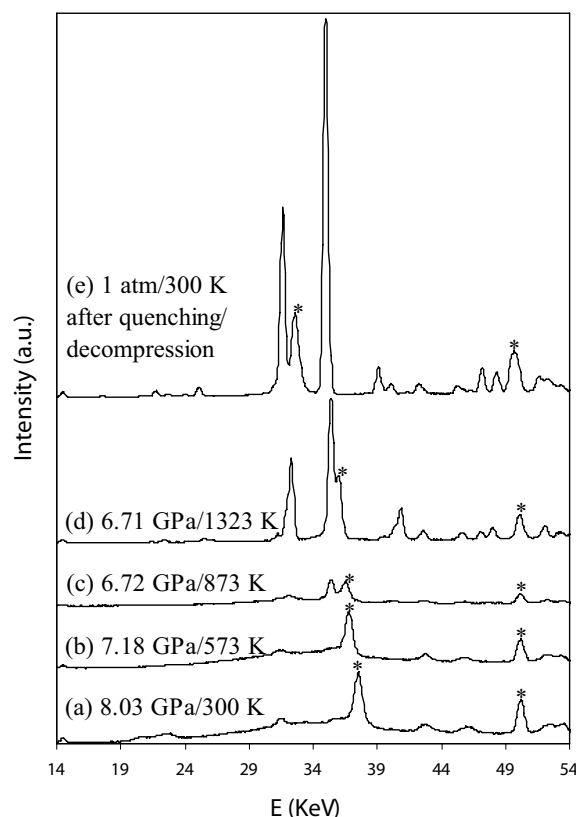


FIGURE 6. Selected XRD patterns of guest-free melanophlogite during heating at 8.03 GPa. Stars indicate peaks from the boron nitride container. The pressure drop during heating was due to the release of deviatoric stress at high temperatures.

(e.g., 2.5–9 GPa at room temperature) (e.g., Zhang et al. 1996), the formation of coesite only at high temperatures (e.g., >873 K at 8.03 GPa) implies that the pressure-induced amorphous phase at low temperatures is indeed an intermediate, metastable state. In other words, the amorphization of melanophlogite (and probably other clathrasils) under high pressure is likely to be a consequence of kinetic factors. During further heating to 1473 K and then cooling to room temperature, the diffraction pattern remained largely unchanged (except that the peak positions showed changes due to expected variations in cell parameters with temperature/pressure), and thus the crystallized coesite was stable at these conditions. Upon decompression, coesite crystals remained present (Fig. 6), which is consistent with the known recoverability of this high-pressure polymorph at ambient conditions.

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