

Shock wave effects on kaolinite and other clays

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ABSTRACT

XRD, TEM, thermoponderal, and infrared spectra of postshock kaolinite and aluminous smectite indicate the presence of a multiphase region under shock effects near 30 GPa. A glass is formed, as has been found in postshock tectosilicates. The data reported here indicate that there is a transfer of a part of the crystalline H₂O of the clays to the new glass phase. This study indicates that even a totally nonalkali composition can form glass under these special conditions and that the glass does not devitrify under postshock conditions.

Comparison of these shock stability results for different clays indicates that the hierarchy of stability of shock events follows the outlines of thermal stability of clays at atmospheric or low-pressure conditions.

INTRODUCTION

The investigation of the effect of shock waves on clays or phyllosilicates has been performed several times in the past (Boslough et al., 1980; Sekine et al., 1991), and compression data have been given for several clay-rich shales (Al'tschuler and Povlowskiy, 1971). However, details of the structural changes of the solids, and hence the mechanism of transition, have not been furnished in these studies. Because the clay structure is highly anisotropic (phyllosilicates form essentially two-dimensional crystalline arrays), one could expect that they would behave in a different manner than the much more studied three-dimensional tectosilicates, quartz and feldspar. The striking thing about shock wave response in tectosilicates is their great compressibility in the range of 30–50 GPa. It has been proposed that this compressibility is due to the formation of a glass structure in an essentially crystal to glass transition (see Tattevin et al., 1990; Ahrens and Rosenberg, 1968, among others).

The present study investigates the shock phase transition of phyllosilicates similar in composition to tectosilicates (i.e., mineral compositions dominated by Si and Al cations).

Clays are known to occur in meteorites, whose histories could include shock events. They are one of the rare instances in nature where one could find clays in shocked environments. The shock experiment results may or may not be relevant to the stability of clay minerals found in carbonaceous chondrite meteorites where they form a large part of the matrix (see Barber, 1985). Two origins are generally proposed for the presence of clays in meteorites: one is that they form through the alteration of preexisting high-temperature phases by hydration, and another is that they form from interstellar dust by some process causing

them to occur as individual particles in space. If the meteorite mother bodies that contain clays formed by accretion of clay-bearing material (the second hypothesis), the shock stability of the clays puts a limit on the size and energy of participating objects in the process of their formation and hence gives information concerning the origin of these extraterrestrial bodies (see Lange and Ahrens, 1984, for a discussion of such problems).

EXPERIMENTAL METHODS

The experimental observations reported here are primarily on shocked kaolinite, AlSi₂O₅(OH)₄, with some data on a smectite having the composition Ca_{0.3}-(Al_{1.7}Mg_{0.3})Si₄O₁₀(OH)₂·*n*H₂O. These represent the 1:1, 7-Å minerals and the 2:1 10-Å expanding minerals.

Various amounts of the clay material (1–175 mg) were dispersed in KBr, which was pressed into a glassy state using typical infrared preparation techniques (see Farmer, 1974). The KBr pellets were shocked using a gas gun system, according to the experimental protocol described by Goto and Syono (1984). Peak shock pressures were from 20 to 39 GPa.

Because of the low shock impedance of KBr, the first shock wave transmitted from the stainless steel container in the multistage process used reduced the amplitude greatly, i.e., 40–15 and 30–11 GPa. The estimated temperature increase from such a process under peak shock pressures would be 2800 and 1500 K for Hugoniot and isothermal compression data (Bridgman, 1924; Marsh, 1980). The KBr material obviously went through the B1-B2 transition to produce the glassy state in the initial preparation procedure (1.8 GPa), which is taken into account in these calculations.

The clay particles are in intimate contact with the KBr,

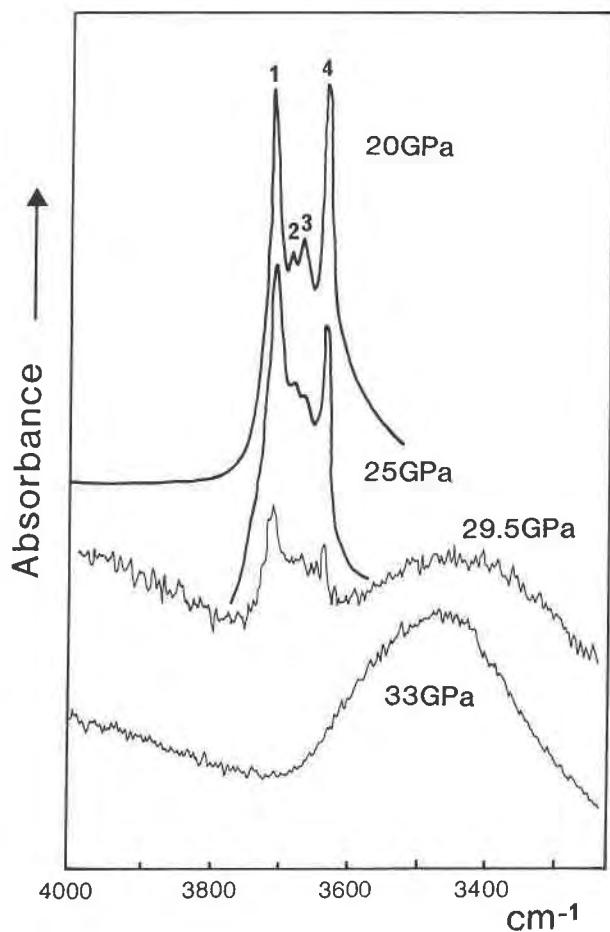


Fig. 1. Infrared spectral region of OH stretch vibrations of shocked kaolinite. The 20-GPa sample is identical with untreated material (band 1 = 3697 cm^{-1} , 2 = 3670 cm^{-1} , 4 = 3620 cm^{-1}). Bands 1–3 are associated with vibrations of the surface OH molecules, which join the 7-Å structural layers in the kaolinite structure through H bonding. The 33-GPa sample shows no sign of crystalline OH vibrations but gives a large diffuse hump in the region of molecular H_2O vibrations. Molecular H_2O is assumed to be present in the glass formed from the kaolinite.

they have a similar shock impedance to KBr, and they represent a small mass compared with the KBr matrix. Thus they are expected to have experienced the same shock conditions as the KBr. The advantage of the pressed pellet method is to ensure good contact of the clay particles with a solid substrate during the shock event and thus avoid voids and air spaces that would change the shock conditions drastically during the transmission.

TEM observations were carried out with a JEM 4000 and JEM 2000 EX-II machine. X-ray diffraction analysis using monochromated $\text{CuK}\alpha$ radiation on a Rigaku Geigerflex was made on the postshock materials after they had been separated from the KBr by washing the products in H_2O . Thermal analysis of a 50-mg sample was carried out using a differential thermal balance Shinku

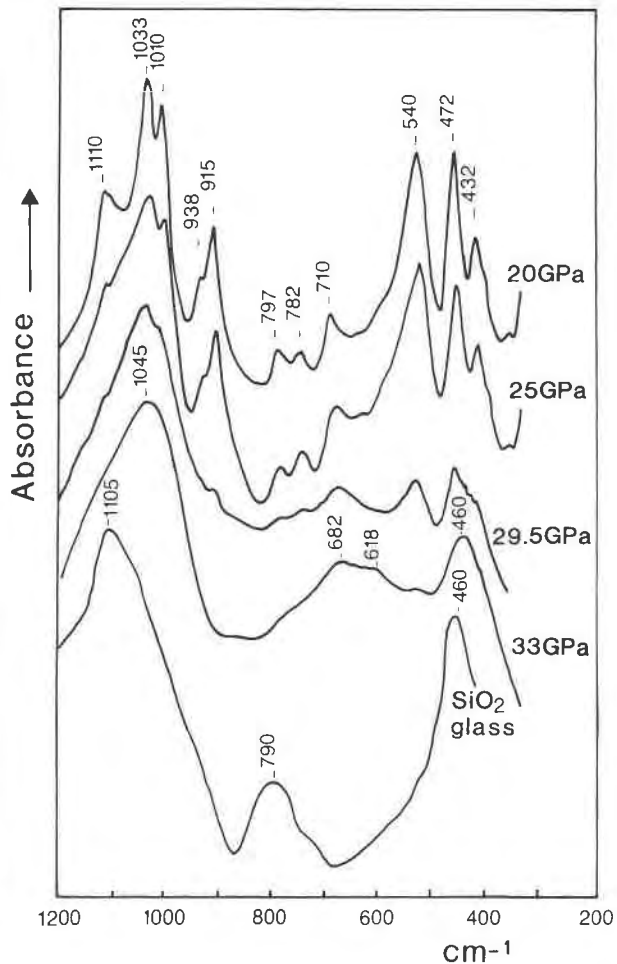


Fig. 2. Infrared spectra in the range of Si-O and Al-O bending and stretching. The major vibrational mode regions for kaolinite are indicated in the figure. The spectrum at the bottom is that of amorphous silica, which serves as a reference.

Riko TGD-5000 apparatus with a rate of heating of $5\text{ }^\circ\text{C}/\text{min}$ under a N atmosphere.

EXPERIMENTAL RESULTS

Experiments on kaolinite

Infrared. The spectra of the shocked products indicate a gradual change in the material, which is due to the production of an increasingly large portion of recovered postshock glass. The spectra are taken to indicate the existence of a two-phase region under shock pressure. Spectra in the OH-stretch band region (Fig. 1) show that there is a progressive loss in detail for two of the OH stretch bands, at 3670 and 3650 cm^{-1} (numbered 2 and 3 in the figure), which is due to vibrations of the outer or surface OH units located on the interfaces of the 7-Å layers in the kaolinite structure (Farmer, 1974, p. 340). Bands 1 and 4 persist at approximately equal intensity while diminishing with shock pressure. Such a change in relative intensity of the OH stretch bands has been noted by Velde

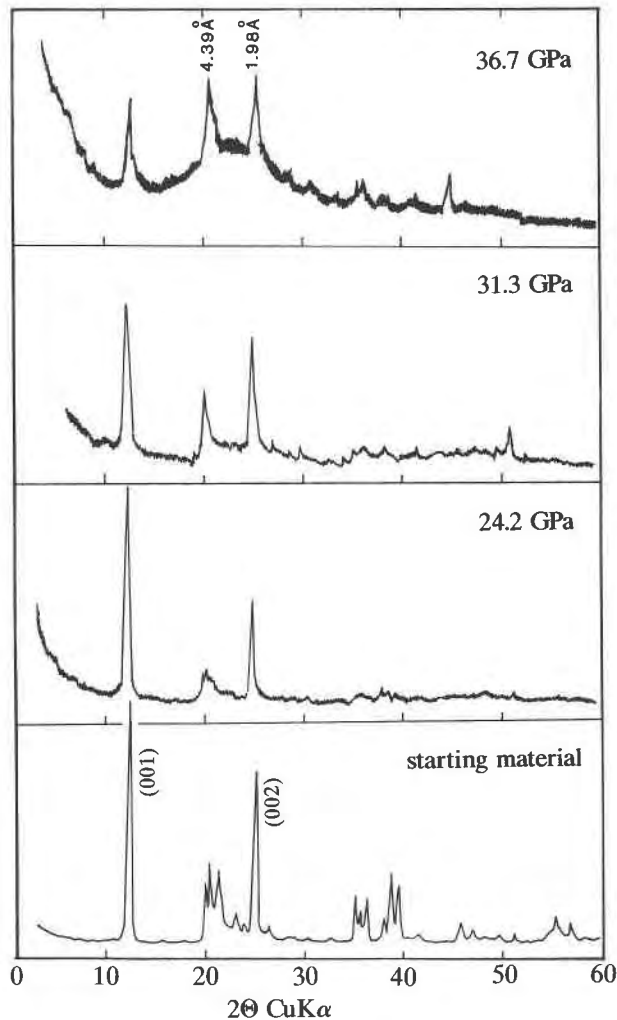


Fig. 3. X-ray diffraction ($\text{CuK}\alpha$ radiation) of shocked samples of kaolinite. The new peaks at 4.39 and 1.98 Å are indicated.

and Martinez (1981) for kaolinite under static pressure and by Maiti and Freund (1981) for kaolinite under heating. Loss of definition in bands 2 and 3 suggests a loss in the coherence or stacking order of the sheet structure. The interlayer contacts of the sheets become disordered in the *c* crystallographic direction. The observation of a concomitant general increase in intensity of the wide band at 3400 cm^{-1} in the recovered specimens as shock pressure increases, due to free H_2O , suggests that there might be some transfer of OH as H_2O into a nonkaolinite phase. This suggestion cannot be verified using infrared alone because even moderate heating of the sample leads to dehydration and destabilization of the shock glass. Some of the OH vibrational band of free H_2O could well be that of the KBr pellet, which is highly hygroscopic. It could have acquired H_2O either in the preparation and loading procedure or in the postshock phase of the experiments. Thus another method of investigation is necessary.

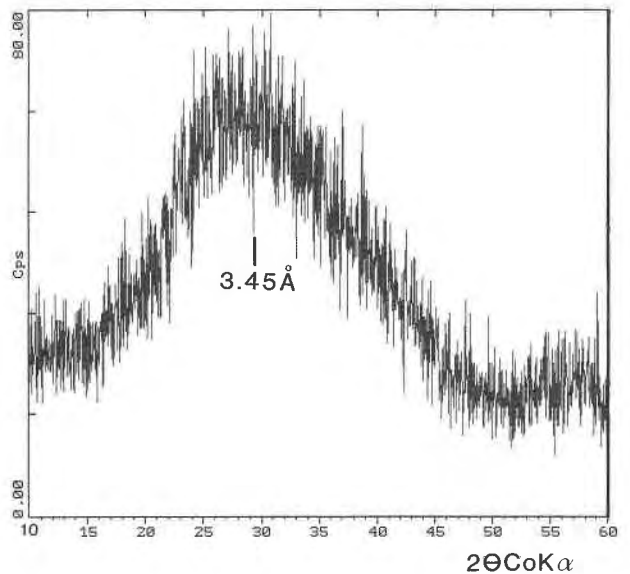


Fig. 4. X-ray diffraction of sodium glass, $\text{CoK}\alpha$ radiation.

Formation of increasing amounts of a glass phase is seen in Figure 2, where the major bands of the silicate structure are shown. The presence of a strong, wide band near 600 cm^{-1} shows the new glass structure. Loss of detail in the 1100-cm^{-1} region, loss of the Al-OH bands at 900 cm^{-1} , and Si-Al-O bands in the regions of 750 and 400 cm^{-1} are typical of the crystal to glass transition seen in tectosilicates using Raman techniques (see Velde et al., 1989). In the shocked clay samples, the difference between the 25- and 39.5-GPa pressure products is striking, indicating a rapid change in the proportions of the crystalline and noncrystalline portions of the sample. A spectrum of silica glass is shown for comparison in Figure 2. The 33-GPa sample shows a spectrum essentially identical to that of glasses, with a loss of lattice bands to form a simplified pattern with basically four bands. Such a change is typical of tectosilicates as they form glasses under heating (Velde and Couty, 1987) or shock pressures (Velde et al., 1989).

X-ray diffraction (XRD). XRD spectra of the samples indicate a strong change in structure in the sample shocked at pressures below 31 GPa (Fig. 3).

The *hkl* bands, near 20 , 37 , and $39^\circ 2\theta$, decrease in intensity in the postshock experimental products. This suggests the loss of crystalline continuity in the *c* crystallographic direction, which is also suggested by the loss of definition of vibrations in the infrared spectra of the OH stretching region at 3600 cm^{-1} . The XRD spectra of the 31- and 36-GPa materials indicate another change, one where a new type of organization is possible. A strong band occurs near 4.39 Å, and another is present at 1.98 Å. A large hump in the background centered near 3.85 Å indicates the presence of a glass. However, this diffuse band is usually centered near 3.45 Å in silica-dominated glass (Fig. 4). The longer distance in band spacing of the

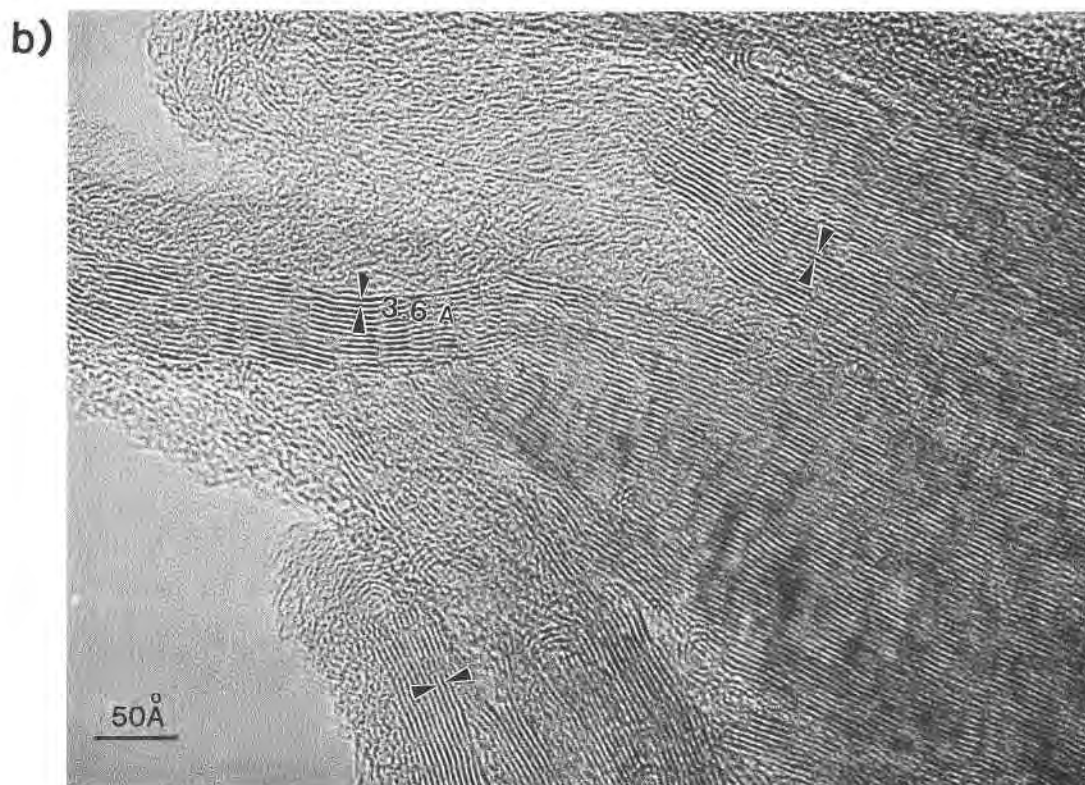
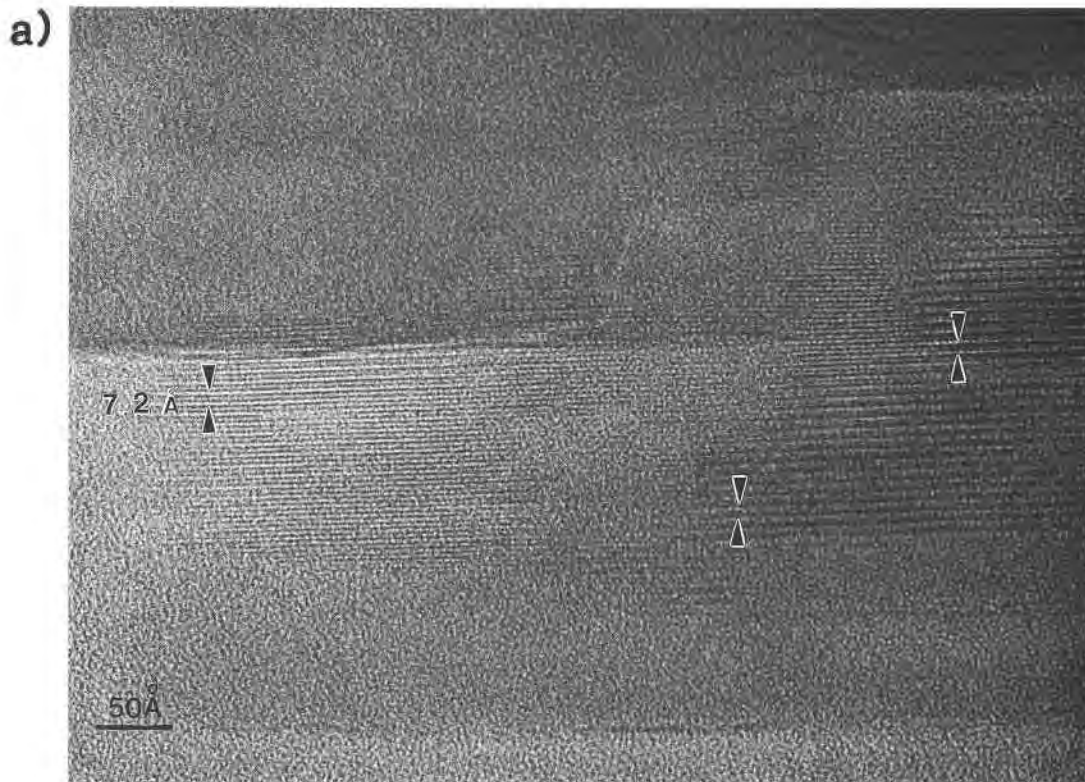


Fig. 5. TEM photographs showing the change in overall structural arrangement of the layers in the kaolinite. (a) Structure dominated by a 7.2-Å linear lattice. (b) The shocked specimen (27.7 GPa) shows a curled structure with a common 3.6-Å repeat distance for the layers.

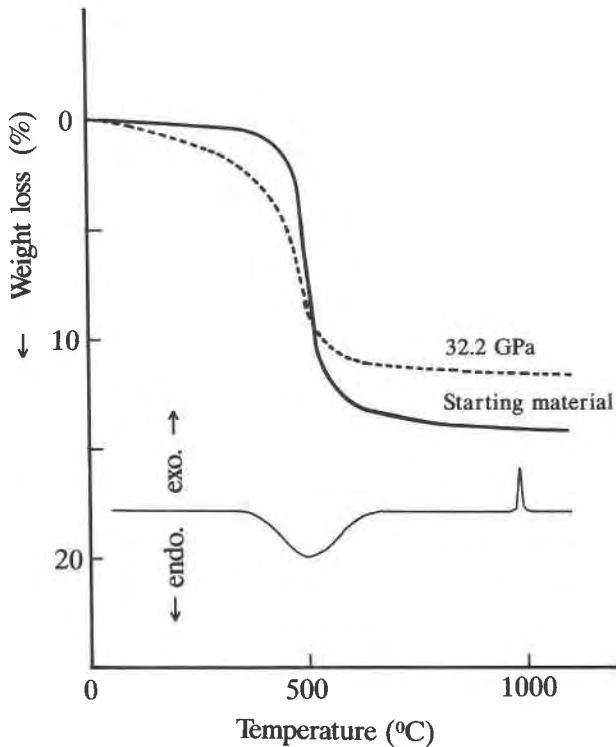


Fig. 6. Thermoponderal curves for normal and shocked kaolinite. The widening of the temperature range of dehydration and the overall loss of H_2O indicate loss of volatiles and disturbance of the crystal structure. Even though other identification methods indicate loss of structural continuity, it is evident that H_2O remains held in the shocked samples.

kaolinite glass could reflect the fact that half of the cations in the kaolinite composition are Al. Al-O distances are assumed to be about 1.70 Å, whereas Si-O distances are nearer 1.62 Å (Geisinger et al., 1985; DaSilva et al., 1975).

As there are only two new bands present in the diffraction diagram of the highly shocked sample (4.39 and 1.98 Å), it is not possible to attribute these to a new, crystalline phase. However, the band positions are very close to those given for the partial dehydration phase meta-kaolin (Brown, 1972, p. 134), which occurs typically in the thermal dehydration process of the destabilization of kaolinite. This phase is considered to be disordered in the *c* crystallographic direction, but significant order remains in the *ab* plane.

Electron microscope (TEM). TEM shows that the crystalline material in the kaolinite samples changes from a structure dominated by a 7-Å linear lattice to one with a repeat distance near 3.6 Å, which tends to be curled (Fig. 5). The structure becomes wavy instead of planar. These observations suggest that the basic 00/ stacking structure remains intact, but it is highly and systematically disturbed in other crystallographic directions by the shock effects.

Thermoponderal measurements. The weight loss of a shocked specimen from a glass-dominated product com-

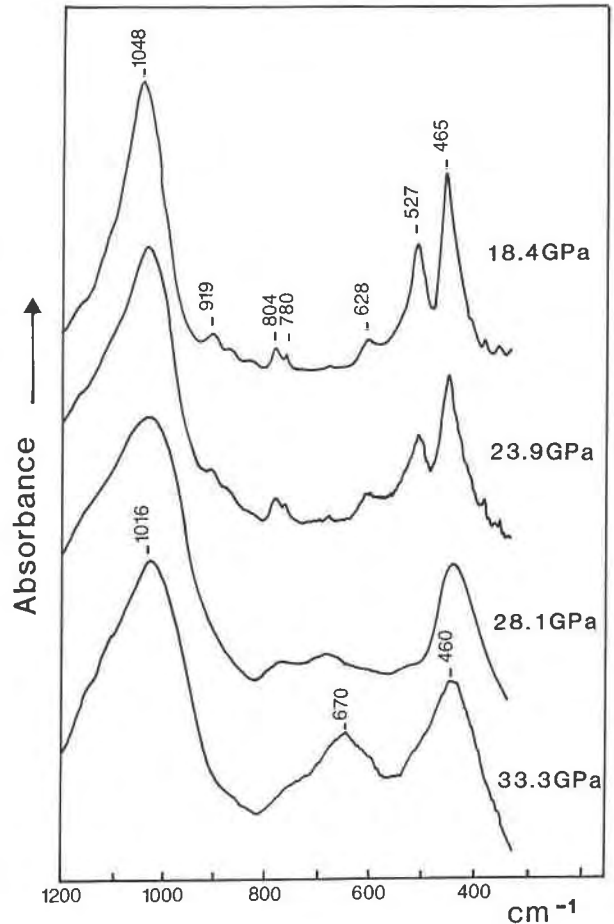


Fig. 7. Infrared spectra of shocked aluminous smectite with a small amount of quartz contamination. The 18.4-GPa sample is identical with unschooled material. The 28.1-GPa sample is essentially a glass that changes somewhat at 33.3 GPa, with a better defined band at 670 cm^{-1} .

pared with normal kaolinite, which contained almost the ideal 14 wt% H_2O , is shown in Figure 6. The shocked specimen contains 20% less H_2O than normal kaolinite, and it loses its H_2O more gradually in the earlier stages of the thermoponderal heating cycle. This again indicates disorder in the structural sites where the OH is held. A large portion of the initial H_2O of kaolinite is held in the new shock phase assemblage. The above observations by several methods of detection indicate that the transition between kaolinite and glass occurs over a range of shock pressures, as is the case for tectosilicates. The intermediate stages produce a multiphase assemblage including kaolinite, a meta-kaolin, and glass. During the whole process only 20% of the initial H_2O is lost from the solids, probably in a vapor phase.

Experiments on other phyllosilicates

Aluminous smectite. Experiments were performed for this study on an aluminous dioctahedral smectite. X-ray

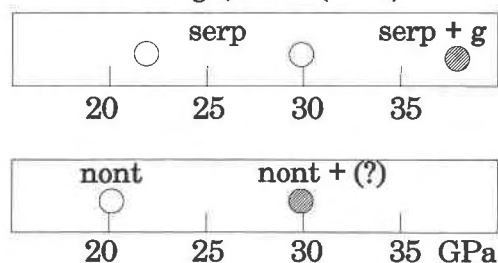
diffraction does not reveal any striking structural information. Infrared spectra (Fig. 7) allow only a determination of the presence of crystalline or glass phases. The highest shock pressure, 33.3 GPa, indicates that the sample was largely transformed into a glass. The spectrum is very similar to albite glass of shock or thermal origin (Velde and Couty, 1987; Velde et al., 1989). The simple structure with three bands at 1016, 670, and 460 cm^{-1} shows a total loss of long-range order. It is interesting to note that the small amount of quartz impurity is also transformed to glass under the same shock conditions as the smectite. Since the two structures, tectosilicate and phyllosilicate, are very different, it is apparent that the transition to glass is not dependent on the three-dimensional structure of the mineral but upon bond strengths and other chemical factors that produce glasses.

Serpentine. Boslough et al. (1980) gave infrared spectra for shocked samples of serpentine, a trioctahedral analogue of kaolinite. It is evident that the recovered shocked material, even after the passage of a 38-GPa shock wave, still retains much crystalline material. In this data, the presence of glass is seen in the strong intensity band at 1100 cm^{-1} . Other lattice bands, especially for the $^{61}\text{Mg-O}$ and $^{61}\text{Mg-OH}$ vibrations near 600 cm^{-1} (Farmer, 1974), are strongly suppressed. This suggests the same effect as that observed in kaolinite, where the Al-O and Al-OH bands were strongly disturbed by the shock event. In both minerals, these bands show the disturbance of atomic position in the external surface site of the octahedral layer, i.e., in the **ab** plane of the structure. In the serpentine spectra, a strong OH band resulting from H_2O is present, as in the kaolinite. It could well indicate the presence of H_2O in a glass phase.

Boslough et al. (1980) also presented X-ray data for shock experiments on ferric smectite, which indicated a higher stability for the crystalline phase than for the aluminous phase aluminum smectite investigated in the present study. Figure 8 shows the experimentally determined phase assemblages for the samples of the present study and those of Boslough et al. (1980). It is apparent that the magnesian and ferric phyllosilicate minerals resist change under shock pressure more than their aluminous counterparts. That is to be expected if one can extrapolate thermal stabilities into shock pressure realms. For aluminous and magnesian 7-Å minerals, the upper limit of thermal stability at low static pressures (<0.1 GPa) for kaolinite is near 300 °C (Frey, 1987), whereas that for serpentines is near 600 °C (Bailey, 1988, p. 302, 264) at hydrostatic pressures between 0.8 and 2 GPa. The magnesian phase has a higher thermal stability than the aluminous one. The aluminous phyllosilicates investigated here appear to be stable only up to 30 GPa.

The timing of the loss of volatiles can be questioned. Sekine et al. (1991) in performing nonrecovery experiments indicated that the hydrous phyllosilicate muscovite remains stable to near 30 GPa but suggested that it devolatilizes upon adiabatic release of pressure below 80 GPa. We cannot determine the point where H_2O leaves

INFRARED-IDENTIFIED PHASES Boslough, et al. (1980)



INFRARED-IDENTIFIED PHASES IN KBr

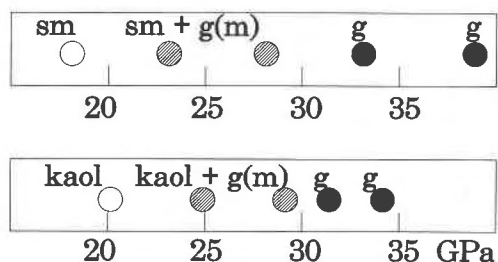


Fig. 8. Graphic representation of the phase assemblages in recovered shock experiments on clay minerals. Sm = aluminous smectite, g = glass, serp = serpentine, kaol = kaolinite, nont = nontronite (ferric smectite).

the kaolinite phase and enters the glass in our experiments, but it seems logical that it would occur at the height of the pressure cycle of the shock wave where the glass is produced.

Another point of interest is the fact that the phyllosilicates form multiphase glass-bearing assemblages in recuperation experiments at about the same shock pressures as do tectosilicates. Even though the phyllosilicates are hydrated, it would appear that their shock stability is not affected by their hydrous composition. Thus the crystal to glass transition is not a function of the presence of H_2O or OH, but one of structural or, more precisely, bond control. The observed effect of shock pressure on clay minerals (phyllosilicates) is very similar to that observed in the transitions of tectosilicates.

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REFERENCES CITED

- Ahrens, T.T., and Rosenberg, J.T. (1968) Experiments on quartz and plagioclase. In B.M. French and N.B.M. Short, Eds., *Shock metamorphism of natural materials*, p. 59–81. Monobook, Baltimore, Maryland.
- Al'tschuler, L.V., and Povlovskiy, M.N. (1971) Response of clay and clay shale to heavy dynamic loading. *Journal of Applied Mechanics and Technical Physics*, 1, 161–165.
- Bailey, S.W. (1988) Hydrous phyllosilicates (exclusive of micas). *Mineralogical Society of America Reviews in Mineralogy*, 19, 726 p.

- Barber, D.J. (1985) Phyllosilicates and other layer-structured materials in stony meteorites. *Clay Minerals*, 20, 450–454.
- Boslough, M.B., Weldon, R.J., and Ahrens, T.J. (1980) Impact-induced water loss from serpentine, nontronite and kernite. *Proceedings of the Lunar Planet Science Conference*, 11, 2145–2158.
- Bridgman, P.W. (1924) Compression data of KBr, *American Journal of Science* (not seen; compiled in S.P. Clark, Ed., *Handbook of physical constants*, Memoir 97, p. 97–173, 1966).
- Brown, G. (1972) X-ray identification and crystal structure of clay minerals, 544 p. The Mineralogical Society, London.
- DaSilva, J.G.R., Pinatti, D.G., Anderson, G.E., and Rudees, M.L. (1975) A refinement of vitreous silica. *Philosophical Magazine*, 713–717.
- Farmer, V.C. (1974) Infrared spectra of minerals, monograph 4, 539 p. The Mineralogical Society, London.
- Frey, M. (1987) Low temperature metamorphism, 351 p. Blackie, London.
- Geisinger, K.L., Gibbs, G.V., and Navrotsky, A. (1985) A molecular orbital study of bond length and angle vibrations in framework structures. *Physics and Chemistry of Minerals*, 11, 266–283.
- Goto, T., and Syono, Y. (1984) Technical aspect of shock compression experiments using the gun method. In I. Sunagawa, Ed., *Materials sciences of the Earth's interior*, p. 605–619. Terra Scientific, Tokyo, Japan.
- Lange, M., and Ahrens, T.J. (1984) FeO and H₂O and the homogeneous accretion of the Earth. *Earth and Planetary Science Letters*, 71, 111–119.
- Maiti, G.C., and Freund, F. (1981) Dehydration-related proton conductivity in kaolinite. *Clay Minerals*, 16, 395–413.
- Marsh, S.P., Ed. (1980) *LASL shock Hugoniot data*, 327 p. University of California Press, Berkeley, California.
- Sekine, T., Rubin, A.M., and Ahrens, T.J. (1991) Shock wave equation of state of muscovite. *Journal of Geophysical Research*, 96, 19675–19680.
- Tattevin, H., Syono, Y., Kikuchi, M., Kusaba, K., and Velde, B. (1990) Shock deformation of alpha quartz: Laboratory experiments and TEM investigation. *European Journal of Mineralogy*, 2, 227–234.
- Velde, B., and Couty, R. (1987) High pressure infrared spectra of some silicate glasses. *Chemical Geology*, 62, 35–41.
- Velde, B., and Martinez, G. (1981) Effect of pressure on OH-stretching frequencies in kaolinite and ordered aluminous serpentine. *American Mineralogist*, 66, 196–200.
- Velde, B., Syono, Y., Kikuchi, M., and Boyer, H. (1989) Raman microprobe study of synthetic diaplectic plagioclase feldspars. *Physics and Chemistry of Minerals*, 16, 436–441.

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