

Shock-Enhanced Dissolution of Silicate Minerals and Chemical Weathering on Planetary Surfaces

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Shock-recovery experiments were performed on samples of bytownite, oligoclase, and hornblende in order to assess the interrelationships between shock-activation and chemical weathering of natural materials. The three silicate minerals were recovered from peak pressures of 7.5, 16, and 22 GPa, and were subjected to analysis by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction, and BET gas adsorption. The dissolution response of three major elements (silicon, aluminum, and calcium) into a pH-buffered aqueous solution was examined for the shocked and unshocked samples. The rate of mass-normalized silicon release increased for all three minerals and, in some cases, was enhanced by a factor of more than 20. Only part of this behavior was due to increased surface area; all three minerals demonstrated an enhancement in surface-area-normalized dissolution of silicon, with two- to seven-fold increases of the rate. The results imply that shock-activation may play a significant role in the chemical weathering of planetary surfaces (e.g., Mars) where impact-cratering and rock-water interactions are both important processes. Estimates of volume amounts of material shocked by impacts onto Mars suggest that the unmelted fraction of ejecta can play an important role in soil formation. Selective weathering of meteoritic material can explain the mafic composition of the Martian regolith. Shock-enhanced authigenesis may also explain the smaller-than-expected quantity of crystalline ejecta associated with the clay layer at the Cretaceous-Tertiary boundary. Shock-enhanced dissolution rates may have an effect on groundwater chemistry near nuclear test sites and natural impact craters on Earth.

INTRODUCTION

There is evidence that when many materials are subjected to intense shock-loading, they undergo changes that affect subsequent chemical reaction processes (see *Grabam et al.*, 1986, for recent review). In some cases, chemical reaction rates in the shocked materials are increased by orders of magnitude (e.g., catalysis of CO and methanol by TiO₂ and ZnO; *Golden et al.*, 1982; *Williams et al.*, 1986a). Recent research suggests that this chemical response is due to the shock-induced generation of unusually high densities of defects and dislocations, increasing the number of reactive sites on grain surfaces (e.g., *Adaduro and Gol'danskiĭ*, 1981, for polymerization and thermal decomposition reactions). Other research has also demonstrated that shock-loading of crystalline solids can increase defect densities by orders of magnitude (*Davison and Grabam*, 1979; *Grabam*, 1981), and defects are known to affect the dissolution process (*Lasaga and Blum*, 1986; *Casey et al.*, 1987). Chemical reactions that are controlled by surface processes will certainly be affected by shock-loading. Both net increases and decreases in specific surface areas have been observed for shocked inorganic powders due to comminution or agglomeration of grains, respectively, with an increase of over an order of magnitude in the case of shocked aluminum oxide (*Williams et al.*, 1986b).

Boslough et al. (1986) suggested that this "shock-activation" may be an important surface process for minerals on planets where impact-induced shocks and atmosphere-regolith and/or groundwater-regolith interactions are significant. For example, a shock-induced enhancement of weathering and hydrothermal alteration rates of the Martian surface material would have affected the evolution of the regolith and determined its present mineralogical composition. Shock-activation of minerals would also have a bearing on the evolving

chemistry of groundwaters and other solutions associated with the weathering of shocked phases near terrestrial impact craters and nuclear test sites.

Although no comprehensive study has been performed on shock-modified silicate minerals, research on ore-processing alternatives by *Murr and Hiskey* (1981) examined the enhanced leaching rates of sulfide minerals with shock pressure. They subjected samples of chalcopyrite to well-defined shock states of 1.2 and 18 GPa, and found that leaching rates correlated with dislocation density. However, their observations were complicated by variations in chemisorption mechanisms on the mineral surface and interference of a precipitation product.

We have undertaken the present study to examine the effect of shock-loading on rock-water interactions and, in particular, to determine if there is experimental evidence to support shock-enhancement in the dissolution of silicate phases. We have not yet attempted to determine detailed mechanisms for such shock-enhancement, nor have we attempted to quantify dislocation densities, strains and other material properties modified by shock-loading; our present goal is merely to identify and quantify changes in dissolution rate in a small sample of rock-forming minerals, and to correlate them with shock pressure.

EXPERIMENTAL

We carried out shock-recovery experiments on three silicate minerals using the Sandia "Bear" explosive loading fixtures to achieve well-characterized shock states. The recovery fixtures allow samples to be shocked in a controlled, reproducible manner, and the peak shock states were determined by numerical simulations (*Grabam and Webb*, 1984, 1986). Two plagioclase minerals (oligoclase and bytownite) and one mafic

TABLE 1. Schedule of experiments.

Shot	Mineral	Fixture	Explosive	Sample Compact Density (Mg/m ³)	Sample Compact Density (%)	Peak Pressure (GPa)	Estimated Mean Bulk Temp. (K)
1B866	Oligoclase	Momma Bear	Baratol	1.70	65	5-10	90-110
2B866	Oligoclase	Momma Bear A	Baratol	1.70	65	14-20	125-175
3B866	Oligoclase	Momma Bear A	Comp B	1.70	65	19-26	250-500
1B876	Bytownite	Momma Bear	Baratol	1.40	51	5-10	300-325
2B876	Bytownite	Momma Bear A	Baratol	1.40	51	14-20	300-410
3B876	Bytownite	Momma Bear A	Comp B	1.40	51	19-26	450-700
4B866	Hornblende	Momma Bear	Baratol	2.30	77	5-10	25
5B866	Hornblende	Momma Bear A	Baratol	2.30	77	14-20	50-75
6B866	Hornblende	Momma Bear A	Comp B	2.30	77	19-26	125-275

mineral (hornblende) were examined. The oligoclase is from Bancroft, Ontario, and the hornblende is from Mineral County, Nevada. Both of these minerals were obtained from Wards Natural Science Establishment, Inc., and were ground and sieved to a size distribution of 37 to 149 microns. Electron microprobe analyses indicated that the hornblende has an approximate composition of $\text{Ca}_2(\text{Mg}_{3.3}\text{Fe}_{1.7})(\text{Si}_{7.5}\text{Al}_{0.5})\text{O}_{22}(\text{OH})_2$ (hornblende-tremolite solution) and the oligoclase has a plagioclase composition of An_{25} . The bytownite is from Pueblo Park, New Mexico, and has been characterized by Casey (1987). The initial grain size range of the bytownite was from 125 to 425 microns, and the composition is An_{60} . All three minerals were recovered from mean peak shock pressures of 7.5, 16, and 22 GPa. Mean-bulk shock temperatures were estimated from the calculations of *Grabam and Webb* (1986) and depend on initial sample packing density (see Table 1).

The dissolution experiments were performed after characterizing each sample with BET specific surface area measurements, X-ray diffraction, and optical and electron microscopy. The unshocked control sample and the three shocked samples for each of the three minerals were reacted in batch dissolution cells with a pH-buffered standard solution of 0.01 N potassium hydrogen phthalate (pH = 4). Approximately one gram of sample was reacted with 200 mL of the standard solution. The shocked mineral samples were hand-selected from the recovery fixtures in order to ensure that material came from the most uniformly shocked ("bulk" of *Grabam and Webb*, 1984) portion of the compact. Samples were sonically washed in distilled water and acetone prior to dissolution. The dissolution cells were placed in a constant temperature bath at 25°C and were kept agitated at a frequency of 1 Hz. Continuous agitation of the cells disrupts any chemical diffusion layer in the solution at the mineral interface and thereby promotes a surface-controlled dissolution mechanism. The experiments were maintained at these conditions for up to 21 days. One milliliter of the reacted solution was periodically (initially daily) sampled from each of the dissolution cells with a precision micropipette; identical volumes of the standard solution were added to replenish the sampled solution. The extracted solution was diluted and split for analysis. Silicon analyses were completed using the molybdate-blue spectros-

copic method and plasma emission spectroscopy was used to determine aluminum and calcium concentrations.

RESULTS

Scanning electron microscopic (SEM) examination of the unshocked and shocked silicate samples indicates substantial brittle disaggregation to have occurred in some of the phases due to shock-loading. This is most apparent for the case of bytownite, in which significant comminution and reduction in mean grain size is obvious from the sequence of photomicrographs (Fig. 1). Still apparent, but less obvious from the photomicrographs, is the disaggregation of the shocked oligoclase (Fig. 2). By contrast, the hornblende does not show any discernable change under SEM examination due to shock (Fig. 3). This result may be due to the differences in elastic/plastic response between the double chain silicate structure of the hornblende and the dense framework structure of the plagioclase phases.

These changes in microstructure were quantified to some extent by the determination of specific surface areas by the BET (multipoint gas adsorption) method (Table 2 and Fig. 4). We assigned a 6.5% uncertainty to the surface area measurements, which corresponds to the overall coefficient of variation in a series of BET area determinations for various powders by *Ace and Parsons* (1979). This uncertainty includes both instrument and powder sampling variation and is a conservative estimate. The laboratory that performed the analyses (Quantachrome Corp.) assigned an uncertainty of 1% to the values determined for our samples. The bytownite demonstrated the largest gain in specific surface area, with an increase of nearly seven-fold for the 7.5 GPa sample. The oligoclase showed increases by factors between about 3 and 4 in all cases, and the hornblende surface areas increased by no more than 36%. The decrease in specific surface area of the hornblende at the high shock pressure may represent the agglomeration of the mineral grains due to localized shock-melting and/or plastic deformation. However, the observed decrease is small (less than the 6.5% measurement uncertainty).

X-ray diffraction analysis of the shocked samples failed to demonstrate the occurrence of any additional crystalline phases.

BYTOWNITE

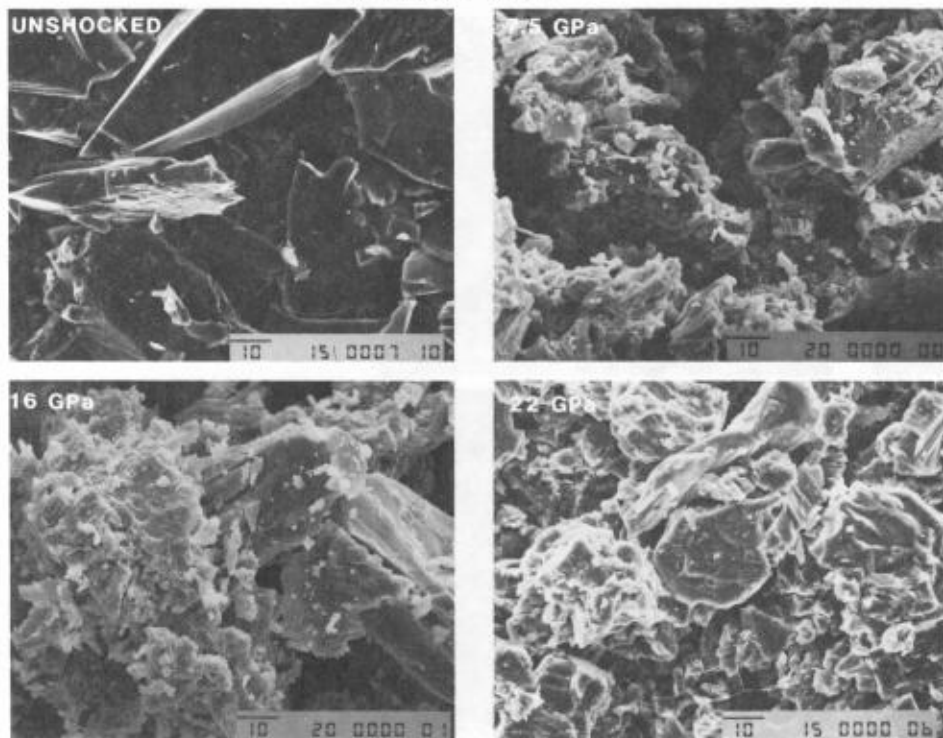


Fig. 1. Scanning electron photomicrographs of bytownite prior to shock and as recovered from three shock experiments. Bar in lower right-hand corner of each photomicrograph indicates scale in microns.

OLIGOCLASE

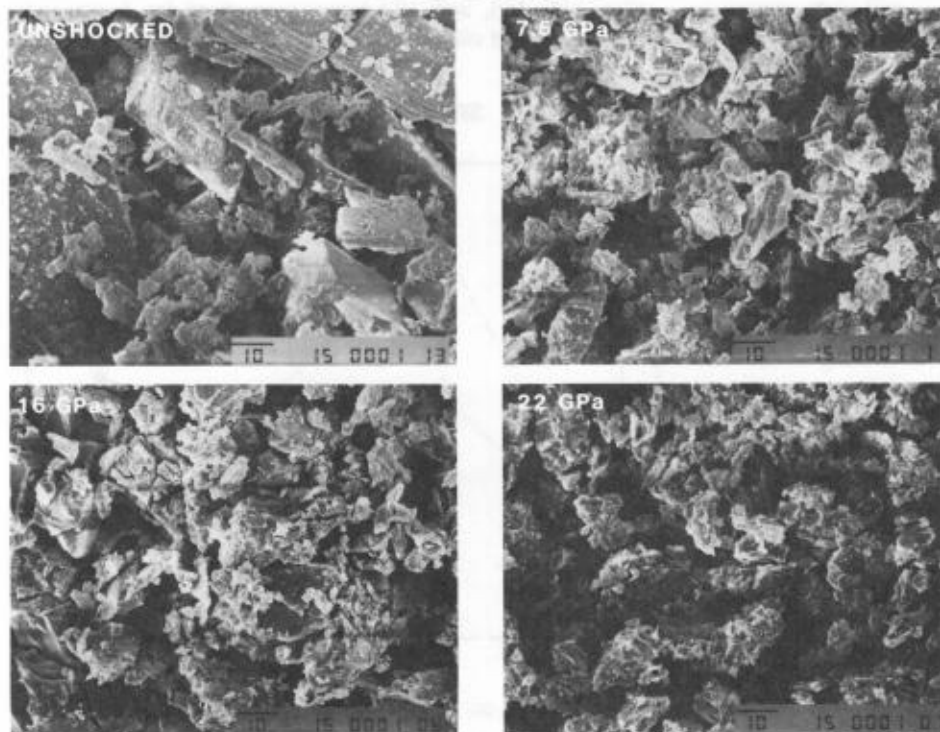


Fig. 2. SEM photomicrographs of unshocked and shocked oligoclase.

HORNBLLENDE

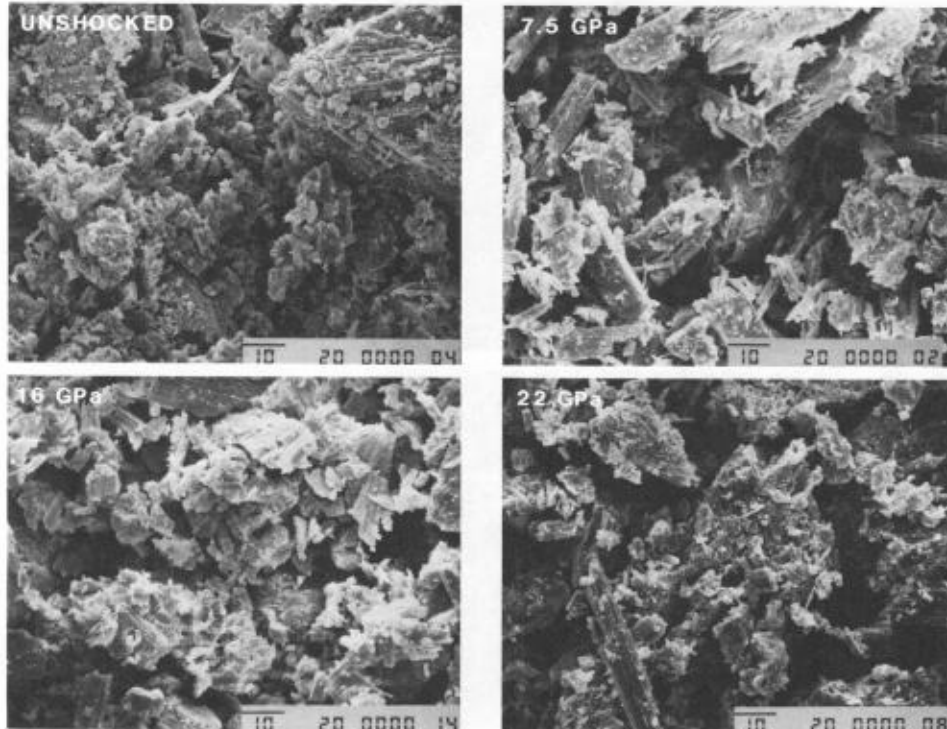


Fig. 3. SEM photomicrographs of unshocked and shocked hornblende.

There was significant line-broadening observed in the shocked samples, implying the introduction of residual strain, and/or increase in dislocation densities by the shock loading; this has not yet been quantified. There was no evidence of shock-generated glass from the X-ray data, despite the microscopic observation of small quantities of glass and melt texture in the highest pressure oligoclase sample (Fig. 5). Care was taken to use only a glass-free sample in the dissolution experiment.

Examples of the dissolution behavior for the three analyzed elements (aluminum, silicon, and calcium) are shown in Figs. 6 and 7, respectively, for unshocked and shocked (16 GPa) hornblende. Similar data were obtained for bytownite and oligoclase. In both cases, the calcium is easily leached into solution with its concentration rapidly approaching a constant value, implying that a saturation level has been reached. However, the aluminum and silicon concentrations show continuous increases, and approach an approximately linear dependence on time, in agreement with existing models and observations for various minerals (e.g., *Holdren and Berner, 1979; Lasaga, 1984*). It is notable that the ratio of Si and Al molar concentrations is not equal to 15, which would be expected if the dissolution process were congruent, but is about one-fourth of that value, implying that Al enters the solution at a higher rate than Si, relative to their abundances in the mineral. Furthermore, this ratio is greater for the shocked sample than for the unshocked sample by a factor of about two. Thus, the dissolution process is incongruent, and the dissolution response for silicon is more strongly enhanced by the shock than that for aluminum. Because silicon is the major structural component of these minerals, we will emphasize the silicon kinetics in the following discussion.

In Figs. 8-10, the experimental results are presented for silicon release from the three minerals in each of the four states: unshocked and the three shock conditions. A linear least-squares regression was used to determine the rate of concentration increase in each case. The concentration data after 166, 145, and 122 hours were used for hornblende, bytownite, and oligoclase, respectively, since these appear to

SPECIFIC SURFACE AREAS

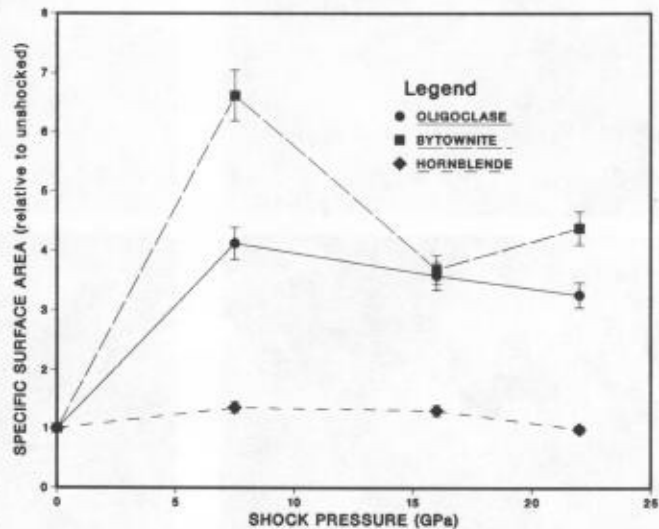


Fig. 4. BET specific surface areas of three shocked minerals relative to the unshocked phases.

TABLE 2. BET specific surface areas and silicon dissolution rates.

Mineral	Mean Shock Pressure (GPa)	Mass-normalized Dissolution Rate (10^{12} mol/g sec)		BET Specific Surface Area (m^2/g)		Area-normalized Dissolution Rate (10^{12} mol/ m^2 sec)	
		Absolute	Relative	Absolute	Relative	Absolute	Relative
Oligoclase	0.0	0.6 ± 3.0	1.0	0.73 ± 0.05	1.00	0.8 ± 4.2	1.00
Oligoclase	7.5	14.7 ± 1.6	25.4 ± 2.7	3.01 ± 0.20	4.12 ± 0.27	4.9 ± 0.8	6.18 ± 1.06
Oligoclase	16.0	12.3 ± 2.6	21.3 ± 4.6	2.61 ± 0.17	3.58 ± 0.23	4.7 ± 1.3	5.95 ± 1.67
Oligoclase	22.0	14.3 ± 1.9	24.8 ± 3.3	2.38 ± 0.15	3.26 ± 0.21	6.0 ± 1.2	7.61 ± 1.49
Bytownite	0.0	1.0 ± 0.6	1.0	0.26 ± 0.02	1.00	3.9 ± 2.7	1.00
Bytownite	7.5	22.7 ± 1.0	22.4 ± 1.0	1.72 ± 0.11	6.62 ± 0.43	13.2 ± 1.4	3.39 ± 0.37
Bytownite	16.0	22.2 ± 0.8	21.9 ± 0.8	0.96 ± 0.06	3.69 ± 0.24	23.1 ± 2.4	5.72 ± 0.59
Bytownite	22.0	19.4 ± 0.8	19.2 ± 0.8	1.14 ± 0.07	4.38 ± 0.28	17.0 ± 1.8	4.37 ± 0.45
Hornblende	0.0	6.0 ± 2.2	1.0	4.93 ± 0.32	1.00	1.2 ± 0.5	1.00
Hornblende	7.5	17.3 ± 1.0	2.9 ± 0.2	6.72 ± 0.44	1.36 ± 0.09	2.6 ± 0.3	2.12 ± 0.26
Hornblende	16.0	25.8 ± 0.7	4.3 ± 0.1	6.44 ± 0.42	1.31 ± 0.09	4.0 ± 0.4	3.31 ± 0.30
Hornblende	22.0	21.8 ± 2.0	3.7 ± 0.3	4.86 ± 0.32	0.99 ± 0.06	4.5 ± 0.7	3.71 ± 0.58

be the times at which the data approach linearity. The hornblende (7.5 GPa) datum at 238 hours was discarded as a bad analytical point. The slope of the linear fit to Si concentration-versus-time data was used in each case to determine the first-order kinetics of the dissolution process, and the mass-normalized and specific-area-normalized dissolution rates.

The mass-normalized rate, which does *not* correct for surface area effects, is given by

$$r = \frac{\Delta c}{\Delta t} \frac{V}{m}$$

where $\Delta c/\Delta t$ is the slope of the linear section of the dissolution curve in molar concentration increase per second, V is the solution volume in liters, and m is the initial mass of mineral in grams. This rate is divided by the initial specific surface

area (A) in m^2/g to obtain the proper specific (surface-area-normalized) rate ($k = r/A$) in moles/ m^2 s. In principle the sample mass and specific surface areas are variables during the course of the dissolution experiments; however, the rates are so low and times so short that changes in these values are extremely small and can be ignored. Both of these dissolution rates are listed in Table 2 and plotted in Figs. 11 and 12. The plotted rates are relative to the rates of the unshocked materials. Because the dissolution process associated with unshocked samples is so slow, the concentrations remain low and the fractional errors are large. This is especially true for the oligoclase, as the unshocked sample had particularly noisy data. For this reason, the rate data plotted in Figs. 11 and 12 are plotted with the upper bound of the rate range for the unshocked samples (the best fit rate plus the standard deviation). This emphasized that, even under the most conservative interpretation, the rates are enhanced by the shock.

OLIGOCLASE
22 GPa SHOCK
OUTER LAYER OF SAMPLE CAKE



Fig. 5. SEM photomicrograph of oligoclase shocked to 22 GPa, showing morphology indicative of glass formation.

Note, however, that the dissolution rates for the shocked samples in these figures are relative to the best fit unshocked sample rates.

Figure 13 shows SEM photomicrographs of unshocked and shocked (22 GPa) oligoclase. The highly deformed surface of the shocked material with a greater number of edge sites is evident in the comparison of reacted material. We believe that the increased defect densities normally associated with such plastic deformation is responsible for the observed increases in dissolution rate.

HORNBLLENDE (UNSHOCKED)

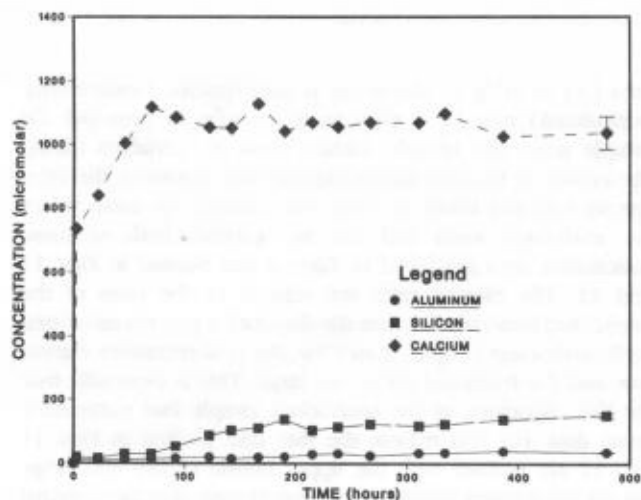


Fig. 6. Concentration history for three elements entering solution from unshocked hornblende.

HORNBLLENDE (SHOCKED TO 16 GPa)

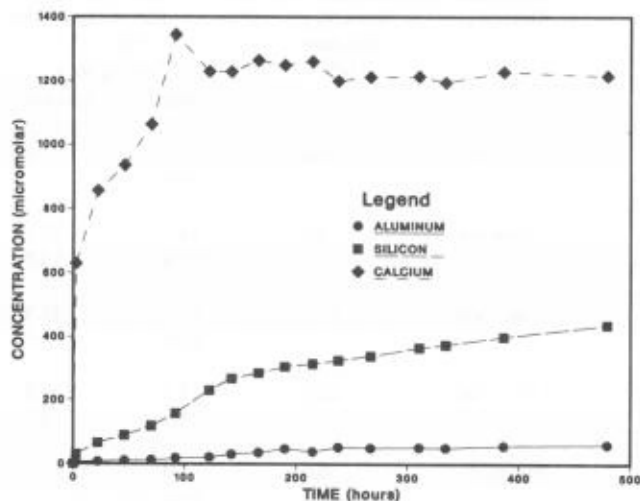


Fig. 7. Concentration history for three elements entering solution from hornblende recovered from a shock pressure of 16 GPa.

HORNBLLENDE

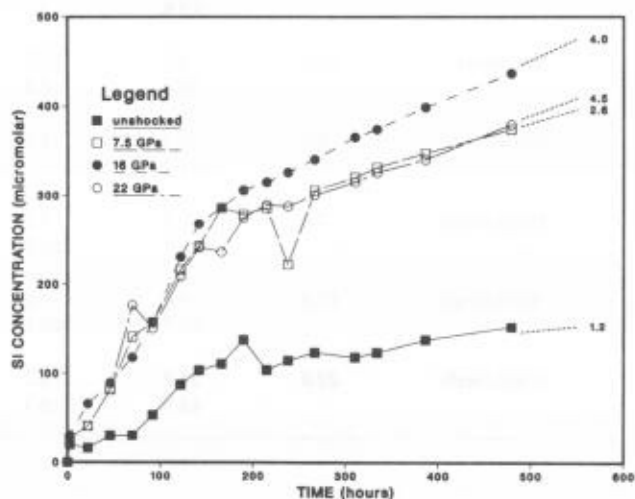


Fig. 8. Silicon concentration history for dissolution from hornblende in each of four conditions: unshocked and recovered from three shock states. Dotted line is least-squares fit to last nine data points. Associated numeral represents surface-area-normalized dissolution rate in $10^{-12} \text{ mol/m}^2 \text{ sec}$.

These results emphasize the *relative* change in dissolution rate of three silicate minerals as a function of shock pressure. Although the absolute rates are of the same order-of-magnitude as those obtained by previous dissolution studies of the plagioclase phases (Busenberg and Clemency, 1976; Holdren and Berner, 1979), it is difficult to directly compare the kinetic data. Sample characterization, solution chemistry, organic complexing, precipitating phases, and other phenomena associated with dissolution experiments cannot be appropriately addressed here, and will be the subject of a future paper

BYTOWNITE

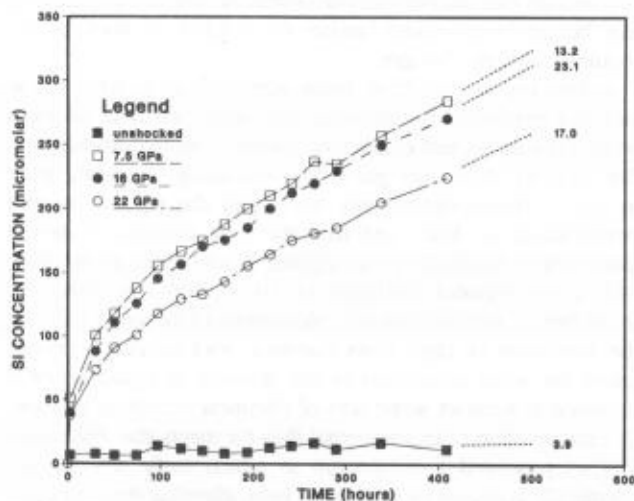


Fig. 9. Silicon concentration history for dissolution from bytownite in each of its four conditions.

OLIGOCLASE

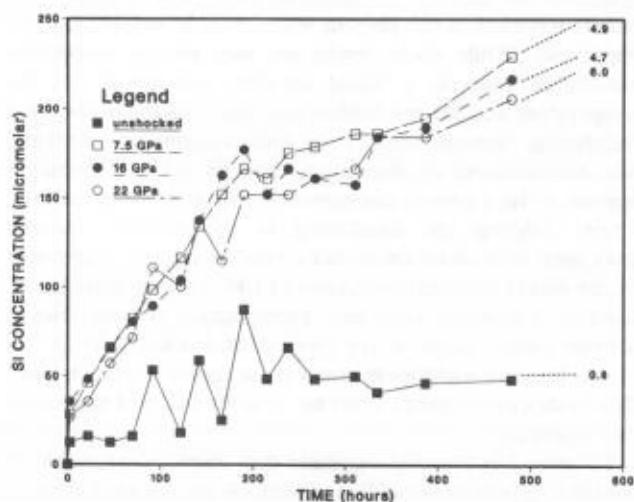


Fig. 10. Silicon concentration history for dissolution from oligoclase in each of its four conditions.

by Cygan and Boslough (in preparation, 1987). Nevertheless, by maintaining identical conditions for each of the dissolution experiments, this study provides a means of directly comparing the relative rates for three different silicate minerals.

DISCUSSION

Implications for the Martian Surface

There is a consensus among planetary geologists that the Martian soil consists mainly of mafic silicate alteration products, but the details of the mineralogy are still under debate. The

MASS-NORMALIZED DISSOLUTION RATE (Silicon)

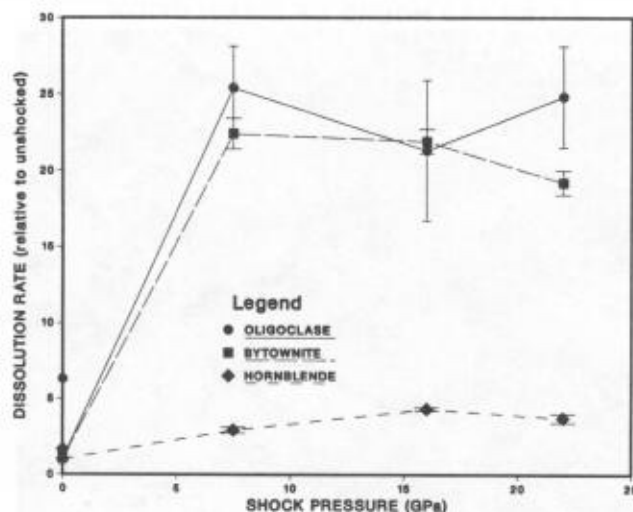


Fig. 11. Mass-normalized silicon dissolution rates for three shocked minerals, relative to the unshocked phases. Symbols on vertical axis represent upper bound of measurement error for associated unshocked phases.

initial interpretation, based on Viking X-ray fluorescence data, was that the fine surface material consists mainly of iron-rich smectite clays and their degradation products, along with ferric oxides, probably in the form of maghemite (Toumin et al., 1977). These researchers suggested a hydrothermal alteration source for the smectite due to interaction between basaltic magmas and subterranean ice deposits. However, according to Singer (1982), Earth-based spectral reflectance data are not consistent with iron-rich clays, but instead strongly suggest the presence of palagonite, an X-ray amorphous weathering product of mafic volcanic glass. Because palagonite is also consistent with the observed bulk chemistry and particle size of the

SURFACE-AREA-NORMALIZED DISSOLUTION RATE (Silicon)

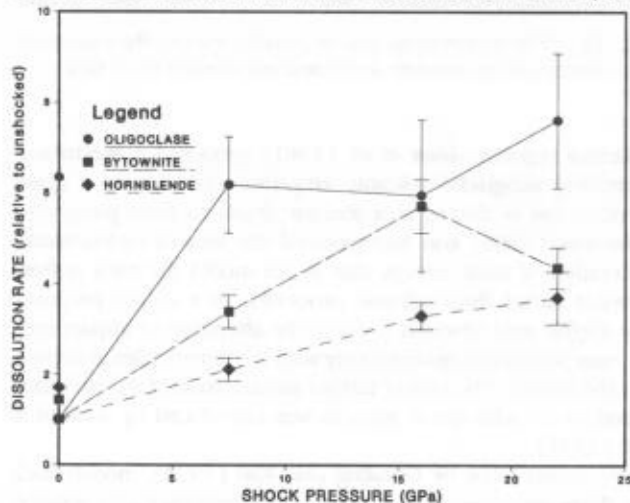


Fig. 12. Surface-area-normalized silicon dissolution rates for three shocked minerals, relative to the unshocked phases.

REACTED OLIGOCLASE

AFTER 480 HOURS OF DISSOLUTION

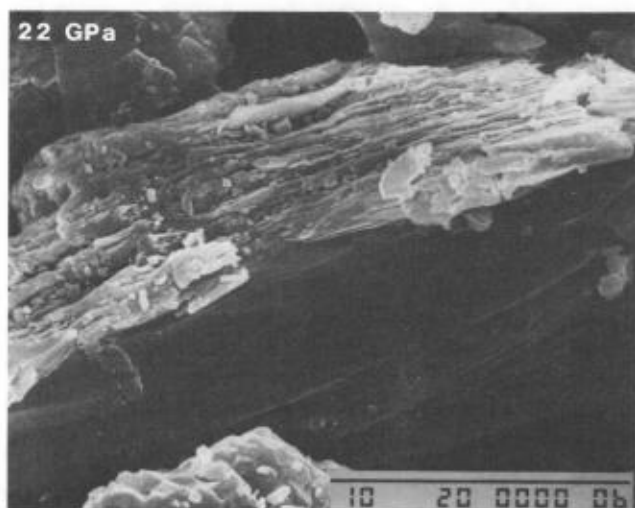
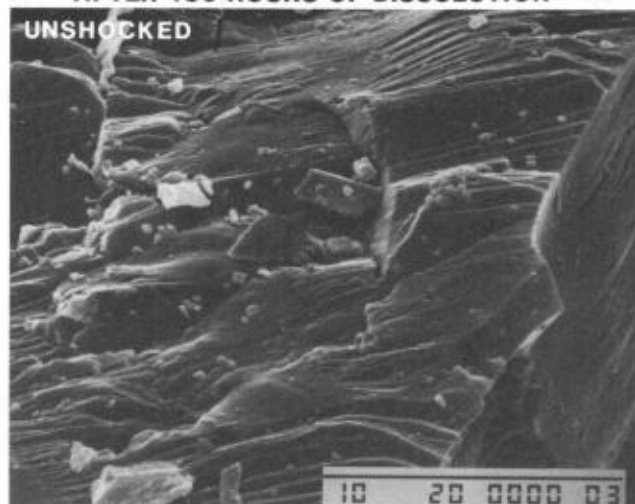


Fig. 13. SEM photomicrographs of partially reacted oligoclase from two dissolution experiments: unshocked and shocked to 22 GPa.

Martian regolith, *Allen et al.* (1981) proposed a mechanism involving subglacial volcanic eruptions resulting in a glassy tephra that is altered at a shallow depth to form palagonite. *Newsom* (1980) also incorporated the idea of hydrothermal alteration of melt, except that in his model the melt is from impact rather than volcanic processes. In a model proposed by *Kieffer and Simonds* (1980), the alteration of impact melt occurs penecontemporaneously with the hot volatiles generated by the impact. The idea of further modification of the alteration product by subsequent impacts was introduced by *Weldon et al.* (1982).

As pointed out by *Gooding and Kell* (1978), models such as those mentioned above assume the existence of a volatile-bearing regolith on Mars, which "presupposes extensive alteration of the regolith to hydrous phases by unspecified

weathering processes." One way to achieve such a state is to postulate that the Martian paleoenvironment was more Earth-like, but any such model "invites the burden of proof for the required climatic changes."

A few hypotheses have been advanced that avoid these inherent problems by allowing alteration products to form under present Martian conditions. Calculations by *Gooding and Kell* (1978) show that gas-solid weathering of silicate glass to clay is thermodynamically favored in the present surface environment on Mars, and that the total amount of altered glass from a lunar-like protoregolith would yield a clay layer with a mean-global thickness of 10 to 100 cm. However, according to thermodynamic calculations of *Gooding* (1978), the formation of clays from common rock-forming minerals under the same conditions in the absence of liquid water is unfavorable without some sort of chemical activation process. By extrapolation of experimental data for magnetite, *Huguenin* (1974) proposed a mechanism in which mafic silicates are chemically activated by ultraviolet light, allowing them to react with atmospheric water vapor to form hydrates as well as to oxidize.

Boslough et al. (1986) proposed shock-modification of minerals due to impacts as another possible means of chemical activation to enhance weathering rates. The experimental results reported in the present study provide support for this hypothesis. While these results are very limited, comparing dissolution rates in a liquid aqueous solution at specific temperature and pH, we believe the shock-enhanced chemical weathering demonstrated by the measurements is significant. The enhancement of dissolution rates for all three minerals appears to be a general phenomenon that must be considered when analyzing the weathering of the relevant minerals associated with planetary surfaces. Further support is provided by the data of *Tyburczy and Abrens* (1987) on the dehydration kinetics of shocked serpentine. Extrapolation of these data to Martian surface temperatures implies that shocked material will reach chemical equilibrium under these conditions much faster than unshocked material; faster by 20 to 30 orders of magnitude for serpentine.

To make a convincing argument that shock-enhancement of weathering rates of crystalline minerals is an important process on Mars, it is important to determine both volumes and rates of production of shock-modified minerals. These calculations are beyond the scope of the present paper, but it is reasonable to assume that the volume of shock-activated minerals would be within an order of magnitude of the volume of impact melt, estimated by *Newsom et al.* (1986) to be equivalent to a global layer 46 m thick. Since most of the cratering of the Martian surface occurred during the period of early bombardment (*Hartmann, 1977*), most of the shocked material was generated at that time, and has had at least 3.5 b.y. to become chemically altered. However, impact-generated material that has been hydrothermally altered was limited to the time over which the impact ejecta remained hot—on the order of years. Since the present results for the dissolution of shocked minerals in liquid water indicate increased alteration rates by factors of around 20 (cf. mass-normalized dissolution rates, with increased surface area effects included), a

substantially greater volume of altered minerals can be produced than if there were no such effect. Perhaps more important, it is possible that, as a result of the shock modification, energy barriers are sufficiently decreased that the decomposition of the minerals might be allowed thermodynamically under ambient conditions on Mars.

One argument can be made for the relative importance of shock-enhanced weathering of crystalline material on the basis of impact energy partitioning. The calculations of *O'Keefe and Abrens* (1977) show that for an impact at 5 km/sec, 50% of the impact energy goes to comminution and plastic work, 40% goes to heating of the target and projectile, and the remaining 10% goes to ejecta kinetic energy. Part of the heat fraction goes toward melting material that is subsequently quenched to glass, but most will be radiated and conducted away as the hot matter comes back to thermodynamic equilibrium with its surroundings. The kinetic energy fraction will eventually be divided between the other two categories, except for any fraction that escapes the planet. Of the 50% that goes toward comminution and plastic work, some is given up as heat when annealing takes place, but the rest is available to increase the specific free energy of the crystalline material, thereby chemically activating it.

It is interesting to note that the most highly shocked material, and the majority of the melt, will come from the meteoroid itself. This implies that the composition of the Martian fines should have a large meteoritic component. In the early paper by the Viking inorganic chemistry team, *Toulmin et al.* (1977) point out that one of the good matches of possible mixtures with Martian regolith samples consists of approximately equal proportions of average tholeiitic basalt and type I carbonaceous chondrites. While they believed that the basalt is likely to be a common rock type on Mars, they found no explanation for a large chondritic component. They dismissed this as a coincidence, stating "the apparent good match of about equal proportions of tholeiitic basalt and type I carbonaceous chondrites to Mars soil is probably fortuitous and does not necessarily imply occurrence of large amounts of primitive, undifferentiated material."

We propose a scenario by which the Martian regolith is enriched in undifferentiated material by selective weathering. A significant fraction of the shock-activated material comes directly from the meteorites, and only shock-activated minerals can weather on Mars. This scenario is also consistent with known production rates of fine-grained material on Mars. According to *Arvidson* (1986), Mars has had a "decidedly non-linear history of debris production," and most of the debris was produced in the first billion years of geologic time. This period is coincident with heavy meteorite bombardment. Similarly, *Guinness et al.* (1987) conclude from spectral reflectance studies at Viking lander sites that "soils are created globally by a number of processes that operated at higher rates earlier in geologic time."

There is some evidence for chondritic enrichment of terrestrial craters, which were formed by much higher impact velocities. The highest meteoritic contamination is found in impact melts, up to 8% for Clearwater East, according to *Palme* (1982). With increasing impact velocity, the amount of

meteorite contamination decreases, so one would expect greater enrichment on Mars where impact velocities are lower. Unless the Martian soil is entirely volcanogenic, it should be chondritically enriched. The fact that most of the regolith dates from the first billion years argues against a volcanogenic origin, since significant volcanic activity has taken place since that time. In fact, according to *Plescia and Saunders* (1979), the main shield of Alba Patera, one of the earliest of the huge Martian shield volcanoes, is only 1725 m.y. old.

Implications for the Cretaceous-Tertiary Boundary

The fact that weathering of shocked minerals is enhanced also has a bearing on the Cretaceous-Tertiary boundary on Earth. One of the criticisms of the impact hypothesis of *Alvarez et al.* (1980) comes from mineralogical studies of the boundary clay layer. According to *Rampino* (1982) and *Rampino and Reynolds* (1983), if such an impact occurred, the clay would be expected to contain fine-grained mineral fragments derived from the asteroid and impact area, since *O'Keefe and Abrens* (1982) calculate that there should be about five times as much submicron ejecta in the form of highly shocked solid mineral and rock fragments as glass from melt and condensed vapor. *Rampino* (1982) allows that the glassy fraction might be altered to smectite, in agreement with *Kastner et al.* (1984). The resulting smectite would be hard to distinguish from the volcanogenic clay present in the layer, but *Rampino* (1982) argues that "diagenetic elimination of fine-grained non-clay minerals from the boundary clay seems unlikely because the degree of diagenesis for the clays is very mild," based on the highly smectitic composition of the clays. However, because the mineral grains are highly shock-activated, the conditions and times required for alteration can be relaxed, and this argument is weakened.

Implications for Nuclear Test Sites and Impact Craters

The observed shock-enhanced dissolution has implications for very long-term effects of underground nuclear testing on groundwater chemistry. According to pressure decay functions determined from nuclear explosion data by R. C. Bass (unpublished data, 1987), a 20-kt explosion in wet tuff or dry alluvium will generate a 9080 m³ volume of material shocked above 7.5 GPa. However, redistribution of the excess energy from the nuclear device melts significantly more rock than would be melted by the shock alone. According to *Schwartz et al.* (1984), 740 metric tons are melted per kiloton of yield. Thus for tuff, with a density of about 1.8 g/cm³, a 20-kt explosion will melt 8220 m³ of rock, nearly all of that shocked above 7.5 GPa. If, however, significant shock-activation occurs at pressures above 1 GPa, the data of R. C. Bass (unpublished data, 1987) indicate that a volume of 5.7×10^4 m³ of rock is shock-activated for a 20-kt explosion in tuff. The amount of melt is small compared to this volume. It may be useful to carry out further experiments in this pressure range on the minerals found in the tuff at the Nevada test site, to see if shock-enhanced dissolution is significant.

Similar estimates can be made of volumes of shocked material near natural impact craters. For impact craters there is no excess thermal energy beyond that generated by shock heating, so the large volumes of highly shocked material are not melted. However, the material that experiences the highest stress is ejected and widely dispersed, and the local groundwater chemistry will be controlled by interaction with minerals that experience lower peak stresses. A comparison of groundwater from known impact sites to that from undisturbed terrain would be useful.

Other Implications

Our observation of variable incongruent dissolution has possible ramifications for chemical fractionation that is dependent on shock history. It implies that shocked and unshocked terrains may differ not only in rate of chemical weathering, but may also differ in chemical composition of the resulting alteration products.

There are other possible consequences of shock modification of silicates that, although unrelated to weathering, should be mentioned here for completeness. Shocked minerals experience large increases in specific free energy, due to high defect densities and increased specific surface areas. Thus we would expect other physico-chemical properties to be altered in addition to dissolution rate. Among the possible effects might be a depression of the melting point, leading to unusual partial melts. Also affected could be diffusion properties, which might result in different trace element partitioning and isotope chronology than would be expected for unshocked material. These speculations provide suggestions for further experiments, as well as a note of caution for interpretations based on properties of planetary materials for which shock effects cannot be ignored.

CONCLUSIONS

This study provides data that demonstrate that there is direct correlation between shock modification of minerals and enhanced weathering rates. Since shock-enhanced dissolution was observed for three different minerals shocked above 7.5 GPa, it is reasonable to expect other minerals relevant to planetary surfaces to demonstrate the effect in this pressure range.

In order to quantify the effects of shock-enhanced dissolution and determine their relative importance in planetary surface evolution, considerable experimentation is necessary on a variety of relevant minerals. Hydrothermal alteration studies should be performed, as well as an investigation of gas/solid weathering processes on shock-activated silicates. Studies of weathering products from naturally shocked minerals will also provide data that may have a bearing on calculations for very long-term effects of underground nuclear tests.

Shock-weathering experiments on chondritic material would also be particularly useful with regard to the composition of the Martian regolith because, according to the weathering scenario suggested in this paper, the Martian regolith should be highly enriched in alteration products of meteoritic minerals.

Any future sample-return mission to the Martian surface should include the capability of measuring platinum-group elements in the regolith at the parts-per-billion concentration level, in order to determine if it is truly enriched in chondritic material.

Since shocked minerals undergo chemical alteration at a higher rate, any restrictions on the quantity of crystalline ejecta in the clay layer of the Cretaceous-Tertiary boundary can be relaxed, thereby weakening one argument against the impact-extinction hypothesis.

There are a number of other possible implications of this study that should be explored, such as the effects of shock-dependence of incongruent dissolution. Effects of shock history on other physico-chemical properties should also be considered.

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