SHOCK-CHEMISTRY IN NATURAL MATERIALS AND EVOLUTION OF PLANETARY SURFACES[*]

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There are two possible types of chemical reactions that can take place due to shock-loading of a
mineral. The first type is one that takes place on a longer time scale than the shock event,
and is due to "shock activation" of the mineral, i.e. the increase in specific free energy due
to increased densities of defects and dislocations. An example of this type was experimentally
studied by measuring shock-enhanced dissolution rates of three silicate minerals. The second
type is the reaction that occurs immediately, or upon release to ambient pressure, and is due to
the large increase in internal energy provided by the shock, together with the shift in chemical
equilibrium brought about by increased pressure and temperature. The clay mineral nontronite
was the subject of an experimental study of such reactions. Both processes can affect planetary
surfaces, either independently or together. The two processes, acting in synergy, are invoked
to explain the composition, mineralogy, color, and physical properties of the Martian soil.

1. INTRODUCTION

Chemical activation of shocked solids is of increasing interest in materials synthesis.[1] Catalysis, polymerization, and decomposition are among the reactions observed to experience rate increases due to shock-loading. In some cases reaction rates have increased by orders of magnitude. Recent work has shown that increased chemical reaction rates are due to the shock-induced generation of extremely high defect and dislocation densities (e.g. ref. 2), and that defect densities can be increased by orders of magnitude when inorganic crystals are shocked (e.g. ref. 3). Because dissolution rates of minerals are dependent on defect densities,[4] one would expect shock-loaded minerals to experience enhanced rates of chemical weathering. This idea is supported by new experimental results of Casey et al.[5] for rutile which suggest that the dissolution rate is an increasing function of shock-generated point defect density for that material.

It is now known that prompt chemical reactions can occur in materials when they undergo shock-loading. For example, post-shock analysis has shown that nickel and aluminum react to form nickel aluminides.[6] Examples of decomposition reactions in geological materials include the release of water from hydrous minerals (e.g. ref. 7), and of carbon dioxide from carbonates (e.g. ref. 8). These reactions have been invoked in models of impact devolatilization of evolving planets, resulting in the generation of early oceans and atmospheres.[9]

This paper is concerned with the evolution of planetary surfaces by the combination of shock-alteration and chemical weathering. Recent data on both processes are summarized and discussed in the context of the Martian surface, emphasizing the possibility that shock-induced chemistry played a key role in the formation and evolution of Martian soil.

2. CHEMICAL ALTERATION OF SHOCK-MODIFIED MINERALS

To quantify the effect of shock activation on chemical weathering in nature, we subjected three rock-forming minerals to controlled shock-loading followed by laboratory dissolution experiments.

2.1 Experimental

Samples of three silicate minerals (bytownite, oligoclase, and hornblende) were experimentally shocked to peak pressures of 7.5, 16, and 22 GPa using the explosive recovery method of Graham and Webb (10 and references therein). Shocked and unshocked minerals were subjected to analysis by scanning electron microscopy, x-ray diffraction, and BET gas adsorption surface area measurements. In addition, the release of three major elements (silicon, aluminum, and calcium) into pH-buffered solutions was measured. This was done by placing one gram of material in an agitated constant temperature (25°C) bath consisting of 200 ml of a standard solution made up of water buffered by potassium hydrogen phthalate (pH-4). A small portion of the solution was withdrawn approximately daily for three weeks, and analysed for silicon with molybdate-blue spectroscopy and for the other elements with plasma emission spectroscopy.

2.2 Results

In Figs. 1 and 2, scanning electron micrographs illustrate the salient effect of a 22 GPa shock on the mineral bytownite. It is clear that significant disaggregation and comminution has taken place, which would tend to increase the specific surface area.

In Fig. 3, the results of the BET surface area measurements on unshocked and shocked bytownite are plotted. These results confirm and quantify the specific surface area increases implied by the photomicrographs. Specific surface areas increase by factors from 3.7 (for 16.5 GPa) to 6.6 (for 7.5 GPa) for shocked bytownite. The shock-activation is not apparent from the photomicrographs; however, x-ray diffraction studies show substantial line-broadening which suggests the introduction of residual strain and/or increases in defect densities. For a surface-controlled dissolution process, the increased surface area will allow the mineral to dissolve faster, even in the absence of shock-activation.

The actual (specific surface area-normalized) dissolution rates were determined from the concentration-versus-time data obtained for the three elements. One set of

FIGURE 1
SEM micrograph of unshocked bytownite. Scale bar at lower right indicates 10 microns.

FIGURE 2
SEM micrograph of bytownite shocked to 22 GPa. Scale is the same as for Figure 1.

such data is plotted in Figure 4, for the dissolution of silicon from bytownite in its unshocked and three different shock conditions.
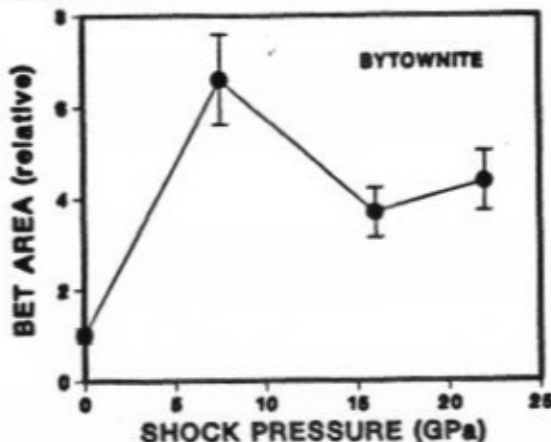

FIGURE 3

Specific surface areas for shocked bytownite relative to that of the unshocked condition.
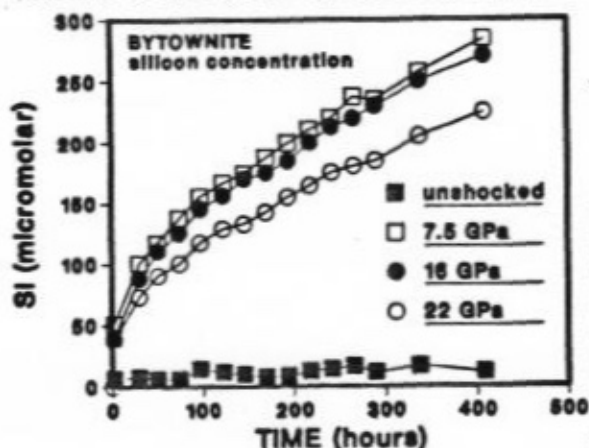

FIGURE 4

Time history of silicon concentration entering solution from bytownite in each of four conditions: unshocked and recovered from three shock states.

We obtained the same type of data for the three elements for all three minerals in their shocked and unshocked states. From Fig. 4 it can be seen that the rate of concentration increase approaches an approximately linear time dependence. This behavior is in agreement with existing models and observations for surface-controlled dissolution of various minerals (e.g. ref. 11). The specific surface

area-normalized dissolution rates were obtained using the equation:

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

where $\Delta c/\Delta t$ is the slope of the linear part of the dissolution curve, V is the solution volume (200 ml), m is the mineral mass (about 1 gm), and A is the specific surface area. A linear least squares method was used to determine $\Delta c/\Delta t$, resulting in relative dissolution rates plotted in Fig. 5.
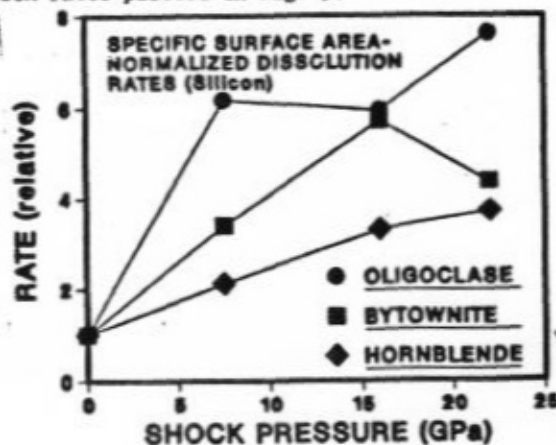

FIGURE 5

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

It is seen from Fig. 5 that specific area-normalized rates increased by up to seven-fold. When the effect of comminution is included, the specific surface area is included, and the mass-normalized dissolution rate increase (which reflects true weathering rate) is over 20-fold in some cases. Results are described in more detail by Boslough and Cygan.[12]

3. SHOCK MODIFICATION OF CHEMICALLY ALTERED MINERALS

To study the effect of immediate shock-induced chemical reactions on natural materials, we performed explosive shock loading experiments on the mineral nontronite, which is an alteration product of crystalline silicate minerals.

3.1 Experimental

Samples of nontronite were shocked to peak pressures between 7 and 32 GPa using the techniques described in section 2.1. By varying the initial packing densities of the clay, the peak mean-bulk shock temperatures were controlled. These temperatures were determined from the calculations of Graham and Webb.[10]

Recovered samples were analyzed with static magnetization measurements, x-ray diffraction, Mössbauer spectroscopy, and comparative color determination. These techniques were also applied to samples of nontronite heated in air to the same temperatures as achieved by shock.

3.2 Results

The room temperature magnetic moment (M) for samples of shocked nontronite is plotted as a function of applied magnetic field in Fig. 6. The data were accurately fit by a function that describes the magnetic moment as the sum of two distinct components: (1) a paramagnetic contribution which is a linear function of the applied field, and (2) a ferromagnetic part that approaches a field-independent saturation magnetization (M_s) at sufficiently high applied fields. The approach to saturation is empirically described by the equation:

$$M_r = M_s/(1 + 4\pi A/H)$$

where A is the magnetic hardness parameter.

The saturation magnetization determined by fitting this equation to the data in Fig. 6 is plotted as a function of mean-bulk shock temperature in Fig. 7. For comparison, we have also plotted saturation magnetization determined in the same way for unshocked nontronite which was heated in air for one hour at various temperatures. It is interesting to note that the magnetization has a strong peak at about 700°C for both sets of data, implying that the clay's magnetic properties can act as a shock thermometer. However, the x-ray diffraction data demonstrate that the shocked and heated

nontronite samples are distinctly different materials, so this correlation is may be fortuitous.
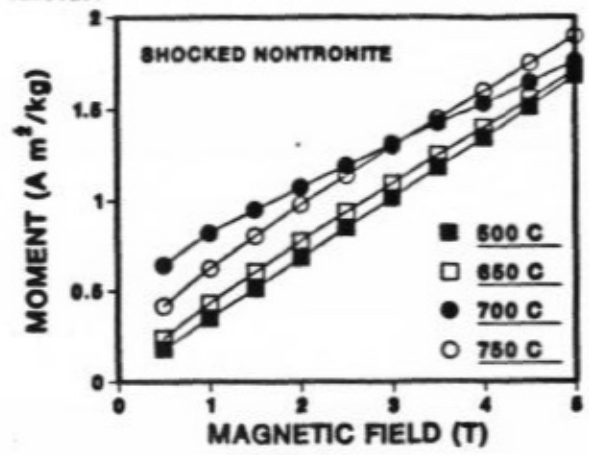

FIGURE 6

Magnetic moment versus applied magnetic field for nontronite samples shocked to four different calculated peak mean-bulk temperatures.
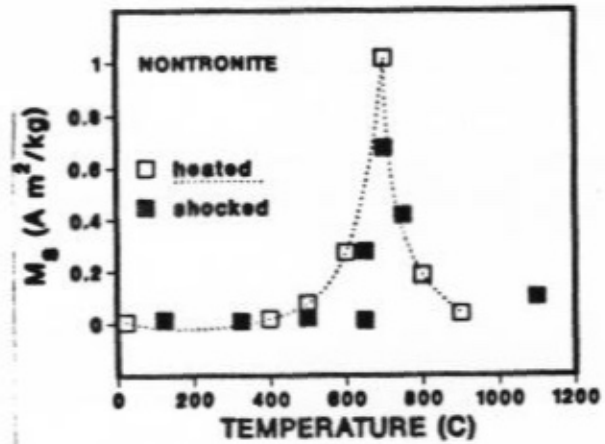

FIGURE 7

Saturation magnetization plotted as a function of peak temperature experienced by shocked and heated nontronite samples.

The most obvious change in the x-ray diffraction data of shocked nontronite is the progressive decrease in the interlayer d-spacing from 12.5 Å to 9.7 Å with increasing shock temperature. This is apparently due to the release of interlayer molecular water.[9] Other x-ray diffraction lines are modified, but no substantial structural change takes place, inferring that the shocked clay retains a

dehydrated nontronite-like structure. By
contrast, thermally altered unshocked non-
tronite abruptly losses its nontronite x-ray
pattern above 700°C, where the corundum pattern
appears, presumably indicating the presence of
hematite. At higher temperatures, the cris-
tobalite pattern also appears, as well as weak
x-ray lines that probably correspond to minor
oxide or silicate phases.

According to ^{57}Fe Mössbauer measurements,
the shocked nontronite undergoes a change in
local symmetry, and there is an increase in
disorder in the local Fe^{3+} environments. One
shocked sample (peak pressure = 19 GPa, peak
temperature = 700°C) was subjected to detailed
Mössbauer analysis with an expanded velocity
range and improved statistics to look for minor
magnetic phases (Fig. 8). A weak spectrum
similar to α-Fe is observed. The size of the
resonance indicates that the metallic Fe con-
stitutes 2% ± 1% of the total Fe present in the
shocked material. There is also evidence for
another magnetic phase, either magnetite or
maghemite.

The color of the shocked nontronite showed a
strong correlation with calculated mean-bulk
shock temperature. The color changes were
quantified to some extent with the aid of the
Munsell Soil Color Charts.[13] The starting
material was light olive brown (Munsell color =
2.5 Y 5/4). With increasing shock pressure the
color became both redder and darker, to strong
brown (7.5 YR 5/6). Weldon et al.[14] attributed
these color changes to a shift in the optical
and near-infrared absorption spectrum, brought
about by a change in the energy of the 0^{2-}-Fe^{3+}
charge transfer. These spectra are reproduced
in Fig. 9. Additional experimental details and
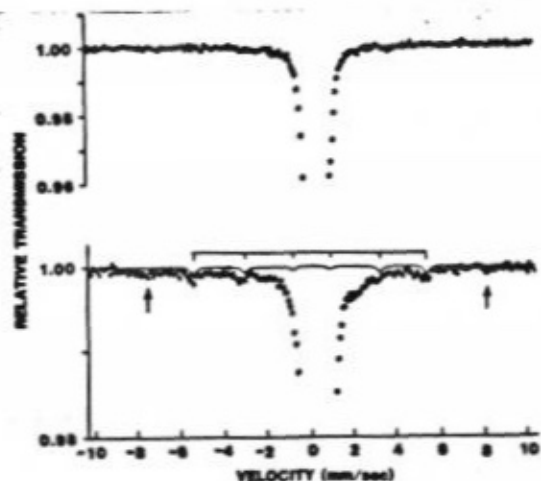results are given by Boslough et al.[15]

FIGURE 8
Mössbauer spectrum of unshocked nontronite
(upper) is compared to that of nontronite
shocked to 19 GPa and 700°C (lower). The
strong paramagnetic resonance is truncated.
There is evidence for minor magnetic phases in
the shocked sample, but none in the unshocked.
Arrows indicate magnetite or maghemite, super-
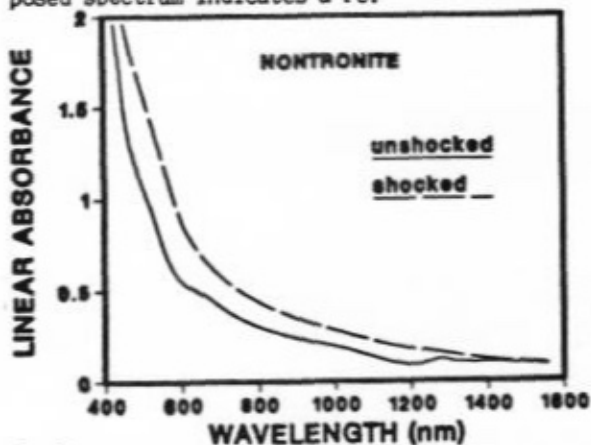posed spectrum indicates α Fe.

FIGURE 9
Optical and near-infrared absorption spectra of
unshocked nontronite and nontronite shocked to
30 GPa, from reference 14.

4. DISCUSSION

According to x-ray fluorescence data, the
fine material on the surface of Mars consists
mainly of iron-rich alteration products, i.e.
clays and clay-like minerals.[16] Two important
questions arise: (1) How were alteration
products formed, when crystalline solids are
stable under present Martian conditions? (2)

Why does the elemental composition of the Martian soil give it the appearance of consisting of 50% meteoritic material? The results of the shock-dissolution experiments may lead to an answer to the first question. The kinetics of alteration are enhanced by shock-activation. If the shock-induced changes also generate thermodynamically unstable solids, the accelerated kinetics will allow more chemically weathered material to form. The second question can be addressed by calculating the amount of material activated by an impact-induced shock. As much as 70% of the most highly shock-activated material from an impact on Mars comes from the meteorite itself.[12] If this material is selectively weathered, the soil will be highly enriched in meteoritic material.

Since the composition of nontronite so closely matches the elemental abundances measured in the Martian soil, it is a candidate for the major mineralogical component. However, in its normal state it is neither red nor magnetic, as is the Martian surface material. Our data show that shocked nontronite more closely matches the physical, as well as chemical, properties of the Martian soil. If the Martian regolith has experienced substantial impact-induced shock, then nontronite cannot be precluded as a major component on the basis of its color or magnetic properties.

5. CONCLUSIONS

Shock-chemistry plays an important role in earth and planetary science. The observation of shock-enhancement of dissolution rates of silicates implies that shock-activation of minerals on the surface of Mars by meteorite impact may be the source of the soil. The dehydration and presence of magnetic phases in nontronite suggest that further shock-modification of chemically altered minerals may

also be an important planetary surface process. It is possible that the combined effects of shock-chemistry and chemical weathering could give rise to planetary surface materials with unusual properties, as observed on Mars.

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