

Mechanisms of hydrogen generation during the mechanochemical treatment of biotite within D₂O media

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The mechanism of hydrogen generation during the mechanochemical treatment of biotite was examined by grinding experiments using a ball mill in H₂O or D₂O as a grinding media. From the linear relationship between the amount of generated hydrogen and the increase of the surface area of ground powders, the hydrogen productivity of biotite is estimated to be 0.036 μmol/m², which agrees with the previous results in spite of the difference in the grinding conditions. D₂ analyses by a mass spectrometry indicate that the produced amount of D₂ accounts for only 10% of the total hydrogen and that more than 90% of hydrogen takes a form of a mixture of HD and H₂. The observed isotope distribution clearly indicates that hydroxyls within the crystal structure can be a major source for the generation of hydrogen. Hydrogen generation originated from hydroxyls may indicate the higher hydrogen productivity of phyllosilicates than those of quartz and alkali feldspar.

Key words: Hydrogen generation, mechanochemical treatment, biotite, hydrogen isotope.

1. Introduction

There are many reports on hydrogen anomaly associated with seismic events (e.g. Wakita *et al.*, 1980; Sugisaki *et al.*, 1983; Sugisaki and Sugiura, 1986; Ito *et al.*, 1999). Hydrogen observed along active faults is thought to be generated by mechanochemical reactions within the fault zones (Wakita *et al.*, 1980). This unique origin of hydrogen has attracted extensive interests. Since hydrogen is produced by chemical reactions where fault rocks are destructed, it is expected that hydrogen may carry valuable information concerning the seismogenic regions (Koizumi, 1997).

Hydrogen generation by mechanochemical reactions between a crushed rock surface and water has been confirmed by means of crushing experiments using quartz and granite powder in the presence of water vapor (Kita *et al.*, 1982). Sugisaki *et al.* (1983) also reacted several kinds of powdered samples with water in a flask and detected molecular hydrogen generation. According to the recent grinding experiments using a ball mill by the present authors (Kameda *et al.*, 2003), hydrogen productivity for some single crystals was evaluated by comparing the amount of generated hydrogen and the freshly created surface area of ground samples. It is reported that phyllosilicates such as biotite and muscovite can effectively produce hydrogen and that more than 60% of hydrogen can be attributed to biotite and chlorite in the case of granite. Thus, it is important to interpret the high hydrogen productivity of phyllosilicates in order to understand the natural occurrences and origin of hydrogen

along active faults. Kameda *et al.* (2003) suggested that the high productivity seems to be correlated with the existence of hydroxyls within the crystal structures. If the hydroxyls actually cause hydrogen production, the observed hydrogen can be thought to have two origins: one is hydrogen atoms from the grinding liquid media (water molecules) and the other from the hydroxyls in a crystal.

In this study, we have conducted the wet grinding experiments of biotite within D₂O as a grinding liquid media in order to elucidate the role of hydroxyls for hydrogen generation. The analyses of stable isotopes for the generated hydrogen may provide a clue to the origin of hydrogen and its generation mechanisms.

2. Experimental

2.1 Milling of the powders and analysis

Grinding was conducted by using a rotational ball-mill (Fritsch P-6), zirconia mill pot (80 cc) and zirconia beads (10 mmφ × 20) at room temperature (25°C) under atmospheric pressure. Processed samples were prepared from the single plate-like crystals of biotite (about 10 cm × 10 cm × 0.5 cm). The chemical compositions (in weight percentage) were determined by electron-probe microanalyzer (EPMA) and Fe (II) and Fe (III) contents measured by wet analyses: Na₂O, 0.153; Al₂O₃, 17.93; FeO, 19.26; Fe₂O₃, 0.26; K₂O, 8.397; MgO, 8.576; SiO₂, 36.818; TiO₂, 2.384; MnO, 0.056; Cr₂O₃, 0.002 (±0.5% accuracy). A single crystal of biotite was gently crushed by a tungsten-carbide motor and washed ultrasonically in ethanol for three times. A dried powder was sieved to grain sizes ranging from 0.15 to 0.512 mm. A starting powder was preheated at 150°C for more than 2 hours to remove adsorbed surface water.

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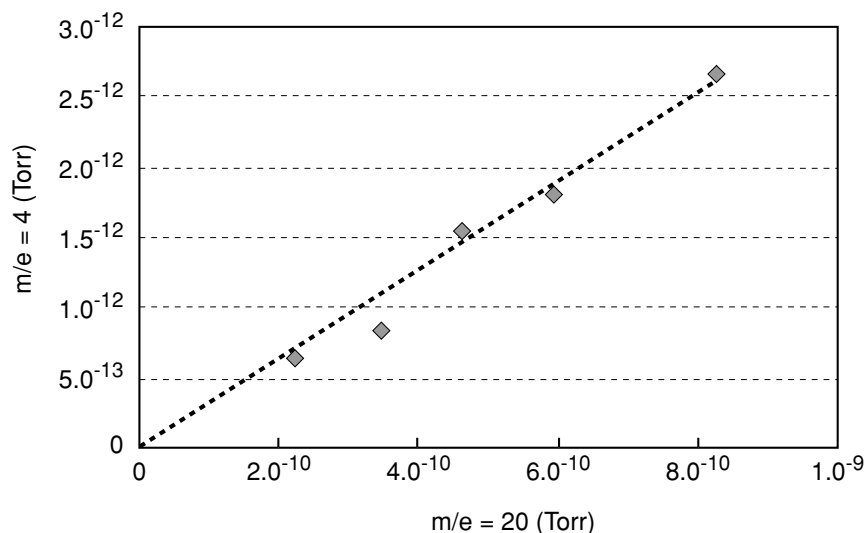


Fig. 1. The relationship between the partial pressures of $m/e = 4$ (D_2^+) and $m/e = 20$ (D_2O^+).

3 g of biotite powder and 10 cc pure of either H₂O (Millipore water; 15M Ω or D₂O (Wako chemicals; 99.5% purity) were put in a mill pot within a glove box (Unico UN-650F) in order to exchange an internal gas phase by Ar (99.995% purity) for H₂O experiments and by N₂ (99.9995% purity) for D₂O experiments, respectively. O₂ content within the glove box was estimated to be <100 ppm as was monitored by an O₂ meter (Toray LC-750). Duration of milling was 15, 30, 45 and 60 minutes at 500 rpm. A gas phase after grinding was sampled by gas-tight syringe (Ito MS-GAN 250). The total hydrogen content was analyzed by gas chromatography (Yanaco G-2700; MS-5A column) equipped with a thermal conductivity detector (TCD). D₂ content was analyzed by mass spectrometer as described in the succeeding section. The ground sample was separated by centrifugation at 4500 rpm for 20 min and the surface area of a ground powder was measured by the BET (Brunauer-Emmet-Teller) method (Beckman Coulter SA-3100) at liquid nitrogen temperature (77 K).

2.2 Mass spectrum

A generated amount of D₂ in a N₂ matrix was measured by quadrupole mass spectrometer (QMS, HIDEN HAL-201). For the measurements, 1 cc of gas sample was injected into the vacuum line ($\sim 1.0 \times 10^0$ Pa) attached to the QMS. A sample was thereafter carried into the analyzer ($\sim 1.0 \times 10^{-7}$ Pa) through a flow control valve. During measurements, gas pressures in the line and analyzer were kept around 5.5×10^3 Pa and 7.3×10^{-5} Pa, respectively. An electron energy of 80 eV and an emission current of 20 μ A were used for analyses. Seven scans were averaged to obtain a peak area. Because there was D₂O vapor in the gas sample, a D_2^+ ion ($m/e = 4$) was always detected as a blank due to the fragmentation of D₂O molecules. In order to evaluate the effect of D₂ originated from D₂O, a D₂O gas sample without D₂ was measured at various concentrations for determining the peak area ratio between $m/e = 20$ (D_2O^+) and $m/e = 4$ (D_2^+). Figure 1 shows the linear correlation between the peak area of D_2^+ ($[D_2^+]_{\text{blank}}$) and that of

D_2O^+ ($[D_2O^+]$), leading to the following regression line:

$$[D_2^+]_{\text{blank}} = 0.0032 \times [D_2O^+] \quad (1)$$

The amount of original D₂ ($[D_2^+]$) was obtained by subtracting the area of blank D_2^+ ($[D_2^+]_{\text{blank}}$) from the total area of D_2^+ ($[D_2^+]_{\text{total}}$):

$$[D_2^+] = [D_2^+]_{\text{total}} - [D_2^+]_{\text{blank}} \quad (2)$$

Neglecting the change of N₂ partial pressure during experiments, $[D_2^+]$ can be corrected by the area of $m/e = 14$ (N^+) as a reference, which was produced by the fragmentation of N₂. From a calibration curve using a standard D₂ gas, the peak area was converted to the D₂ concentration. Unfortunately, because of the high blank of $m/e = 2$ (H_2^+) and $m/e = 3$ (DH^+) caused by fragmentation of D₂O and H₂O in the analyzer, the amounts of DH and H₂ could not be determined successfully in this analytical method.

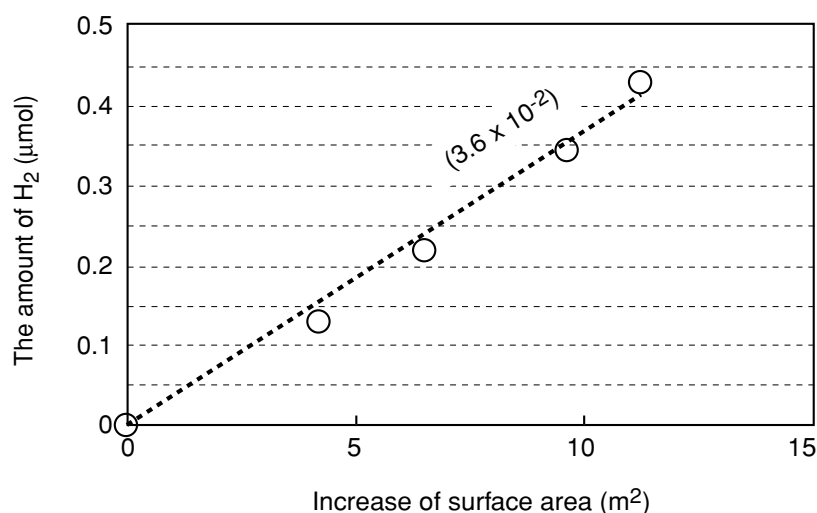
3. Results and Discussion

3.1 Wet grinding within H₂O media

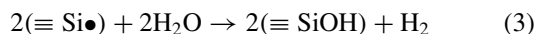
Table 1 shows the results of H₂ measurements and surface area analyses after grinding biotite in H₂O liquid media. Both the H₂ concentration and the specific surface area monotonically increase with the duration of grinding. After 60 minutes, the H₂ concentration reaches 168 ppm, which is smaller than 648 ppm at the same duration observed in a previous study (Kameda *et al.*, 2003). The specific surface area after 60 minutes grinding is determined to be 4.42 m²/g, which is also lower than the results obtained by Kameda *et al.* (2003). Such lower values seem to be caused by the smaller amounts of samples, fewer balls and slower milling conditions. Comparing these results, the relationship between the increase of the total surface area of ground powders and the generated amount of H₂ in molar quantity can be obtained (Fig. 2). The amount of H₂ is linearly correlated with the increase of a total surface area with the slope of 0.036 μ mol/m². Although the grinding conditions are different from those by Kameda *et al.* (2003), the H₂ productivity fairly agrees with each other.

Table 1. The experimental results of H₂ and D₂ analysis. The specific surface areas of the ground biotite are also shown.

Grinding time (min)	H ₂ concentration		D ₂ concentration		Specific surface area (m ² /g)
	(ppm)	(μmol)	(ppm)	(μmol)	
0	—	—	—	—	0.691
15	50.3	0.12	2.4	0.0072	2.09
30	84.5	0.22	5.5	0.0165	2.86
45	135	0.35	7.4	0.0222	3.9
60	168	0.43	12.7	0.0381	4.42

Fig. 2. The linear relationship between the amount of generated H₂ (μmol) and the increase of the surface area of ground biotite (m²). The values in the parentheses indicate the H₂ productivity of biotite.

As presented previously in Kameda *et al.* (2003), the hydrogen productivity of biotite is much higher than those of quartz ($1.0 \times 10^{-3} \mu\text{mol}/\text{m}^2$) and alkali feldspar ($3.9 \times 10^{-3} \mu\text{mol}/\text{m}^2$). Hydrogen generation during grinding of quartz or alkali feldspar can be explained by the chemical reactions between the mechanoradicals on a fresh surface of minerals and grinding liquid media as follows (Schrader *et al.*, 1969; Kita *et al.*, 1982):



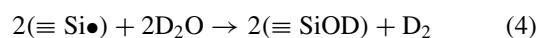
Higher hydrogen productivity of biotite is likely related to the existence of hydroxyls in its structure (Kameda *et al.*, 2003). The prospect was supported by dry grinding experiments using kaolinite (Kameda *et al.*, 2004). Hydrogen generation during the grinding of kaolinite was observed even under dry conditions. Furthermore, infrared (IR) absorption measurements reveal that the intensity due to hydroxyls decreases in accordance with the hydrogen generation. If this is the case, the observed hydrogen during grinding biotite in H₂O liquid media may be produced by hydrogen atoms from grinding media and/or from hydroxyl groups.

3.2 Wet grinding within D₂O media

For the quantitative discussion on the origin of hydrogen atoms, D₂O liquid media were used for grinding procedures. In this case, we can suppose that the generated hydrogen may be composed of a mixture of H₂, HD and D₂.

At first, the apparent hydrogen concentration after 60 minutes grinding in D₂O was analyzed by gas chromatography. Assuming all of hydrogen atoms were from H₂, 154 ppm of hydrogen was detected and this seems a little lower than the result in H₂O experiments (168 ppm). Since the thermal conductivity detector (TCD) was used for GC measurements, the slightly lower concentration may suggest that D₂ or DH whose thermal conductivity is lower than that of H₂ was mixed in the apparent hydrogen peak.

Because it is difficult to separate a mixture of hydrogen (H₂, HD and D₂) into each component by the present GC measurements, mass spectrometry was adopted to determine the amount of generated D₂. Figure 3 shows the relationship between the D₂ concentration and the grinding time. The concentration increased with the duration of grinding time until 12.7 ppm of D₂ was detected after 60 minutes. Surprisingly, this value indicates that only ~10% of total hydrogen was generated by D₂O grinding media according to the following equation:



To obtain the D₂ productivity, the generated amount of D₂ (μmol) was compared with the increase of the total surface area (Fig. 4). Although the points are scattered, the slope of the regression line between them indicates that the D₂ productivity is within 0.002–0.0035 μmol/m². Although the structural change due to the destruction of biotite lay-

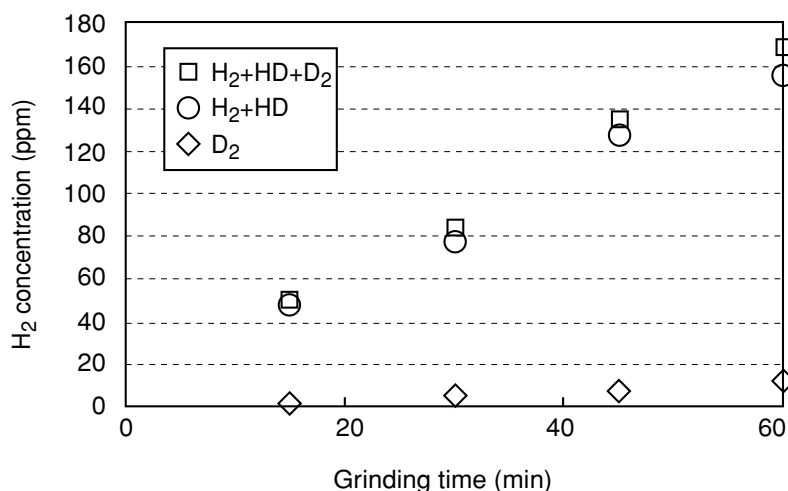


Fig. 3. The relationship between the amount of the generated hydrogen concentration (ppm) and the increase of the specific surface area of ground biotite (m²).

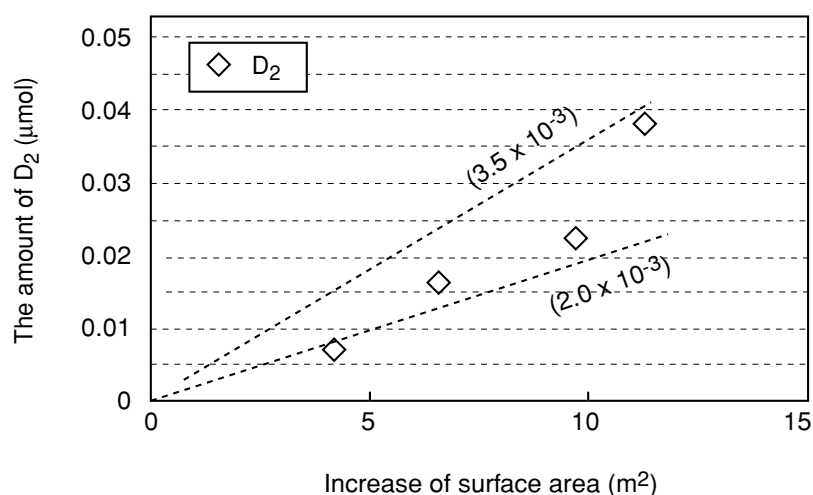
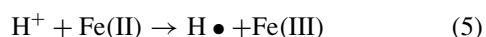


Fig. 4. The increase of the amount of D₂ with the total surface area of ground biotite.

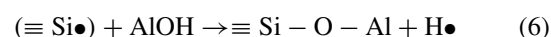
ers may be different from that of quartz and K-feldspar, the amount of generated hydrogen from grinding media is comparable with those of quartz and K-feldspar.

On the other hand, more than 90% of the observed hydrogen can be attributed to HD and H₂ (Fig. 3) and the existence of such large amounts of HD and H₂ indicates that hydroxyls are considered to be an important source for the hydrogen formation. Because the surface of biotite was always in contact with D₂O media during milling, H atoms as a precursor for H₂ or HD molecules should be formed within the crystal structure. One possible mechanism is the reduction of a proton by Fe (II) in a biotite crystal:



Miller and Oulton (1970) observed a collapse of hydroxyl groups of kaolinite on IR spectra during the percussive milling and explained it by a *prototropy* effect, i.e. the transfer of protons within a kaolinite structure to form H₂O molecules. Such dehydroxylation (mechanochemical dehydroxylation) accompanied with the crystal destruction was also reported for montmorillonite (Blahoslav and

Gunther, 1981) and pyrophyllite (Sánchez-Soto and Pérez-Rodríguez, 1989). It can be supposed that prototropy effects also proceed within a biotite crystal during grinding in this study. If proton transfer does occur, a Fe (II) ion possibly reduces the proton to form a H atom. Since the FeO content of biotite is 19.26% as given in the experimental section, the molar quantity of Fe (II) corresponds to 7.9×10^{-3} mol for 3 g sample, which is sufficiently large (about two orders) to produce the observed H₂. However, Kameda *et al.* (2003) observed that muscovite with the about 1/6 smaller content of Fe (II) than biotite (unpublished data) also exhibits the higher H₂ productivity ($0.022 \mu\text{mol}/\text{m}^2$). This inconsistency between the Fe (II) content and the amount of generated H₂ may suggest that not all H• radicals are produced by proton reduction. This leads us to the postulation of another possible mechanism or the direct interaction between Si• and Al-OH in the octahedral layer of biotite within the crystal as below.



This reaction seems to be reasonable because it can explain

the high hydrogen productivity of muscovite, although further studies should be performed to validate this model. In any cases, it is postulated that the mechanochemical treatment of biotite causes the destruction of a crystal structure to lead to the reaction of the hydroxyls successively producing a H atom to form hydrogen.

4. Conclusions

Pure biotite powders were ground within H₂O or D₂O as a liquid media. The H₂ productivity of biotite obtained in the present experiments agrees with that of the previous study in spite of the difference in the grinding conditions. D₂ analyses revealed that more than 90% of hydrogen was composed of HD and H₂, suggesting that the hydroxyls in a layer are a major source for the generation of hydrogen during the mechanochemical treatment of biotite. Furthermore, it can be pointed out that the present results are principal for studying the stable isotopic analyses of H₂ along active faults to discuss the reaction temperature or the origin of H₂ in a future work.

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