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Generation of oxidising fluids by comminution of fault rocks

J. Kameda^{1*}, A. Okamoto²

Abstract





Mechanochemical reactions exert a crucial control on the chemical environments of crustal fault zones during co-seismic and post-seismic periods. Comminution due to faulting causes activation of fault rock surfaces, such as the production of reactive radical species. In this study, we report on the generation of H_2O_2 by immersion of comminuted sedimentary, igneous, and metamorphic rocks that are broadly representative of those present at a variety of depths in subduction zones. Our experiments demonstrate that fresh surfaces of these rocks have an H_2O_2 productivity of 1.3–10.4 nmol m⁻² (mean = 5.4 nmol m⁻²). In a natural fault zone environment, H_2O_2 produced after a slip event is likely to react with Fe-bearing mineral surfaces or Fe²⁺ in

porewater, or thermally decompose to produce more oxidative ·OH. The oxidising fluid produced by fault rupture in one patch may spread and induce corrosion and degradation of surrounding fault zones. These chemical processes are likely to be important factors influencing the interaction between neighbouring seismic activities.

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Introduction

Frictional slip on a fault zone causes comminution and wearing of fault rocks, producing highly reactive fine particles (Sammis et al., 1986; Scholz, 2002). Radical species such as Si- and SiO- are commonly created on such particles of silicate minerals owing to homolytic rupture of Si-O covalent bonds (Hochstrasser and Antonini, 1972; Narayanasamy and Kubicki, 2005). Hydrogen (H₂) is a typical product that is generated by reaction between Si and water molecules within a fault zone. The production of H₂ by the interaction of fluids and comminuted rocks has been demonstrated by laboratory experiments (Kita et al., 1982; Kameda et al., 2003; Hirose et al., 2011) and that associated with seismic activity has been observed by field survey (Wakita et al., 1980; Ito et al., 1999). In addition, numerous studies have demonstrated that pulverisation of pure powders of minerals forming igneous rocks can produce oxidising compounds such as hydrogen peroxide (H₂O₂), superoxide (O₂ \cdot ⁻), and hydroxy (·OH) radicals (Schoonen et al., 2006; Hurowitz et al., 2007; Hendrix et al., 2019), which are termed "reactive oxygen species" or "ROS". ROS are formed by human activities such as mining, which produces fine particles of rocks and minerals (Schoonen et al., 2006). ROS are also formed due to reaction with reactive secondary minerals and photochemistry in soils and sediments (e.g., Georgiou et al., 2015). Because fault activity causes comminution of fault rocks, it can be assumed that ROS are also produced within fault zones. Moreover, such ROS may modify the chemical and even physical state of the fault zone. For example, some lithologies such as shales have been shown to undergo a variety of degradation on interaction with H₂O₂ (formation of cracks and voids, decomposition and dissolution of constituent materials, etc.), which results in modification of their hydromechanical properties at varying rates depending on temperature (Chen *et al.*, 2017; Zhou *et al.*, 2018; Yu *et al.*, 2019). Thus, the production and diffusion of oxidising compounds by a seismic event can potentially degrade surrounding fault zones and stimulate subsequent fault activity.

In this study, we examine the production of H_2O_2 by reaction between water and ground rock samples at ambient conditions. The samples are sedimentary, metamorphic, and igneous rocks that may constitute plate boundaries at various depths in subduction zones (Hacker *et al.*, 2003; Kimura *et al.*, 2012; Kameda *et al.*, 2017). Our results show that oxidising fluid can be easily produced throughout the plate boundary zone after an earthquake. On the basis of our findings, we discuss the importance of the chemical aspects of fluids on fault behaviours.

Samples and Experimental Methods

We analysed five natural rock samples: shale and oceanic basalt from the Cretaceous accretionary complex (Shimanto belt, Japan), and three basic schist samples from the high pressure Sanbagawa metamorphic belt, Japan. The basic schist samples (basic schist 1, basic schist 2, and basic schist 3) were taken from the chlorite, garnet, and albite–biotite zones of the Sanbagawa belt, respectively, which correspond to pressure-temperature (*P*-*T*) conditions ranging from greenschist to epidote-amphibo-lite facies (~300 to ~550 °C; Enami *et al.*, 1994). For comparison, quartz sand (Wako Purer Chemicals) was also used for the experiments.

Whole rock major element concentrations of the rock samples were determined by an X-ray fluorescence spectrometer (XRF; Rigaku 25X Primus IV) using the conventional glass bead method. The Fe²⁺/ Σ Fe ratios were determined by wet chemical

^{1.} Department of Earth and Planetary Sciences, Faculty of Science, Hokkaido University, N10 W8, Sapporo, 060-0810, Japan

^{2.} Graduate School of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan

^{*} Corresponding author (email: kameda@sci.hokudai.ac.jp)

analyses. Mineral compositions were analysed by X-ray diffraction analysis (XRD; MAC Science MX-Labo), and the obtained XRD patterns were used for quantitative analysis by RockJock software (Eberl, 2003).

The grinding experiments were carried out by using a planetary-type ball mill apparatus (P6; Fritsch). An amount of 3 g of each powder was loaded into a zirconia mill pot and was processed at 250-300 rpm for 5 min. The freshly ground powders with the post-grinding grain size of ~0.5 µm (estimated from the surface area data described below, assuming uniform spherical particles) were then mixed with pure water (Direct-Q 3UV, Merck; pH = 5.84) in a Teflon beaker at room temperature (~22 °C), and settled for 10-20 min. The H₂O₂ concentrations of the filtered solutions were then measured with the Scopoletin-Horseradish peroxidase (HRP) Fluorometric method using a fluorometer (RF-5300PC; Shimazu). The postexperiment pH of the solutions was also measured. The specific surface areas of the processed powders were measured by the Brunauer-Emmett-Teller (BET) method using an automated sorption analyser (Autosorb, Quantachrome Instruments). More details on the samples and experimental methods are described in the Supplementary Information.

Results

Our experiments demonstrated that all of the studied samples were able to produce H₂O₂ by mechanical activation and subsequent immersion in water. Figure 1 shows the H₂O₂ productivity of each sample (nmol m^{-2}), which is calculated from the H₂O₂ concentration of the reacting fluid (the background H_2O_2 concentration of 0.060 µmol L^{-1} was subtracted from the measured concentration) normalised to the total surface area of the ground powders, as well as pH of the reacted solution and Fe²⁺ content in the solid samples (Tables S-1, S-2). The two analysed quartz samples have values of 0.55 and 0.44 nmol m^{-2} , which are slightly higher than previous results (0.2–0.3 nmol m^{-2} ; Hurowitz et al., 2007). Factors such as different temperatures, pH of the matrix, reaction time, hydration state of the samples, etc. could explain the differences. The H2O2 productivities of the natural rock samples are generally one order of magnitude greater than those of quartz, ranging from 1.3 nmol m^{-2} (shale) to 10.4 nmol m⁻² (basic schist 3) with a mean value of ~5.4 nmol m⁻².



Figure 1 H_2O_2 productivity of the analysed samples. Error bars for H_2O_2 productivity were estimated from the equation for the standard addition method (Larsen *et al.*, 1973). The pH of the solution after the experiment (during the duplicate analyses) and the concentration of FeO in the rock samples are also shown.

No obvious correlation was found between the H_2O_2 productivities and pH or Fe²⁺ content.

Discussion

Although the actual mechanism of H_2O_2 production from pulverised mineral surfaces is not completely understood, Hendrix *et al.* (2019) argued that Si–O· on a newly created mineral surface reacts with H_2O to generate H_2O_2 as follows:

$$2 \equiv Si - O \cdot + 2H_2O \rightarrow 2 \equiv Si - OH \cdot + H_2O_2 \qquad \text{Eq. 1}$$

Hurowitz et al. (2007) conducted pulverisation experiments using various pure mineral types and found that H₂O₂ productivity depends on the crystallographic nature of silicate minerals, with productivity increasing with a decreasing number of corners shared between Si (Al) tetrahedra (here termed the "c" number; Fig. 2). For example, tectosilicate minerals such as guartz and plagioclase have c = 4 and show the lowest H₂O₂ productivity of <1.0 nmol m⁻² of other types of silicate minerals with *c* < 4 (Hurowitz *et al.,* 2007; Fig. 2). As the present work used rock samples that included different types of silicate minerals, the weighted mean of c of each sample was estimated by XRD analysis (Table S-3). Figure 2 presents the relationship between H_2O_2 productivity and *c* of the analysed rock samples, and shows that the data are broadly consistent with the results of Hurowitz et al. (2007). Our results reveal that H_2O_2 can be generated by activation of natural rocks irrespective of their type (i.e. sedimentary, metamorphic, and igneous rocks), and the amount generated is likely to depend on the mineral composition of the rock.

Stability of H_2O_2 in fault zones following slip. Since fault movement causes comminution of fault rocks, H_2O_2 is expected to be produced by the reaction with porewater after an earthquake event. Furthermore, larger slip events may also lead to greater amount of comminution (Scholz, 2002; Hirose *et al.*, 2012), which would produce more H_2O_2 . In a natural fault zone environment, generated H_2O_2 reacts with Fe-bearing mineral surfaces or Fe²⁺ in porewater to produce more oxidative \cdot OH, as follows (*i.e.* the Fenton reaction):

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \qquad \text{Eq. 2}$$



Figure 2 H_2O_2 productivity vs. number of corners shared between silica tetrahedra (weighted mean) for the analysed rocks. The open symbol is data for the experiment using 0.01 M NaCl solution. Data and regression line from Hurowitz *et al.* (2007) are also shown.

In addition, H_2O_2 decomposes to two ·OH at high temperature conditions. The rate coefficient of the decomposition reaction is described as $k = 6.4 \times 10^5 \exp(-71 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ (Takagi and Ishigure, 1985). This suggests that the half-life of H_2O_2 (*i.e.* $\ln(2)/k$) is 158 min at 100 °C but is only ~1 min at 200 °C. In the supercritical condition (T > 374 °C), the activation energy of the decomposition reaction can be higher (182 kJ mol⁻¹; Croiset *et al.*, 2004), but the half-life is again very short (*e.g.*, several seconds at 400 °C). Thus, it is presumed that H_2O_2 quickly decomposes to ·OH after an earthquake, and fluid containing these oxidative compounds may diffuse along the fault zone.

Influence of oxidising fluid generation on surrounding fault zones. In general, an earthquake does not occur in isolation but occurs as part of a sequence controlled by physical processes such as stress perturbation (Scholz, 2002). Porewater diffusion is usually invoked as a reason for aftershock sequence (e.g., Nur and Booker, 1972), but only the physical aspect of water (i.e. fluid pressure) has been argued in these models. Our study indicates the importance of chemical interaction between the fluid and surrounding fault zones. Specifically, generation of highly oxidising fluid can potentially promote corrosion of nearby fault zones and stimulate further fault activity. Such oxidising fluid is thought to interact with Fe-bearing minerals as well as organic compounds (Chen et al., 2017; Zhou et al., 2018). OH oxidises even graphite (Wang and Zhang, 2018), a common product of the thermal maturation of organic compounds in metamorphic rocks, and may therefore degrade fault zones containing such minerals and materials. In natural examples, degradation or consumption of graphite has been observed in some fault zones (Nishiyama et al., 1990; Kretz, 1996; Nakamura et al., 2015), and the involvement of oxidising fluids in these processes has been suggested (Nishiyama, 1990; Okamoto et al., 2021). In addition to mechanical processes, oxidative corrosion could promote such graphite degradation. However, it has not been fully clarified how the redox state of a fault temporally and spatially changes during the seismic cycle. For a more quantitative consideration, the kinetics of the reaction between oxidising fluid and various types of fault rocks and the lifetime of oxidising state of the fluid need to be clarified in future work, as well as how such fluid can affect the shear strength and frictional properties of the rock.

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Additional Information

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Supplementary Information

The Supplementary Information includes:

- Materials and Methods
- ➤ Tables S-1 to S-3
- ➢ Figure S-1
- Supplementary Information References

Materials and Methods

Samples

We analysed five natural rock samples collected from an ancient plate subduction boundary (Table S-1): two samples from the Cretaceous accretionary complex in the Shimanto belt, southwestern Japan (shale and oceanic basalt); and three metabasic rock samples from the high-pressure Sanbagawa metamorphic belt, southwestern Japan. The shale and basalt from the Shimanto belt were taken from ancient plate boundary fault rock (tectonic mélange) within the seismogenic subduction zone (Kimura *et al.*, 2012; Kameda *et al.*, 2017). The basic schist samples (basic schist 1, basic schist 2, and basic schist 3) were taken from the chlorite, garnet, and albite–biotite zones, respectively, which correspond to pressure-temperature (*P-T*) conditions ranging from greenschist to epidote-amphibolite facies (Enami *et al.*, 1994). The paleo-temperatures of the samples range from ~150 to ~550 °C (Enami *et al.*, 1994). For comparison, quartz sand (Wako Purer Chemicals; grain diameter is ~1 mm) was also used for the experiments. The natural rock samples were gently crushed and sieved to a particle size range of 1.4–8.0 mm before conducting the experiments.



Experimental methods

The grinding experiments were carried out by using a planetary-type ball mill apparatus (P6, Fritsch). An amount of 3 g of each powder was loaded into a zirconia mill pot and was processed at 250–300 rpm for 5 min. The freshly ground 0.2 or 0.3 g powders were then mixed with 10 mL of pure water (Direct-Q 3UV, Merck; pH = 5.84) in a screw-top Teflon beaker, and settled for 10–20 min. The reacted solution was filtered to separate it from solid phases by using a 0.45 μ m filter attached to a syringe tip.

The H₂O₂ concentrations of the filtered solutions were measured with the Scopoletin–Horseradish peroxidase (HRP) Fluorometric method using a fluorometer (RF-5300PC, Shimazu) at excitation and emission wavelengths of 380 nm and 460 nm, respectively. Scopoletin (Wako Purer Chemicals) and HRP (Type II, 181 p.u. mg⁻¹; Sigma Aldrich) were used as received. Analytical procedures followed those described by Hurowitz et al. (2007). We also applied the standard addition method with 1 mmol L⁻¹ of H₂O₂ spike, whose concentration was adjusted by measuring the H₂O₂ concentration of stock solution by spectrophotometry (V-650, JASCO). The background H₂O₂ concentration of the pure water was determined to be 0.060 µmol L⁻¹ by the above method. The measurement error *Sz* for the standard addition method was estimated using the equation described in Larsen *et al.* (1973): $Sz = \pm \frac{Sr}{M}\sqrt{A+B}$, where A = (n+1)/n (*n*)

= 3 for this study),
$$S_r = \pm \sqrt{\sum(Y_0 - \bar{Y})^2 / (n-2)}$$
, $B = (Z - \bar{X})^2 / \sum (Z - \bar{X})^2 = D(Y_0 - \bar{Y})^2 / M^2$, and

Z = -I/M. \overline{Y} is the mean of the Y readings (apparatus response); Y_0 and I are the intercepts of the fitted line

for three data points to the abscissa and the ordinate axis, respectively, from each analysis; and M is the slope of the fitted line.

The specific surface areas of the processed powders were measured using an automated sorption analyser (Autosorb, Quantachrome Instruments). Prior to measurement, the ground powder separated from the solution was dried and degassed at 120 °C for 1 h. Nitrogen adsorption assessed at 77 K provided isotherms for Brunauer–Emmett–Teller (BET) analysis.

Whole-rock major element concentrations and gravimetric loss on ignition (LOI at 950 °C for two hours) were determined by an X-ray fluorescence spectrometer (XRF; Rigaku 25X Primus IV) using the conventional glass bead method at Tohoku University. Wet chemical analyses for determination of the Fe²⁺/ Σ Fe ratios were performed by the chemical laboratory of Palynosurvey Co.

The XRD patterns were obtained using a MAC Science MX-Labo with monochromatised Cu K α radiation at 40 kV and 30 mA, with 1° divergence and antiscattering slits, and a 0.15 mm receiving slit in continuous scan mode at a rate of 1° 2 θ min⁻¹. The powders, mixed with an internal standard (corundum, AX-5H,



Hinomoto Kenmazai Co.) at a weight ratio of 4:1, were mounted by side-loading to minimise the development of a preferred alignment of clay minerals. XRD patterns were quantitatively analysed using RockJock software (Eberl, 2003).



Supplementary Tables

	Qtz1	Qtz2	Basalt	Basalt- a	Shale	Shale- a	Basic schist 1	Basic schist 1-a	Basic schist 2	Basic schist 2-a	Basic schist 2-b	Basic schist 3	Basic schist 3-a
Powder weight (g)	4	4	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Solution volume (mL)	8	8	10	10	10	10	10	10	10	10	^b 10	10	10
Concentration (μmol L ⁻¹)	0.08	0.06	0.94	0.72	1.30	0.72	0.48	0.46	0.64	0.72	0.66	0.74	0.51
Specific surface area (m ² g ⁻¹)	0.46	0.46	9.01		17.76		6.19		4.47		3.56		
H2O2 productivity	0.55	0 44	5.23	3 99	2 4 4	1 35	3.86	3 70	7 1 7	8.04	7 37	1040	7 51
(nmol m ⁻²)	0.55	0.11	5.25	0.77	2.11	1.55	5.00	5.70	/.1/	0.01	7.07	10.10	7.51
error	0.046	0.014	0.094	0.179	0.064	0.035	0.193	0.286	0.072	0.181	0.000	0.522	0.229
pН	-	-		10.04		8.71		8.76		9.92	9.72		9.52
^a Temp. (°C)	-	-	130-190		175-200		300-360		420-500			500-550	

Table S-1 H_2O_2 production from surfaces of comminuted samples.

^a Palaeotemperature data are from Enami *et al.* (1994), Ohmori *et al.* (1997), and Kameda *et al.* (2017). ^b 0.01 M NaCl solution.

	Basalt	Shale	Basic schist 1	Basic schist 2	Basic schist 3
SiO ₂	49.86	59.12	51.15	41.76	42.69
TiO ₂	1.63	0.76	1.42	0.89	2.99
Al ₂ O ₃	15.07	18.90	14.45	17.70	13.19
Fe ₂ O ₃	9.45	6.45	12.88	9.74	17.64
^a FeO	5.50	4.15	6.63	2.73	8.16
MnO	0.19	0.08	0.21	0.15	0.28
MgO	8.46	2.86	6.73	4.03	6.31
CaO	8.51	0.50	8.25	14.94	6.01
Na ₂ O	3.85	1.23	1.93	1.93	1.72
K ₂ O	0.75	4.49	0.43	1.61	2.01
P2O5	0.15	0.12	0.12	0.11	0.36
LOI	4.37	5.57	3.77	8.11	3.20
Total	102.29	100.08	101.35	100.97	96.40

^a Data from wet chemical analyses.

	Qtz1	Qtz2	^b Basalt	Shale	Basic schist 1	Basic schist 2	Basic schist 3
Quartz (4) ^a	100.0	100.0	0.0	21.7	10.5	15.0	8.3
Plagioclase (4)	0.0	0.0	45.1	11.4	29.8	21.5	13.0
Chlorite (3)	0.0	0.0	23.9	18.3	37.5	34.0	19.5
Mica (3)	0.0	0.0	0.0	48.6	3.6	0.0	17.7
Amphibole (2.5)	0.0	0.0	0.0	0.0	5.1	13.4	33.9
Epidote (1.66)	0.0	0.0	0.0	0.0	11.5	14.6	5.6
Pyroxene (2)	0.0	0.0	24.1	0.0	0.0	0.0	0.0
Non- silicates	0.0	0.0	6.9	0.0	2.0	1.5	1.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Weighted mean of <i>c</i>	4.0	4.0	3.0	3.3	3.2	3.1	2.9

Table S-3Whole-rock chemical compositions.

^a Number in parenthesis is the *c* number of each mineral.

^b Data on mineral composition are from Kameda *et al.* (2017).





Supplementary Figure

Figure S-1 Results of measurements using the standard addition method. Horizontal and vertical axes are H_2O_2 concentration (µmol L⁻¹) and instrumental response, respectively.



Supplementary Information References

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