



# Oxidation of water to hydrogen peroxide at the rock–water interface due to stress-activated electric currents in rocks

Melike Balk<sup>a,1</sup>, Milton Bose<sup>b,2</sup>, Gözen Ertem<sup>c,3</sup>, Dana A. Rogoff<sup>d</sup>,  
Lynn J. Rothschild<sup>a</sup>, Friedemann T. Freund<sup>a,b,d,\*</sup>

<sup>a</sup> NASA Ames Research Center, Code SGE, Moffett Field, CA 94035, USA

<sup>b</sup> Department of Physics, San Jose State University, San Jose, CA 95192-0106, USA

<sup>c</sup> NASA Ames Research Center, Code SSX, Moffett Field, CA 94035, USA

<sup>d</sup> Carl Sagan Center, SETI Institute, 515 N Whisman Rd., Mountain View, CA 94043, USA

## ARTICLE INFO

### Article history:

Received 11 September 2008

Received in revised form 21 March 2009

Accepted 31 March 2009

Available online 6 May 2009

Editor: R.W. Carlson

### Keywords:

hydrogen peroxide

rock–water interface

electric currents

rock battery

oxidation

early Earth

early life

## ABSTRACT

Common igneous and high-grade metamorphic rocks contain dormant defects, which release electronic charge carriers when stressed. Rocks thereby behave like a battery. The charge carriers of interest are defect electrons  $h^{\cdot}$ , e.g. electronic states associated with  $O^{-}$  in a matrix of  $O^{2-}$ . Known as “positive holes” or pholes for short, the  $h^{\cdot}$  travel along stress gradients over distances on the order of meters in the laboratory and kilometers in the field. At rock–water interfaces the  $h^{\cdot}$  turn into  $\cdot O$  radicals, e.g. highly reactive oxygen species, which oxidize  $H_2O$  to  $H_2O_2$ . For every two  $h^{\cdot}$  charge carriers one  $H_2O_2$  molecule is formed. In the laboratory the battery circuit is closed by running a Cu wire from the stressed to the unstressed rock. In the field closure of the circuit may be provided through the electrolytical conductivity of water. The discovery of  $h^{\cdot}$  charge carriers, their stress-activation, and their effect on Earth’s surface environment may help better understand the oxidation of the early Earth and the evolution of early life.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Though most oxygen anions in oxide/silicate minerals occur in their common  $2-$  valence state, some can exist in the more oxidized valence  $1-$ , as  $O^{-}$ . In this paper we present evidence that oxygen anions in the valence state  $1-$  in minerals, which make up the bulk of igneous and high-grade metamorphic rocks, give rise to some unexpected phenomena. The  $O^{-}$  are normally dormant, forming inconspicuous and electrically inactive point defects. However, they can be “awakened” when rocks are subjected to mechanical stress. Once activated, the electronic state associated with  $O^{-}$  can produce an electric current, which was previously unknown.

First we discuss how  $O^{-}$  are introduced into the mineral matrix, why they exist in a dormant form, and how they are become activated when mechanical stresses are applied. Second, we demonstrate that stress-activated electronic charge carriers can flow out of the stressed rock volume and propagate through unstressed rock. When they cross a rock–water interface, they oxidize  $H_2O$  to  $H_2O_2$ .

### 1.1. Dormant electronic charge carriers

It has been shown some time ago that hydroxyl pairs in MgO, introduced into the MgO matrix during crystallization from an  $H_2O$ -laden melt or recrystallization in an  $H_2O$ -laden environment, undergo a previously unknown redox reaction: they split off  $H_2$  and form peroxy anions,  $O_2^{2-}$  (Martens et al., 1976; Freund and Wengeler, 1982):



where  $\oplus$  stands for an  $Mg^{2+}$  vacancy site. In the peroxy anion,  $O_2^{2-}$ , the two  $O^{-}$  are tightly bonded together, forming a self-trapped, localized, electrically inactive point defect.

Evidence suggests that the same type of redox reaction also occurs in fused silica, where  $O_3SiOH$  pairs are converted into  $H_2$  plus peroxy links  $O_3Si-OO-SiO_3$  (Freund and Masuda, 1991; Ricci et al., 2001).

\* Corresponding author. Carl Sagan Center, SETI Institute, 515 N Whisman Rd., Mountain View, CA 94043, USA. Tel.: +1 650 810 0218; fax: +1 650 961 7099.

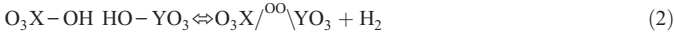
E-mail addresses: [M.Balk@nioo.knaw.nl](mailto:M.Balk@nioo.knaw.nl) (M. Balk), [milton.bose@gmail.com](mailto:milton.bose@gmail.com) (M. Bose), [gozen1ertem@gmail.com](mailto:gozen1ertem@gmail.com) (G. Ertem), [drogoff@mail.arc.nasa.gov](mailto:drogoff@mail.arc.nasa.gov) (D.A. Rogoff), [Lynn.J.Rothschild@nasa.gov](mailto:Lynn.J.Rothschild@nasa.gov) (L.J. Rothschild), [friedemann.t.freund@nasa.gov](mailto:friedemann.t.freund@nasa.gov) (F.T. Freund).

<sup>1</sup> Present address: NIOO-KNAW Centre for Limnology, Rijksstraatweg 6, 3631 AC Nieuwersluis, The Netherlands.

<sup>2</sup> Present address: Department of Physics and Astronomy, University of California, Riverside, CA 92521, USA.

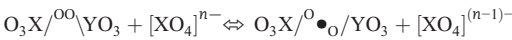
<sup>3</sup> Present address: Karlsruhe Forschungszentrum, Weberstr. 5 D-76133 Karlsruhe, Germany.

Likewise nominally anhydrous silicate minerals (Freund, 1987, 2003) are known to always dissolve small amounts of H<sub>2</sub>O when crystallizing in H<sub>2</sub>O-laden magmas or H<sub>2</sub>O-laden high temperature environments (Wilkins and Sabine, 1973; Rossman, 1996; Koga et al., 2003). The solute H<sub>2</sub>O occurs in the form of O<sub>3</sub>(X,Y)OH, where X, Y = Si<sup>4+</sup>, Al<sup>3+</sup> etc. Hydroxyl pairs are probably the most abundant, but they seem to undergo the same redox conversion, splitting off H<sub>2</sub> and forming peroxy links (Freund, 2003):



Because crustal rocks consist mostly of nominally anhydrous minerals, which invariably contain small amounts of dissolved H<sub>2</sub>O, peroxy links may be very ubiquitous.

From a semiconductor viewpoint, an O<sup>-</sup> in a matrix of O<sup>2-</sup> represents a defect electron or hole, also known as positive hole (Griscom, 1990) or phole for short, symbolized by h<sup>•</sup>. Accordingly, a peroxy link represents a positive hole pair, PHP (Freund et al., 2006), in which two O<sup>-</sup> are self-trapped, immobilized and, hence, electrically inactive. PHPs break apart when rocks are subjected to deviatoric stresses, e.g. to stresses that exceed the elastic limit causing dislocations to be mobilized and new dislocations to be generated (Freund et al., 2006; Takeuchi et al., 2006). As dislocations move through the mineral grains, they intersect a PHP causing the peroxy bond to break:



Eq. (3) describes a process, by which an electron e' is transferred from a neighboring O<sup>2-</sup> anion (here represented by [XO<sub>4</sub>]<sup>n-</sup>) onto the broken peroxy bond, which captures the electron e'. The donor O<sup>2-</sup> turns into O<sup>-</sup> (here [XO<sub>4</sub>]<sup>(n-1)-</sup>), e.g. a defect electron or phole h<sup>•</sup>. In other words, Eq. (3) describes the generation of an electron–hole pair.

In semiconductors like silicon electron–hole pairs recombine very rapidly, often within nanoseconds (Sze, 1981; Van Zeghbroeck, 1997). In the case of the e'–h<sup>•</sup> pairs generated by the break-up of peroxy links in silicate matrices, the broken peroxy bond that has captured electron appears to relax in such a way as to delay recombination. Thus, e'–h<sup>•</sup> pairs formed in silicates and, hence, in rocks are long-lived (Freund et al., 2006; Freund and Sornette, 2007).

### 1.2. Electric currents flowing through rocks

The h<sup>•</sup> charge carriers in the silicates are associated with O 2sp energy levels at the upper edge of their valence bands (Canney et al., 1999). When mineral grains are in physical contact, the valence bands are electrically connected. Though their energies will shift from grain to grain, all valence bands form an energy continuum along which h<sup>•</sup> charge carriers can propagate. The mode of propagation probably involves a phonon-assisted electron transfer, whereby h<sup>•</sup> hop from O<sup>2-</sup>

to O<sup>2-</sup>, maximally at the frequency of thermally activated lattice phonons, ~10<sup>12</sup> Hz (Shluger et al., 1992). The O<sup>-</sup> turn insulating silicate minerals into p-type semiconductors. From a chemistry perspective, an O<sup>-</sup> is a highly oxidizing •O radical.

Hurovitz et al. described experiments, where freshly ground basaltic minerals immersed in aqueous solution produced detectable amounts of H<sub>2</sub>O<sub>2</sub> (Hurovitz et al., 2007). The H<sub>2</sub>O<sub>2</sub> production is thought to occur when water reacts with unspecified defects formed at the mineral surfaces during crushing. Possibly h<sup>•</sup> charge carriers, activated by the high mechanical stresses levels during crushing, contribute to the oxidizing properties of freshly crushed rock surfaces.

In the experiments as described here, where only a subvolume of a large piece of rock is subjected to increased levels of mechanical stress, h<sup>•</sup> charge carriers flow from the stressed into the unstressed rock volume. The stressed rock volume acts as the anode in a battery from where an electric current flows out (Freund et al., 2006). The unstressed rock acts as the electrolyte, through which the h<sup>•</sup> flow to reach the Cu contact at the unstressed end of the rock as depicted in Fig. 1a. This Cu contact acts as the cathode.

The electrons e', co-activated according to Eq. (3), cannot spread from the stressed rock into the unstressed rock. However, they can pass from the stressed rock into a metal contact, in our case the steel pistons, and then proceed through a Cu wire to reach the same Cu contact attached to the far end of the unstressed rock. The Cu wire thereby closes the battery circuit. At the interface between the Cu contact and the unstressed rock the e' "shake hands" with h<sup>•</sup> and recombine. Knowing that h<sup>•</sup> = O<sup>-</sup>, we can write:



In the course of this study we addressed three questions:

- Can the h<sup>•</sup> charge carriers flow not only through solid rock as depicted in Fig. 1a but also through water as depicted in Fig. 1b?
- What happens at the rock–water interface?
- How can the rock battery circuit be closed, if no wire is available to connect the stressed rock volume with the unstressed rock volume?

## 2. Experimental

We used a gabbro from Shanxi, China, ~40 modal% plagioclase, 30% augitic clinopyroxene with alteration rims to amphibole and chlorite, plus 25% opaques, a porosity of about 0.3%, and less than 1% total water mostly due to hydroxyl-bearing minerals such as amphiboles (Parkhomenko, 1967).

Fig. 2 depicts a block of this gabbro, 60 × 7.5 × 7.5 cm<sup>3</sup>, loaded at the center through two rectangular steel pistons with a contact area of 5 × 10 cm<sup>2</sup> covered by Cu tape with graphite-based conductive adhesive (3M). Two water pools 1 and 2 in Plexiglas frames, 5 × 5 × 0.6 cm<sup>3</sup>, symmetrically placed close to the unstressed ends of

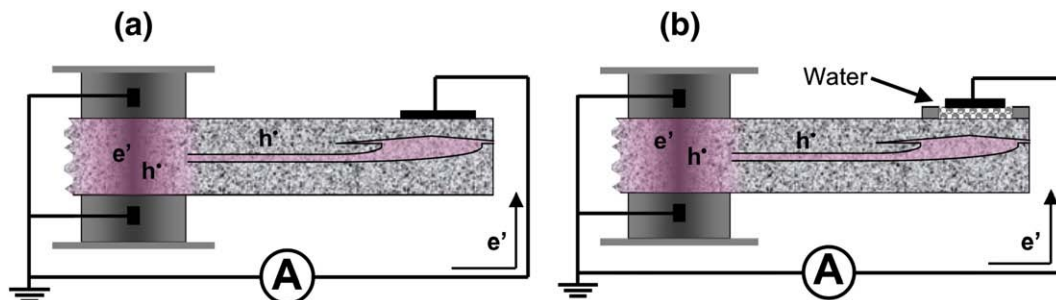
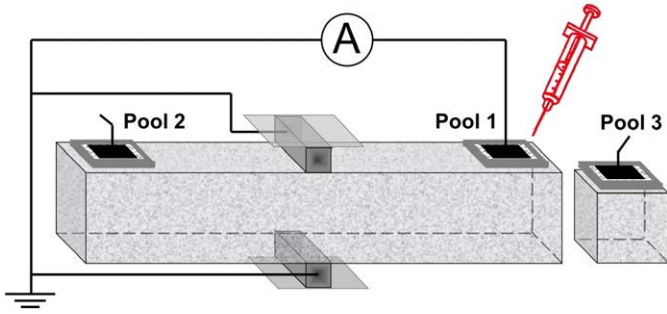


Fig. 1. a: Electric circuit to demonstrate the flow of stress-activated h<sup>•</sup> charge carriers through a slab of rock, forming the "rock battery"; b: circuit to demonstrate that the electric current, transported through the rock by h<sup>•</sup> charge carriers, also flows through water.



**Fig. 2.** Experimental set-up to test the flow of current carried by stress-activated  $h^+$  through water. Gabbro slab,  $7.5 \times 7.5 \times 60 \text{ cm}^3$ , loaded at the center by two steel pistons, electrically insulated from the press with sheets of polyethylene, resistance  $>10^{14} \Omega$ . Two water pools  $5 \times 5 \text{ cm}^2$ , cut out of Plexiglas, each with a  $4 \times 4 \text{ cm}^2$  Cu electrode touching the water surface, Pool 1 and Pool 2, were set on the gabbro slab,  $\sim 20 \text{ cm}$  on either side of the pistons. An identical control Pool 3, also with a  $4 \times 4 \text{ cm}^2$  Cu electrode, was set on a separate piece of the same gabbro not to be stressed. All water pools were filled 6 mm deep with distilled water. Pool 1 was connected to the battery circuit, while Cu electrodes in Pools 2 and 3 were left unconnected.

the rock, as well as an identical Pool 3 on a separate block of gabbro, were filled with distilled water to a depth of 6 mm. All pools had Cu electrodes,  $4 \times 4 \text{ cm}^2$ , touching the water surface.

The rock was loaded using a manually operated hydraulic press. Immediately upon loading a battery current started to flow through the unstressed portion of the rock and through Pool 1. The current increased rapidly reaching a maximum of  $\sim 10 \text{ nA}$  at less than 20 MPa, corresponding to  $<10\%$  of the compressive strength of this rock. A current of  $\sim 10 \text{ nA}$  flowing through our rock sample translates into a current density on the order of  $5 \mu\text{A m}^2$ . The current passed through a maximum and then stabilized at a slightly lower level, around 7 nA, while the load was held constant at  $30 \pm 5 \text{ MPa}$ . After 24 h the current had decayed to  $\sim 4.5 \text{ nA}$ . The current flowing through the water of Pool 1 is of the same magnitude as currents flowing through Cu contacts of the same size attached directly to the dry rock surface (Freund et al., 2006). Pools 2 and 3 acted as references and were not connected to the battery circuit. None of the water pools were stirred.

$\text{H}_2\text{O}_2$  concentrations in Pools 1, 2 and 3 were measured in 50  $\mu\text{L}$  aliquots, taken with a plastic syringe, using the Amplex Ultra Red Hydrogen Peroxide Assay Kit from Molecular Probes Inc. (Catalog # A22188 and A36006). In the presence of horseradish peroxidase, the Amplex Red reagent (N-acetyl-3,7-dihydroxyphenoxazine) reacts with  $\text{H}_2\text{O}_2$  and probably other oxidizing species such as short-lived hydroxyl ( $\bullet\text{OH}$ ) and/or hydroperoxyl ( $\bullet\text{HO}_2$ ) radicals to produce a red-fluorescent oxidation product, resorufin. The intensity of the fluorescence was measured with a SpectraMax Gemini XS Scanning Fluorometer using the SoftMax Pro v. 5.0.1 program from Molecular Devices Corporation) and expressed at  $\text{H}_2\text{O}_2$ . To eliminate background  $\text{H}_2\text{O}_2$  in the deionized water to be used in the fluorometric analysis we treated the water overnight at room temperature with 1 mg/L catalase (1000 U, Aldrich-Sigma Chemical Inc.), then autoclaved it at  $121^\circ\text{C}$  to de-activate the enzyme. The catalase-treated water was used for  $\text{H}_2\text{O}_2$  standards and all analyses. Each fluorometric analysis was repeated four times.

Using Pool 3, we separately determined the rate at which  $\text{H}_2\text{O}_2$  decays as a function of time ( $t$ ) in contact with the rock surface; we started with a  $2 \mu\text{mol}$   $\text{H}_2\text{O}_2$  solution and measured the change in  $\text{H}_2\text{O}_2$  concentration over 22 h. Each  $\text{H}_2\text{O}_2$  analysis was repeated twice. We found the expected exponential  $\text{H}_2\text{O}_2$  decay  $F(t)$  with a time constant 0.179:

$$F(t) = 2.46e^{-0.179t} \quad (5)$$

### 3. Results

Fig. 3 plots the battery current  $I$  flowing into and through Pool 1 integrated over time. After 24 h, the total charge  $C$  passing through the rock–water interface was 0.5 mC,  $\approx 2 \times 10^{15} h^+$  charge carriers.  $C$  as a function of time ( $t$ ) is given by:

$$C(t) = \int_{t=0}^t I(t) dt. \quad (6)$$

When the  $h^+$  current flows into the water, interface reactions have to be considered. Being chemically equivalent to  $\text{O}^-$ , the  $h^+$  charge carriers are expected to act as  $\bullet\text{O}$  radicals at the rock–water interface. One possible reaction for the  $\bullet\text{O}$  radicals in the rock surface is to subtract H from the  $\text{H}_2\text{O}$  in the pool and to form  $\bullet\text{OH}$  radicals:



By binding the  $\text{OH}^-$  into the surface, excess  $\text{H}_3\text{O}^+$  will be left in the water to carry the current to the Cu electrode and discharge at the water–Cu interface:



Two  $\bullet\text{OH}$  radicals from Eq. (7) are expected to combine to hydrogen peroxide:



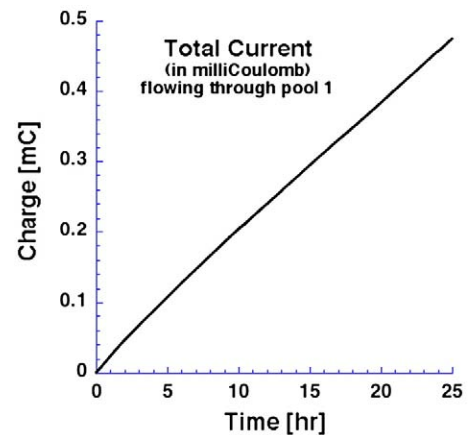
Eqs. (7) and (9) predict that two  $h^+$  charge carriers are needed to form one  $\text{H}_2\text{O}_2$  molecule at the rock–water interface. The total number of  $\text{H}_2\text{O}_2$  per mole,  $G(t)$ , is then given by:

$$G(t) = \frac{C(t)}{2eN_A} \quad (10)$$

where  $e$  is the electron charge and  $N_A$  Avogadro's number.

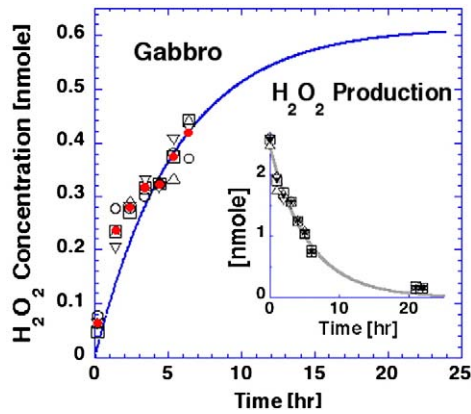
In the reference Pool 2 the  $\text{H}_2\text{O}_2$  concentration became barely detectable shortly after loading the rock, then decreased below the detection limit within 1–2 h. In Pool 3 the  $\text{H}_2\text{O}_2$  remained below the detection limit over the course of the 24 h long experiment.

The symbols in Fig. 4 give the  $\text{H}_2\text{O}_2$  concentrations as measured in Pool 1. The solid curve represents the expected  $\text{H}_2\text{O}_2$  concentrations obtained by using as input the  $\text{H}_2\text{O}_2$  generation function  $G(t)$  according to Eq. (10) and the empirical  $\text{H}_2\text{O}_2$  decay function according to Eq. (5), shown in the insert in Fig. 4. The  $\text{H}_2\text{O}_2$  decay gives an exponent of  $-0.179$ . The reported  $\text{H}_2\text{O}_2$  concentrations are corrected for the removal of the 50  $\mu\text{L}$  samples from the water pools.



**Fig. 3.** Total charge flowing out of the stressed rock at constant stress level, 30 MPa, through the unstressed rock and 6 mm of water to a  $4 \times 4 \text{ cm}^2$  Cu electrode in Pool 1.





**Fig. 4.**  $\text{H}_2\text{O}_2$  concentration in Pool 1 as a function of time. Bold curve: best fit to the experimental data assuming that two  $\text{h}^\bullet$  are needed to form one  $\text{H}_2\text{O}_2$  molecule according to Eqs. (6) and (8). Solid dots: averaged of 4 measurements. Insert:  $\text{H}_2\text{O}_2$  decay in contact with the rock surface in Pool 3.

The amount of  $\text{H}_2\text{O}_2$ ,  $M(t)$ , present at any time in Pool 1 is given by the sum of the  $\text{H}_2\text{O}_2$  generation according to Eq. (10) and the  $\text{H}_2\text{O}_2$  decay according to Eq. (5):

$$M(t) = \alpha G(t) + F(t) \quad (11)$$

where  $\alpha$  is an adjustable constant. Taking into account the 2:1 stoichiometry postulated in Eqs. (7) and (9) we find the numerical expression:

$$M(t) = 0.097te^{-0.177t} \quad (12)$$

which is plotted as the solid curve in Fig. 4.

The  $\text{H}_2\text{O}_2$  decay exponent obtained through the curve fit,  $-0.177$ , agrees well with the exponent  $-0.179$  obtained from the  $\text{H}_2\text{O}_2$  decay measured separately (see insert in Fig. 4). The agreement between the experimental data and calculated  $\text{H}_2\text{O}_2$  concentration is satisfactory, confirming the proposed stoichiometry for the formation of  $\text{H}_2\text{O}_2$ , one  $\text{H}_2\text{O}_2$  molecule formed for every two  $\text{h}^\bullet$  charge carriers crossing the rock–water interface.

#### 4. Discussion

Electric potentials and ground currents are common in nature. Self-potentials can be generated in conductive materials through transfer of charges. Known sources of self-potentials are streaming currents driven by the flow of water through porous rocks, thermo-electric currents associated with temperature gradients, and electro-chemical currents associated with a transfer of electrons during redox reactions or with the diffusion of ions (Cox and Singer, 1986; Bernabé,

1998; Revil and Linde, 2006; Revil, 2007; Crespy et al., 2008). Other mechanisms of generating self-potentials are provided by the piezo-electric effect (Tuck et al., 1977; Bishop, 1981; Lorne et al., 1999; Ogawa and Utada, 2000). In all these cases the currents are weak.

A fundamentally different process to generate electric currents in rocks has recently been described (Freund, 2002; Freund et al., 2006). It is based on the fact that pairs of oxygen anions, which changed their valence from  $2^-$  to  $1^-$ , ubiquitously occur in minerals that constitute the bulk of igneous and high-grade metamorphic silicate rocks. The  $\text{O}^-$  pairs, which are believed to form through a redox conversion as described by Eq. (2), represent point defects in the mineral structure, chemically equivalent to peroxy links  $\text{O}_3\text{Si}-\text{OO}-\text{SiO}_3$  in silica and silicates.

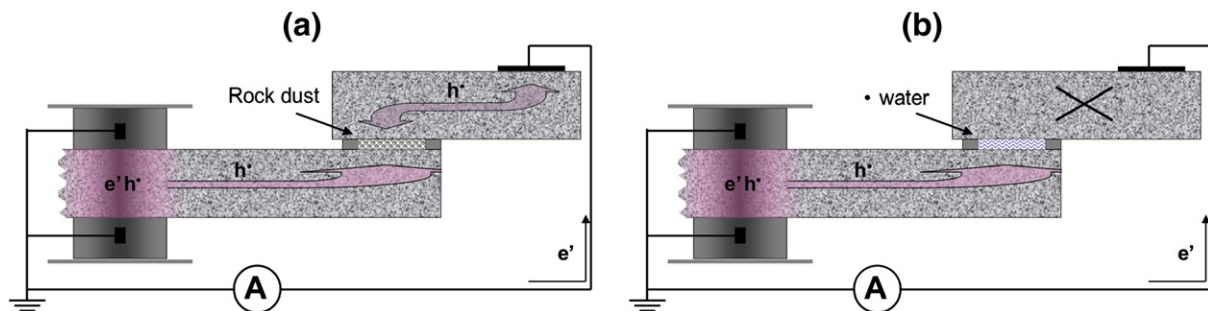
As long as the peroxy links are intact, they are electrically inactive. When stresses are applied beyond the elastic limit and dislocations move through the mineral grains, the  $\text{O}^- - \text{O}^-$  bonds break. In the process, two types of charge carriers are generated as indicated in Eq. (3), electrons  $\text{e}'$  and holes  $\text{h}^\bullet$ .

The electrons are trapped at the broken peroxy bond sites, while the  $\text{h}^\bullet$  are mobile. As outlined in the Introduction, the  $\text{h}^\bullet$  represent an electronic state associated with  $\text{O}^-$  in a matrix of  $\text{O}^{2-}$ . They are known as positive holes (Griscom, 1990) or pholes for short. Chemically they are highly oxidizing. Residing in O 2sp- symmetry energy levels at the upper edge of the valence band, the  $\text{h}^\bullet$  charge carriers can pass from  $\text{O}^{2-}$  to  $\text{O}^{2-}$ , presumably by a phonon-assisted electron hopping mechanism (Shluger et al., 1992). This is consistent with the speed with which a pulse carried by  $\text{h}^\bullet$  charge carriers can propagate through unstressed rock, on the order of 200 m/s (Freund, 2002).

While the electrons remain loosely attached to the broken peroxy links, the  $\text{h}^\bullet$  are highly mobile. They can cross grain boundaries using energy levels at the upper edge of the valence band and flow out of the stressed rock volume (Freund et al., 2006). Therefore, the stressed rock volume behaves as anode from where  $\text{h}^\bullet$  charge carriers flow out. In laboratory experiments the  $\text{h}^\bullet$  flow through meters of unstressed rock. In the field they can probably propagate over distances on the order of kilometers. The unstressed rock does not provide energy levels that the co-activated electrons could use to also flow out. They have to take a different path. In our laboratory experiment we provide a path for the electrons by running a Cu wire from the stressed rock to the unstressed rock.

The concentration of peroxy defects in typical rock-forming minerals and, hence, the number of  $\text{h}^\bullet$  charge carriers a given volume of rock, are still poorly known. If the average peroxy concentration in igneous and high-grade metamorphic rocks is 100 ppm (Batllo et al., 1990), every  $\text{km}^3$  could produce about  $10^{13} \text{ C km}^{-3}$ , equivalent to a battery current of about  $10^6 \text{ A}$  flowing for 6 months.

However, any battery can deliver a current only when the electric circuit is closed. When the effect was first demonstrated (Freund et al., 2006), closure of the electric circuit was provided by the Cu wire as depicted in Fig. 1a.



**Fig. 5.** a: Electric circuit to demonstrate that the “rock battery” works when a layer of rock dust is inserted into the current path between two blocks of rock, indicating that the  $\text{h}^\bullet$  charge carriers can flow through a layer of rock dust. b: When a layer of water is inserted into the current path, the flow of the current is interrupted, suggesting the water does not allow the  $\text{h}^\bullet$  charge carriers to pass through.

In nature the situation is different. Earth's crust is replete with tectonic stresses, which constantly deform rocks and cause dislocations to move (Reimold and Gibson, 2006). Hence,  $h^+$  charge carriers can be expected to be activated in many parts of the crust. They will be available to produce battery currents along stress gradients. However, closure of the battery circuit may not be readily achievable under conditions that prevail in the field. Obviously, there are no Cu wires to connect stressed and unstressed rock volumes.

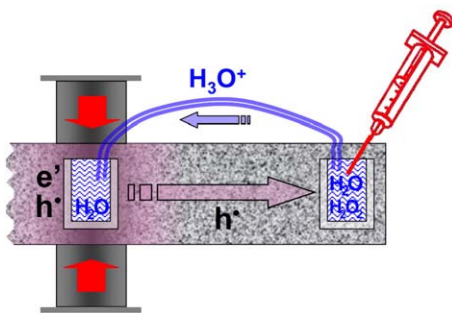
Here we describe an experiment where we inserted a water path into the electric circuit. We find that the water does not stop the current as shown in Fig. 1b. There are two possibilities: either (i) the  $h^+$  charge carriers travel through the water without being altered or (ii) the  $h^+$  charge carriers convert at the rock–water interface into other forms of charge carriers, which can travel through the water.

To learn more about the two possibilities we conducted the following tests. As depicted in Fig. 5a, we filled the Plexiglas frame with fine gabbro dust and weighed it down with a second piece of gabbro to which we had attached a Cu electrode. As indicated by the arrows, the current continued to flow indicating that the  $h^+$  charge carriers are capable of crossing through the dust layer from the first rock into the second rock. This is consistent with the notion that, because every grain–grain contact provides a contact between the valence bands, the  $h^+$  charge carriers can pass through. Next, as depicted by Fig. 5b, we filled the Plexiglas frame with water and repeated the test with the same second piece of gabbro. Under these circumstances no battery current was recorded, indicating that the  $h^+$  charge carriers were unable to pass through the water, at least not unchanged, and thus unavailable to reenter the second rock.

As Eq. (7) states, when  $h^+$  charge carriers arrive at the rock–water interface, they “reveal” their chemical nature as  $O^-$ , e.g. as highly oxidizing  $\bullet O$  radicals, capable of extracting an H from  $H_2O$ . The  $\bullet O$  in the rock surface thereby convert into  $OH^-$ , while one  $H_2O$  is oxidized to  $\bullet OH$ . Two  $\bullet OH$  combine to  $H_2O_2$  as indicated by Eq. (9) and confirmed by the data in Fig. 4. The current in the water continues to flow as an electrolytic current, carried by  $H_3O^+$ , and discharges at the Cu electrode immersed in the water as suggested by Eq. (8).

The result of this experiment is that water can close the battery circuit thanks to its own electrolytical conductivity. This allows us to design a “rock battery” without metal wires, where the outer circuit is provided by an electrolytically conductive water path. Such a situation would be able to close battery circuits in the field.

Fig. 6 shows the set-up. We used a slab of the same gabbro but attached two water reservoirs to its side, one to the portion to be stressed and one to the unstressed part. Both reservoirs were filled with distilled water and connected with a plastic capillary, 0.5 mm inner diameter, filled with dilute NaCl solution (simulated sea water). Instead of using an ammeter to measure the battery current we monitored the formation of  $H_2O_2$  in the water pool attached to the unstressed end of the rock.



**Fig. 6.** Demonstration of a rock battery without use of any metal parts where closure of the battery circuit is achieved through the electrolytical conductivity of a capillary filled with NaCl solution.

Upon loading and keeping the load constant at the 30 MPa level, 50  $\mu L$  aliquots for the  $H_2O_2$  analysis were extracted in 15 min intervals from the water pool attached to the unstressed rock. After about 1 h the  $H_2O_2$  concentration in this water pool began to rise, suggesting that the battery circuit had closed by drawing an electrolytical current through the capillary.

Battery currents flowing in the Earth's crust are probably linked to transient magnetic field changes that happen over time periods of hours, days, months or years. Such magnetic field variations have been reported in connection with the build-up of regional tectonic stresses prior to major earthquakes (Zeng et al., 2002). Battery currents may also be linked to transient changes in the electrical resistivity of the crust (Lu et al., 2004). Though changes in  $H_2O_2$  concentrations in springs in the Yellowstone National Park and other geothermally active regions are thought to indicate UV-driven reactions (Wilson et al., 2000), an electrochemical reaction as described here may also play a role in forming  $H_2O_2$  in natural environments where stresses would activate  $h^+$  charge carriers.

The  $H_2O_2$  production observed during immersion of freshly crushed basaltic rock into water (Hurowitz et al., 2007) may also involve  $h^+$  charge carriers that were activated by the very high mechanical stresses exerted during crushing. When trapped at the rock surface, these  $h^+$  will cause the grain surfaces to become highly oxidizing.

As additional sources of  $H_2O_2$  one has to also consider that, when  $H_2O_2$  is produced according to Eq. (7), causing  $O^-$  at the rock surface to change into  $OH^-$ , cations can be expected to be released changing the spring water chemistry. If  $Fe^{2+}$  is released, it is to be noted that, under aerobic conditions,  $Fe^{2+}$  can react with dissolved  $O_2$  to form superoxide radicals (Wilson et al., 2000):



Superoxide radicals in turn react with  $H_2O$  to  $H_2O_2$  plus  $\bullet OH$  (Espinosa-Garcia, 1993):



Further work will be needed to determine whether or not the reactions described by Eqs. (13/14) take place to a significant extent when battery currents flow across rock–water interfaces.

Though it is still much too early to estimate the magnitudes of battery currents in the Earth's crust, some projection of the potential impact of oxidation processes at rock–water interfaces may be in order. Since Earth is tectonically active, rocks are constantly subjected to stresses and stress gradients (Reimold and Gibson, 2006). Such tectonic stresses surely acted on the crust throughout Earth's history (van Hunen and van den Berg, 2006). Therefore, it is to be expected that stress-activated phole currents have been part of Earth's history for a very long time. In the case described here we reach a current density on the order of only 5  $\mu A$  per square meter cross section. In other experiments, with higher stresses, the current densities reach values on the order of 0.1–1  $mA m^{-2}$  (Freund et al., 2006). Whenever and wherever such currents have been crossing rock–water interfaces, the positive hole charge carriers much have oxidized  $H_2O$  to  $H_2O_2$ . This continuous production of  $H_2O_2$  on the tectonically active Earth may have contributed to the global oxidation. In particular, it may have played a significant, maybe dominant role, in the slow but seemingly unstoppable oxidation over the first 2–3 Gyrs of Earth's history (Goldblatt et al., 2006).

The production of  $H_2O_2$  at the rock–water interface has also implications for early life and how life adapted to the presence of highly oxidizing “reactive oxygen species” (ROS). These ROS certainly became a major challenge to Life when free  $O_2$  appeared in Earth's atmosphere 2.4 to 2.7 billion yrs ago. However, long before,  $O^-$  must have led to powerful ROS whenever stress-activated positive hole charge carriers passed through rock–water interfaces. Early microbial communities forming biofilms on rock–water interfaces were surely exposed to these

$O^-$  in their microenvironments. Exposure to highly reactive and even potentially lethal ROS must have been a daily experience long before the rise of free  $O_2$  in the atmosphere and long before the advent of oxygenic photosynthesis (Pierson, 1994; Towe and Des Marais, 2001; Dismukes et al., 2001; Eigenbrode and Freeman, 2006).

The consequences of exposure to strongly oxidizing conditions at rock–water interfaces early in Life's history may still be recognized today in the phylogeny of archaea, which are deeply rooted in the tree of life (Pace, 1997). A majority of archaea as well as a number of anaerobic bacteria contain distinct enzymatic systems, which evolved early to protect the cell from the detrimental effects of ROS. These enzymes include superoxide reductase to reduce superoxide to hydrogen peroxide and superoxide dismutases to disproportionate superoxide to  $H_2O_2$  plus  $O_2$  (Brines and Kovacs, 2007). Stress-activated positive hole charge carriers in crustal rocks, capable of oxidizing  $H_2O$  to  $H_2O_2$  and producing ROS at rock–water interfaces, could have well provided the driving force for the development of such enzymes in the oldest life forms on Earth.

## 5. Conclusion

By studying the flow of stress-activated battery currents through a rock–water system we simulate oxidation processes that take place in the crust of a tectonically active body like Earth and that may have taken place throughout Earth's history. Electrochemical oxidation driven by stress-activated battery currents at rock–water interfaces may have played an important role in the evolution of the early Earth, specifically in the global oxidation, and in the evolution of early life.

## Acknowledgments

This work was supported in part by a grant from the NASA Astrobiology Institute (NAI) Cooperative Agreement NNA04CC05A (to F.T.F. and L.J.R.). M. Balk acknowledges a travel grant from the Netherlands Organization for Scientific Research (NWO). G.E. acknowledges a NASA Senior Fellowship through the National Research Council and the Oak Ridge Associated Universities (ORAU).

## References

- Batlo, F., LeRoy, R.C., Parvin, K., Freund, F., 1990. Dissociation of  $O_2^-$  defects into paramagnetic  $O^-$  in wide band gap insulators: a magnetic susceptibility study of magnesium oxide. *J. Appl. Phys.* 67, 588–596.
- Bernabé, Y., 1998. Streaming potential in heterogenous networks. *J. Geophys. Res.* 103, 20,827–20,841.
- Bishop, J.R., 1981. Piezoelectric effects in quartz-rich rocks. *Tectonophysics* 77, 297–321.
- Brines, L.M., Kovacs, J.A., 2007. Understanding the mechanism of superoxide reductase promoted reduction of superoxide. *Europ. J. Inorg. Chem.* 27–38.
- Canney, S.A., Sashin, V.A., Ford, M.J., Kheifets, A.S., 1999. Electronic band structure of magnesium and magnesium oxide: experiment and theory. *J. Phys. Condens. Matter* 11, 7507–7522.
- Cox, D.P., Singer, D.A., 1986. Mineral deposit models. *US Geol. Survey Bull.* 1693, 379.
- Crespy, A., Revil, A., Linde, N., Byrdina, S., Jardani, A., Bolève, A., Henry, P., 2008. Detection and localization of hydromechanical disturbances in a sandbox using the self-potential method. *J. Geophys. Res.* 113. doi:10.1029/2007JB005042.
- Dismukes, G.C., Klimov, V.V., Baranov, S.V., Kozlov, Y.N., DasGupta, J., Tyryshkin, A., 2001. The origin of atmospheric oxygen on Earth: the innovation of oxygenic photosynthesis. *Proc Natl. Acad. Sci. USA* 98, 2170–2175.
- Eigenbrode, J.L., Freeman, K.H., 2006. Late Archaean rise of aerobic microbial ecosystems. *Proc. Natl. Acad. Sci. USA* 103, 15,759–15,764.
- Espinosa-Garcia, J., 1993. New theoretical value of the enthalpy of formation of the  $OOH$  radical. *Mol. Phys.* 79, 445–447.
- Freund, F., 1987. Hydrogen and carbon in solid solution in oxides and silicates. *Phys. Chem. Miner.* 15, 1–18.
- Freund, F., 2002. Charge generation and propagation in rocks. *J. Geodyn.* 33, 545–572.
- Freund, F.T., 2003. On the electrical conductivity structure of the stable continental crust. *J. Geodyn.* 35, 353–388.
- Freund, F., Masuda, M.M., 1991. Highly mobile oxygen hole-type charge carriers in fused silica. *J. Mater. Res.* 8, 1619–1622.
- Freund, F.T., Sornette, D., 2007. Electromagnetic earthquake bursts and critical rupture of peroxy bond networks in rocks. *Tectonophysics* 431, 33–47.
- Freund, F., Wengeler, H., 1982. The infrared spectrum of OH-compensated defect sites in C-doped MgO and CaO single crystals. *J. Phys. Chem. Solids* 43, 129–145.
- Freund, F.T., Takeuchi, A., Lau, B.W., 2006. Electric currents streaming out of stressed igneous rocks – a step towards understanding pre-earthquake low frequency EM emissions. *Phys. Chem. Earth* 31, 389–396.
- Goldblatt, C., Lenton, T.M., Watson, A.J., 2006. Bistability of atmospheric oxygen and the Great Oxidation. *Nature* 443, 683–686.
- Griscom, D.L., 1990. Electron spin resonance. *Glass Sci. Technol.* 4B, 151–251.
- Hurowitz, J.A., McLennan, S.M., Schoonen, M.A.A., Tosca, N.J., 2007. Production of hydrogen peroxide in martian and lunar soils. *Earth Planet. Sci. Lett.* 255, 41–52.
- Koga, K., Hauri, E., Hirschmann, M., Bell, D., 2003. Hydrogen concentration analyses using SIMS and FTIR: comparison and calibration for nominally anhydrous minerals. *Geochem., Geophys., Geosyst.* 4, 1–20.
- Lorne, B., Perrier, F., Avouac, J.-P., 1999. Streaming potential measurements 1. Properties of the electrical double layer from crushed rock samples. *J. Geophys. Res.* 104, 17,857–17,877.
- Lu, J., Xue, S., Qian, F., Zhao, Y., Guan, H., Mao, X., Ruan, A., Yu, S., Xiao, W., 2004. Unexpected changes in resistivity monitoring for earthquakes of the Longmen Shan in Sichuan, China, with a fixed Schlumberger sounding array. *Phys. Earth Planet Inter.* 145, 87–97.
- Martens, R., Gentsch, H., Freund, F., 1976. Hydrogen release during the thermal decomposition of magnesium hydroxide to magnesium oxide. *J. Catalysis* 44, 366–372.
- Ogawa, T., Utada, H., 2000. Coseismic piezoelectric effects due to a dislocation 1. An analytical far and early-time solution in a homogeneous whole space. *Phys. Earth Planet Inter.* 121, 273–288.
- Pace, N.R., 1997. A molecular view of microbial diversity and the biosphere. *Science* 276, 734–740.
- Parkhomenko, E.I., 1967. *Electrical Properties of Rocks*. Plenum Press, New York, NY. 314 pp.
- Pierson, B.K., 1994. The emergence, diversification, and role of photosynthetic eubacteria. In: Bengtson, S. (Ed.), *Early Life on Earth*. Columbia Univ. Press, New York, NY, pp. 161–180.
- Reimold, W.U., Gibson, R.L. (Eds.), 2006. *Processes on the Early Earth*. *Geol. Soc. America*, p. 403.
- Revil, A., 2007. Thermodynamics of transport of ions and water in charged and deformable porous media. *J. Colloid Interface Sci.* 307, 254–264.
- Revil, A., Linde, N., 2006. Chemo–electromechanical coupling in microporous media. *J. Colloid Interface Sci.* 302, 482–694.
- Ricci, D., Pacchion, G., Szymanski, M.A., Shluger, A.L., Stoneham, A.M., 2001. Modeling disorder in amorphous silica with embedded clusters: the peroxy bridge defect center. *Phys. Rev. B* 64 224104 224101–224108.
- Rossmann, G.R., 1996. Studies of OH in nominally anhydrous minerals. *Phys. Chem. Miner.* 23, 299–304.
- Shluger, A.L., Heifets, E.N., Gale, J.D., Catlow, C.R.A., 1992. Theoretical simulation of localized holes in MgO. *J. Phys.: Condens. Matter* 4, 5711–5722.
- Sze, S.M., 1981. *Physics of semiconductor devices*. Wiley, New York, NY.
- Takeuchi, A., Lau, B.W., Freund, F.T., 2006. Current and surface potential induced by stress-activated positive holes in igneous rocks. *Phys. Chem. Earth* 31, 240–247.
- Towe, K.M., Des Marais, D.J., 2001. On the origins of photosynthesis. *Science* 291, 436–437.
- Tuck, B.T., Stacey, F.D., Starkey, J., 1977. A search for the piezoelectric effect in quartz-bearing rock. *Tectonophysics* 39, 7–11.
- van Hunen, J., van den Berg, A.P., 2006. Plate tectonics on the early Earth: limitations imposed by strength and buoyancy of subducted lithosphere. *Lithos* 103, 217–235.
- Van Zeghbroeck, B., 1997. Photocurrents in a metal–semiconductor–metal photodetector. *IEEE J. Quantum Electron.* 22, 2188–2194.
- Wilkins, R.W.T., Sabine, W., 1973. Water content of some nominally anhydrous silicates. *Am. Mineral.* 58, 508–516.
- Wilson, C.L., Hinman, N.W., Sheridan, R.P., 2000. Hydrogen peroxide formation and decay in iron-rich geothermal waters: the relative roles of abiotic and biotic mechanisms. *Photochem. Photobiol.* 71, 691–699.
- Zeng, X., Hayakawa, M., Lin, Y., Xu, C., 2002. Infrastructural analysis of geomagnetic field and earthquake prediction. In: Hayakawa, M., Molchanov, O.A. (Eds.), *Seismo Electromagnetics: Lithosphere–Atmosphere–Ionosphere Coupling*, pp. 463–468. Tokyo.