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Verification of Hole Activation in Gabbro Blocks Subjected to Non-uniform Loading by Means of Hot Point Probe Tests

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Olivine and gabbro has been investigated to understand the electrical conductivity structure of the Earth's lower crust and mantle. To simulate a certain deep environmental circumstance, a rock sample is generally placed under a certain confining hydrostatic pressure at a certain temperature. Nowadays, it is known that the electric conduction property of olivine is p-type, which is driven by the small polaron of $Fe_{Mg}^{\bullet}$ and the V''_{Mg} as the main charge carriers at low and high temperatures, respectively [1]. However, when we turn our eyes to rocks on the crustal scale, the pressure-temperature condition is not homogeneous. The stress-strain distribution in the Earth's crust changes statistically and dynamically accompanied with seismic, volcanic and tidal activities. This may generate new electric phenomena on the crustal scale. In early laboratory experiments, when a part of an air-dried rock volume was uniaxially loaded, an electric current flowed from the unloaded part to the loaded part via the electrometer connecting to both parts, i.e., the generation of the electromotive force (EMF) which the electric potential of the unloaded part became high relative to the loaded part [2-4]. Based on a number of such experiments, it was expected that holes were activated in the loaded volume and diffused into the unloaded volume. However, this activation is not proved yet. Here, we try verification of this activation by means of hot point probe tests; we can judge the increase or decrease of the hole concentration based on the change of thermo-EMF as explained below.

Prior to hot point probe test, we first tried reconfirmation of EMF induced by non-uniform loading. The samples were gabble blocks ($2.5 \times 3.0 \times 10$ cm^3) which were polished with #800 abrasives then dried in a vacuum oven. Fig. 1a depicts the experimental set-up. One end of the blocks was uniaxially loaded by means of a manual hydraulic press at ~20 °C. The load was measured with a load cell. Copper tapes with graphite-based conductive adhesive were pasted on the load areas (2.5×2.5 cm^2 each). The EMF between the loaded and unloaded ends was measured with an electrometer. As expected, it was reconfirmed that the blocks generated EMF V_{emf} when loaded from 0 MPa to 60 MPa under manual control. The V_{emf} increased with an increase of loading and reached ~100 mV at ~50 MPa in case of the sample #1. Such an EMF appeared again when the unloading-loading cycle was repeated.

Next, hot point probe tests were conducted to the same blocks. Fig. 1b depicts the experimental set-up. The cold-probe was a twisted wire made of stainless steel. Its terminal was untwisted, and points of the fine wires were attached to some mineral grains in Area A or B on the backside of the blocks. The cold-probe temperature T_C was ~20 °C. On the other hand, the hot-probe was installed as the point of a soldering iron. Its point was also made of stainless steel. The hot-probe temperature T_H was ~150 °C when heated, so that, the temperature difference $\Delta T = T_H - T_C \approx 130$ °C. The probes were connected each other through the same electrometer to measure thermo-EMF ΔV. The hot-probe was attached to a position in the same area on the opposite side for 50 s until the voltage change became stable. Such an attachment-detachment cycle was repeated 10–20 times. To measure the averaged ΔV for this gabbro formed by various types of minerals, the attachment position was different each time. In case of Area A of the sample #1, ΔV increased approximately from –2100 mV to –1900 mV when loaded. On the other hand, that of Area B (about –2100 mV) did not change remarkably even when loaded.

The $-\Delta V/\Delta T$ ratio is called Seebeck coefficient α and used to judge whether the conduction property of semiconductors under study is p-type or n-type. In case of the sample #1, α of the loaded volume decreased from ~16 mV/°C to ~15 mV/°C when loaded, while α of the unloaded volume kept ~16 mV/°C even when loaded. Because all of α obtained in this study was positive, it was judged that the conduction property of this gabbro was p-type during unloading/loading. This is consistent with previous studies that indicate the conduction property of olivine is p-type [1]. Here, what we should note is the decrease of α of the loaded volume during loading. In the case that the charge carriers of this gabbro are represented by only holes, α is theoretically given by

$$\alpha = k_B/q \cdot \{(\gamma + 5/2) + \ln (N_V/n)\} \qquad (1)$$

where k_B is Boltzmann constant, q is the elementary electric charge, γ is a constant depending on the scattering mechanism of hole charge carriers, N_V is the effective density of states in the valence band, and n is the concentration of hole charge carriers. From eq. 1, the decrease of α means the decrease of the N_V/n ratio. If N_V is almost independent of load, the decrease of the ratio means the increase of n. That is, this test indicated the activation of holes in the loaded volume.

From the viewpoint of band model of solid states, n increases by two mechanisms: (1) downward-shift of energy levels of the existing accepters such as the H'_M site in olivine, resulting in the decrease of the mean excitation energy and (2) downward-shift of some unoccupied energy levels in the middle of the forbidden band, resulting in the increase of the number of effective accepters. One of the unoccupied energy level will be the $3\sigma_u^*$ of peroxy bond ($O_3X{-}OO{-}YO_3$, with X, Y = Si^{4+}, Al^{3+}, etc.). This lattice defect is included in various kinds of igneous rock-forming minerals. This energy level in the band model is expected to shift downward by loading and become an effective accepter [2-4]. As a result, a hole is activated in an O-site and can spread as the electric state of O^- hopping in the matrix of O^{2-}, in other words, a polaron of $O_O^\bullet$. These two mechanisms will cause the downward-shift of the Fermi energy level ε_F, and there appears the difference in ε_F between the loaded and unloaded volumes in the gabbro block during loading.

Now, we consider a simple 1-D model of the gabbro block with the *x*-axis along the block length. The loaded end side is at $x = 0$ cm and the unloaded end side is at $x = L$ (= 10 cm). Because there appears a difference of $n(x)$ between the loaded and unloaded volumes, holes activated in the loaded volume diffuse into the unloaded volume. At the same time, holes are electrically attracted toward the loaded volume because of the electric field $E_{drift}(x)$ that is formed by diffusing holes themselves. When we assume that they are balanced during loading at a slow loading rate, $E_{drift}(x)$ is given by

$$E_{drift}(x) = k_B T/q \cdot d/dx \{\ln n(x)\} \qquad (2)$$

The V_{emf} (≈ 100 mV) observed in the loading test is the summation of two competing effects of the $\varepsilon_F(x)$ difference and $E_{drift}(x)$:

$$V_{emf} = \int_0^L \{d/dx\, V_F(x)\}dx + \int_0^L E_{drift}(x)dx = \{V_F(L) - V_F(0)\} + k_B/q \cdot \ln\{n(L)/n(0)\} \qquad (3)$$

where $V_F(x) = \{\varepsilon_F(x) - \varepsilon_V(x)\}/q$ is the potential difference of the Fermi energy level $\varepsilon_F(x)$ from that of the valence band top $\varepsilon_V(x)$ during loading. On the other hand, $n(x)$ has a relation with $N_V(x)$ and $V_F(x)$:

$$n(x) = N_V(x) \cdot \exp\{-qV_F(x)/k_B T\} \qquad (4)$$

From eqs. 1 and 4,

$$V_F(x) = \alpha(x)T - k_B T/q \cdot \{\gamma(x) + 5/2\} \qquad (5)$$

When $\gamma(x)$ is independent of load, from eqs. 3 and 5,

$$V_{emf} = \{\alpha(L) - \alpha(0)\}T + k_B/q \cdot \ln\{n(L)/n(0)\} \qquad (6)$$

When $V_{emf} \approx 100$ mV and $\alpha(L) \approx 16$ mV/°C and $\alpha(0) \approx 15$ mV/°C are adopted in eq. 6 at $T \approx 20$ °C ≈ 300 K, the $n(L)/n(0)$ ratio ~1/2000, meaning the activation of a number of holes in the loaded volume.

According to early studies, the electrical conductivity of gabbro needs the confining hydrostatic pressure of the order of GPa to become several tens times larger, moreover, the electrical conductivity of some minerals/rocks is almost independent of the confining hydrostatic pressure [5,6]. Therefore, the shear stress/strain by non-uniform loading may effectively shift energy levels in the forbidden band. We can expect that the downward-shift of the Fermi level and the diffusion of activated holes occur in various types of rocks subjected to non-uniform loading, because EMF induced by non-uniform loading has been detected in gabbro, granite and anorthosite at least [2-4]. Therefore, this mechanism must be driven accompanied with various activities of the Earth's crust such as major earthquakes, volcanic eruptions, and earth tides. However, as far as we observe the geoelectric field on or under the ground surface, the

EMF by this mechanism will be partially or completely canceled by other mechanisms related to ground water. We should consider the chemical influence of the activated holes [7] rather than their direct electric influence, i.e., EMF, in the actual Earth's crust.

References

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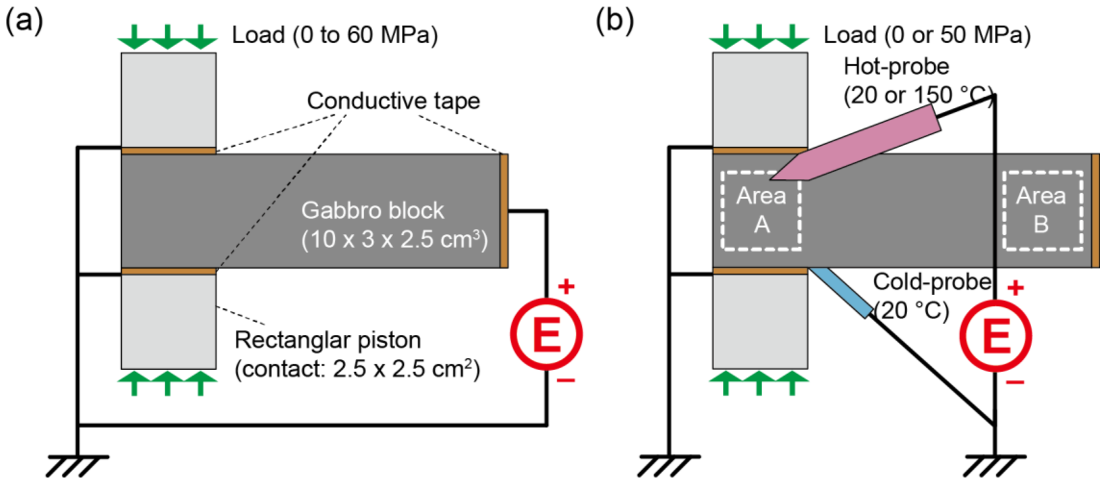

Fig. 1: (a) The set-up of non-uniform loading tests. (b) The set-up of hot point probe tests.