Surface electrification of rocks and charge trapping centers

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Abstract

In order to elucidate mechanisms of seismo-electromagnetic phenomena such as earthquake luminosity, earth potential changes, electromagnetic radiation and ionosphere disturbances, numerous fracture or frictional slip tests using rock samples have been conducted. Fracturing or frictional slipping generates electrification on the affected surfaces. The surface structures and gouges thus generated are generally disordered containing many charge trapping centers, which are important to understand surface electrification. To investigate the state changes of charge trapping centers in surface disordered layers, we measured thermoluminescence (TL) from milled quartz grains with and without surface disordered layers. The TL intensity per unit mass of the quartz decreased with decreasing grain diameter. Moreover, the TL intensity of samples with surface disordered layers decreased with grain diameter more rapidly than of those without such layers. This diameter-dependence can be explained by disturbances of TLs on the grain surfaces and by deformations of Al-hole centers in the surface disordered layers. Al-hole centers release holes as well as the newly formed E' centers in surface disordered layers release electrons. Charges released from charge trapping centers are disturbed in the surface disordered layers during milling. Like milling, fracturing or frictional slipping could generate charge. These charges express themselves on the fractured or frictionally slipped surfaces as surface electrification. On the geological scale, fault zones are characterized by fracturing and frictional slipping. Therefore, the releases of charges from charge trapping centers in surface disordered layers within faults might provide a mechanism to explain seismo-electromagnetic phenomena.
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1. Introduction

It is well known that fracturing and frictional slipping of materials such as metals, polymers and minerals cause electrification, the emission of electrons, ions and neutral species, visible light (luminescence) and/or electromagnetic radiation over a wide wave length region (e.g. Deryagin et al., 1978; Dickinson, 1990 and references therein). Many laboratory studies of these phenomena, using rock samples, have been conducted to investigate the mechanisms of various seismo-electromagnetic phenomena such as earthquake luminosity, earth potential changes, electromagnetic radiation and ionosphere disturbances (e.g. Nitsan, 1977; Ogawa et al., 1985; Brady and Rowell, 1986; Enomoto and Hashimoto, 1990; Hadjicontis and Mavromatou, 1994, 1995;

Freund, 2000, 2002; Takeuchi and Nagahama, 2001, 2002a,b). For centuries seismo-electromagnetic phenomena have been observed before, during and after earthquakes (e.g. Park et al., 1993; Hayakawa, 1999; Hayakawa and Molchanov, 2002 and references therein).

As possible sources of seismo-electromagnetic phenomena, piezoelectricity (e.g. Finkelstein et al., 1973; Nitsan, 1977) and streaming potentials (e.g. Mizutani et al., 1976) have been considered. However, piezoelectricity and streaming potentials require, respectively the presence of piezoelectric minerals such as quartz and water flowing through porous rocks. That is, piezoelectricity and streaming potentials could lead to seismo-electromagnetic phenomena only under limited conditions. On the other hand, all minerals, even of high chemical purity and carefully cleaned, generally contain charge trapping centers (e.g. Kittel, 1953; Varotsos and Alexopoulos, 1986). For example, in quartz crystals Al^{3+} substituting for Si^{4+} acts as a hole trapping center,

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while Ge^{4+} and Ti^{4+} at Si^{4+} sites act as electron trapping centers. The E' center is a dangling bond at an Si^{4+} site, i.e. a lone electron at a three-coordinated Si^{4+}. Takeuchi and Nagahama (2002a,b) found that the surface charge density on fractured or frictionally slipped quartz or granite is of the order of 10^{-4}–10^{-2} C/m^2 which is consistent with the surface charge density estimated from the density of unpaired electron on fractured quartz and in oxide films of silicon wafers. Based on this consistence, the authors pointed out that charge trapping centers should be sources for surface electrification induced by fracturing or frictional slipping of rocks.

To explain the generation of electric currents induced by impacts on rocks, Freund (2000, 2002) considered positive hole pairs (PHPs): $O_3X/^{OO}/XO_3$, where $X = Si^{4+}$, Al^{3+}, Fe^{3+} and where the oxygens in the peroxy link (–O–O–) has converted to the 2− to the 1− oxidation state. The PHP defects can dissociate: $O_3X/^{O\bullet}$ $_{\bullet O}/XO_3$, where $\bullet$ represent holes associated with the O^- state, also known as "positive holes". After dissociation, one hole remains at the defect site, while the other can propagate as an electronic charge carrier through the O 2p-dominated valence band. This process does not involve O diffusion but only the movement of the electronic charge associated with the O^- state. When positive holes reach the surface of rocks, they become be trapped and form a thin charge layer. The attendant electric field can be high enough to cause dielectric breakdown of the surrounding air (Freund, 2000, 2002). Because PHPs are believed to be ubiquitous in common rock-forming minerals, they may explain the electrification induced by fracturing or frictional slipping of rocks. However, minerals contain not only PHPs but also other kinds of charge trapping and charge releasing centers. Therefore, to elucidate the mechanisms of electrification, we investigate here such charge trapping and charge releasing centers in quartz before and after fracturing or frictional slipping.

Early studies of the surfaces of ground or milled quartz grains found that the near-surface layers are generally amorphous and/or highly disturbed (e.g. Gibb

et al., 1953; Rieck and Koopmans, 1964; Burton, 1966). This layer is often called the surface disordered layer and its layer is of the order of 10^1–10^2 nm (e.g. Moody and Hundley-Goff, 1980; Yund et al., 1990). Arends et al. (1963) measured electron spin resonance (ESR) signals from freshly crushed powders of high purity quartz. They found that the ESR signal from E' centers per unit mass increased in intensity with decreasing grain size, strongly suggesting most of E' centers are formed on or near the surface of the quartz grains. In other words, the surface disordered layers contain most of E' centers in quartz grains.

Quartz generally acquires not only E' centers and PHPs, but also Al-hole centers (e.g. Weil, 1975). Al-hole centers are thought to be one of the sources for thermoluminescence (TL) which is the thermally stimulated emission of light from insulator or semiconductor (e.g. McKeever, 1985; Chen and McKeever, 1997 and references therein). TL measurements can be used to investigate the states and properties of charge trapping centers in materials. A schematic diagram of the TL generation mechanism is shown in Fig. 1. When electrons trapped in the forbidden band are thermally excited to the conduction band, they behave as quasi-free electrons. Some of these electrons return to lower trapping states, while others recombine with trapped holes in the forbidden band. Any retrapping or recombination releases energy as radiation corresponding to the energy difference of transition states involved. When the energy difference is small, the transition leads to the emission of phonons that is of heat. When the energy of the emitted radiation is in or near the region of visible light, TL is observed. For example, TL from quartz above room temperature is usually blue and/or red, called blue-TL and red-TL, respectively (e.g. Hashimoto et al., 1986; Krbetschek et al., 1997). The TL intensity is related to the density (number) of charge trapping centers.

Early measurements of TL, especially blue-TL, from quartz or silica above room temperature suggested Ge and/or Ti as electron sources and Al-hole centers as a hole source although these issues are still being discussed
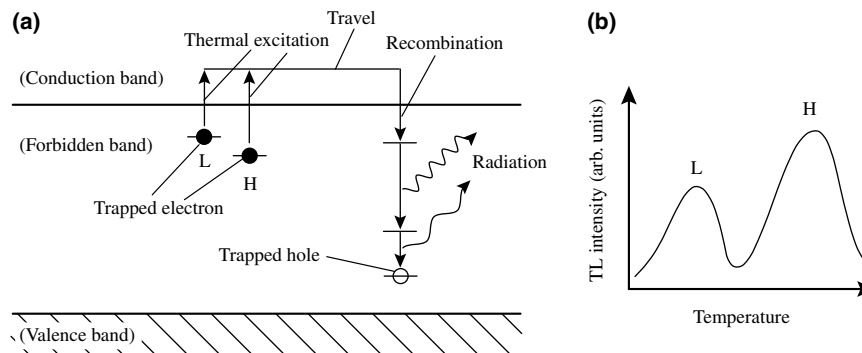

Fig. 1. Schematic diagrams of (a) TL generation mechanisms based on the band theory of solids involving two levels L and H and (b) a schematic TL growth curve as a function of the heating temperature for transitions involving the energy levels L and H.

(e.g. Arnold, 1960, 1973; Schlesinger, 1964; Durrani et al., 1977; Marfunin, 1979; McKeever, 1985; Martini et al., 1995; Hashimoto et al., 2000). Yamaguchi et al. (2003) recognized that the TL color of quartz shifted from blue to red after a 1100 °C for 100 h annealing treatment, and pointed out that deformed Al-hole centers were the hole sources of red-TL. In spite of intensive investigations (e.g. Hashimoto et al., 1986, 1996, 2001; Fattahi and Stokes, 2000), the details of the red-TL sources are not yet fully understood.

While there are extensive studies dealing with the TL of quartz crystals, little attention has been paid to surface disordered layers. If (deformed) Al-hole centers are related to surface electrification induced by fracturing or frictional slipping of quartz, there should be differences between the TL signature of quartz crystals and of their surface disordered layers. In the present investigation, TL from quartz grains with and without surface disordered layers are measured (Section 2) to study Al-hole centers in surface disordered layers due to milling (Section 3) and to discuss generation mechanisms of surface electrification induced by fracturing or frictional slipping (Section 4).

2. Methods

Natural pegmatite quartz from Marumori, Miyagi prefecture, Japan was used in the present TL measurements. This quartz emits mainly red-TL during heating to 50–450 °C. It was crushed to fragments with diameter less than 1 mm by a hammer. Those fragments were treated with 36% HCl for 30 min and then with 6N NaOH for 30 min in an ultrasonic syringe to remove impurities from the fragment surfaces. Half of treated fragments were annealed at 450 °C for 30 min. Another half were dried in an oven at 50 °C. Both were milled again to small grains in an agate mortar. Then, one half of each batch were etched with 48% HF for 15 min to remove surface disordered layers, while the other halves were left untreated. Thus, four batches were obtained: annealed-etched, annealed-unetched, unannealed-etched and unannealed-unetched quartz grains, designated as QAE, QAX, QXE and QXX, respectively. Moreover, the batches were separated into groups with different grain diameter distributions (Fig. 2).

A schematic diagram of the TL measurement system (Hashimoto et al., 2002) is shown in Fig. 3. Each sample with weight of 5 mg was loosely packed in a small Al-pot with 5 mm in diameter and 5 mm in depth. To remove unstably trapped electrons, they were first annealed at 220 °C for 3 min. Thereafter, they were reheated from 50 to 450 °C at a heating rate of 1 °C/s. During heating, red-TL from each sample was measured through two red filters (Hoya, O-58 and Asahi-techno Glass Co. Ltd., CF-50E) and a photomultiplier tube (Hamamatsu
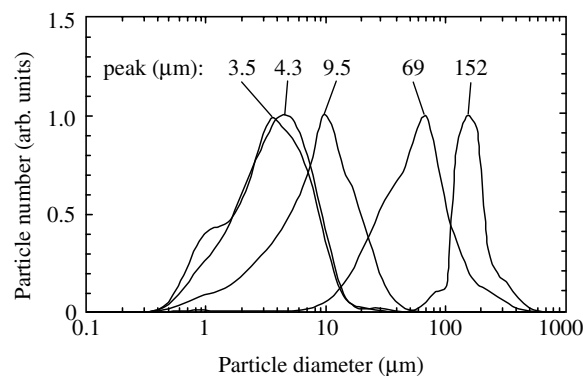
Fig. 2. Diameter distributions of QXX classified in five groups. Other samples (QAE, QAX and QXE) also have similar diameter distributions.
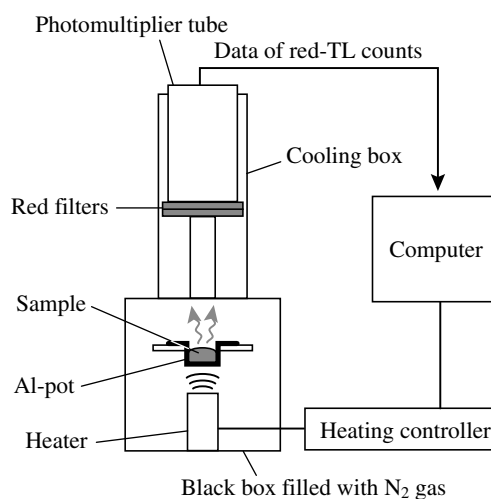
Fig. 3. A schematic diagram of the red-TL measurement system (modified from Hashimoto et al. (2002)).

Photonics, R649S). The data were transmitted to a computer, which also controlled the heating and automatically conducted TL measurements.

3. Results

Typical growth curves are shown in Fig. 4. The unannealed samples (QXE and QXX) exhibit the red-TL with a pronounced peak at approximately 400 °C, while the annealed samples (QAE and QAX) give very weak peaks around 400 °C. For QXE and QXX the TL intensities decreased with decreasing the grain diameter d as shown in Fig. 5 for the red-TL intensity I_{RTL} where I_{RTL} is the integral counts of red-TL from 370 to 430 °C. At $d = 10$–150 μm at least, log–log plots of both samples are like to be linear although there are data for only three grain sizes. At $d > 70$ μm, I_{RTL} of QXX is almost equal to that of QXE. At $d < 70$ μm, I_{RTL} of QXX is slightly lower than that of QXE. However, at $d < 10$
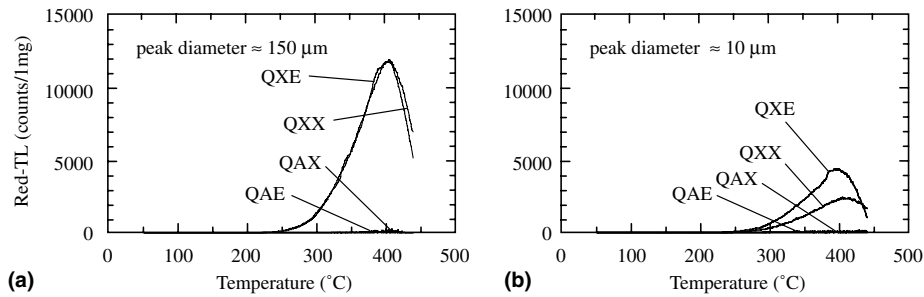
Fig. 4. Red-TL growth curves against the heating temperature for each group of QAE, QAX, QXE and QXX with peak diameters of approximately (a) 150 μm and (b) 10 μm.
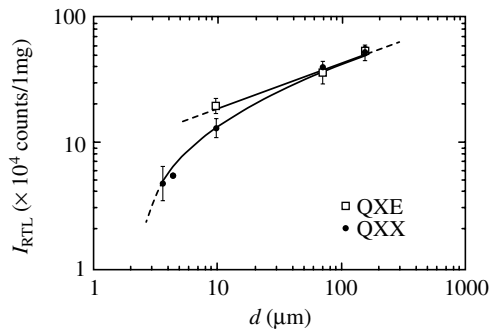

Fig. 5. Plots of the red-TL intensity I_{RTL} against the grain diameter (peak diameter) d for QXE and QXX.

μm, I_{RTL} of QXX decreases rapidly. Here, there is no useful datum for QXE at $d < 10$ μm because of insufficient mass of QXE grains.

Not the entire TL intensity emitted from the quartz grains can reach the photon counter. A portion of the emitted TL will either reach the photon counter directly or pass through surrounding grains, while another portion is lost through reflection. Pandurangi and Seehra (1990) measured the infrared (IR) absorption spectra through crystalline and amorphous silica grains of different sizes ($d = 0.05$–260 μm), and found that the intensity of strong absorption was proportional to $d^{-\delta}$, where $\delta = 0.34$–0.42. Similarly, an increase in the absorption leads to a decrease of photons reaching the photon counter. Therefore, I_{RTL} should also be approximately proportional to d^δ. Log–log plots of I_{RTL} for QXE and QXX in Fig. 5 are like to be concordant with the $d^{-\delta}$-dependence at $d = 10$–150 μm at least. On the other hand, Avnir et al. (1983) found that the specific surface area S' of fractured grains has a fractal relationship with d : $S' \propto (d/2)^{D-3}$ where D is the surface fractal dimension. Now, $D - 3$ has values ranging from -0.63 to -0.36 (Nagahama, 1991), which is approximately consistent with the values of $-\delta$ given above. When $D - 3 = -\delta$, I_{RTL} is proportional to the inverse of S'. This means that the IR absorption and the TL intensity are directly affected by the fractal geometry of fractured grain surfaces.

Sample QXX contains surface disordered layers that may play a role in the rapid I_{RTL} decrease for QXX at $d < 10$ μm in Fig. 5. The disordered layer is generally amorphous and/or highly disturbed (e.g. Gibb et al., 1953; Rieck and Koopmans, 1964; Burton, 1966). Additionally, this layer contains many of the charge trapping centers such as E′ center (e.g. Arends et al., 1963; Fukuchi, 1993, 1996). Therefore, the density of Al-hole center, which is assumed to be a hole source of red-TL from quartz (Yamaguchi et al., 2003), in this layer might be different from that in original quartz (Fig. 6). The outermost surface of this layer is in contact with environmental air containing H_2O molecules. Adsorption of H_2O molecules causes Al-hole centers to disappear (Hashimoto et al., 2000). Therefore, we posit that the density of Al-hole centers in the outermost surface layer will approach zero. The thickness of this "hole-depleted" layer might be of the order of the thickness of a few atoms.

For QXX, the number of Al-hole centers in a quartz grain n_{Al} is given by

$$n_{Al} = \frac{4\pi}{3}\left[(\rho_{OQ} - \rho_{SDL})\left(\frac{d}{2} - t_{OSL} - t_{SDL}\right)^3 + \rho_{SDL}\left(\frac{d}{2} - t_{OSL}\right)^3 \right], \qquad (1)$$

for $t_{OSL} + t_{SDL} \leqslant d/2$, where ρ_{OQ} and ρ_{SDL} are, respectively, the concentration of Al-hole centers in the original quartz and in the surface disordered layer, and where t_{OSL} and t_{SDL} are, respectively, the thickness of the outermost "hole-depleted" surface layer and of the surface disordered layer (Fig. 6). The number of grains per unit mass is inversely proportional to the volume of a grain. Therefore, the total number of Al-hole centers in QXX per unit mass N_{Al} is given by

$$N_{Al} = \left[(\rho_{OQ} - \rho_{SDL})\left(\frac{d}{2} - t_{OSL} - t_{SDL}\right)^3 + \rho_{SDL}\left(\frac{d}{2} - t_{OSL}\right)^3 \right]\left(\frac{d}{2}\right)^{-3}, \qquad (2)$$

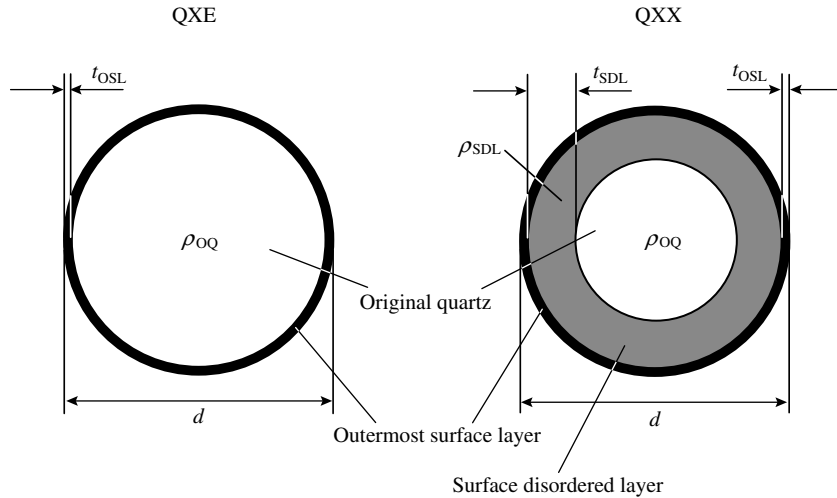QXE   QXX

Fig. 6. Representative diagrams of QXE and QXX grains. Parameters are described in the text.

for $t_{OSL} + t_{SDL} \leqslant d/2$. Because I_{RTL} obeys the d^δ-dependence, I_{RTL} of QXX is given by

$$I_{RTL} \propto \left[(\rho_{OQ} - \rho_{SDL}) \left(\frac{d}{2} - t_{OSL} - t_{SDL} \right)^3 + \rho_{SDL} \left(\frac{d}{2} - t_{OSL} \right)^3 \right] \left(\frac{d}{2} \right)^{\delta-3}, \quad (3)$$

for $t_{OSL} + t_{SDL} \leqslant d/2$. In the case that t_{OSL} and t_{SDL} are constants independent on d, I_{RTL} of QXX becomes a function of d only. Applying the same procedure, I_{RTL} of QXE is then given by

$$I_{RTL} \propto \rho_{OQ} \left(\frac{d}{2} - t_{OSL} \right)^3 \left(\frac{d}{2} \right)^{\delta-3}, \quad (4)$$

for $t_{OSL} \leqslant d/2$. In the case that t_{OSL} is constant and independent on d, I_{RTL} of QXE is also a function of d only.

I_{RTL} curves for QXE and QXX calculated on this basis were fitted with experimental data in the case that $\rho_{SDL} = 0.01 \rho_{OQ}$, $t_{OSL} = 1$ nm, $t_{SDL} = 500$ nm, $\delta = 0.35$, and a measurement datum $(d, I_{RTL}) = (150$ μm, 50×10^4 counts/1 mg) for both QXX and QXE is adopted as an initial condition. Solid lines in Fig. 5 express these curves. Parameters $t_{SDL} = 500$ nm and $\delta = 0.35$ are consistent with previous data from independent measurements (e.g. Moody and Hundley-Goff, 1980; Pandurangi and Seehra, 1990; Yund et al., 1990). A significant difference between the densities of Al-hole centers in surface disordered layers and in original quartz $(\rho_{SDL} = 0.01 \rho_{OQ})$ indicates that, if the Al-hole centers are a source of red-TLs in surface disordered layers, they nearly disappear during the formation of surface disordered layers during milling in an agate mortar.

4. Discussion

Milling treatment produces quartz grains with surface disordered layers and generates numerous E' centers in these layers (e.g. Gibb et al., 1953; Arends et al., 1963; Rieck and Koopmans, 1964; Burton, 1966; Fukuchi, 1993, 1996). However, Al-hole centers in the surface disordered layer can also be eliminated during formations of surface disordered layers. Al–O bonds in this layer can be expanded or contracted due to disorder of around lattice structure. The energy states of these deformed Al-hole centers can be unusual. Since TL is strongly related to a part of the energy difference between states of a released electron and a hole center (Fig. 1), TL from deformed Al-hole centers can be beyond the region of visible light. In this case, the photon counter of the measurement system as used here cannot detect them. In the case that expansion or contraction of Al–O bonds are further intense or strong, Al-hole centers are broken rather than deformed. These broken Al-hole center sites may then release holes into more stable energy levels rather than store trapped electrons. On the other hand, Al-hole centers in this layer can recombine with electrons or ions like OH^-, H^+, Li^+ and Na^+ that are released from around deformed lattice structure (Yamaguchi et al., 2003). These recombined Al-hole centers show no longer property of hole centers even if they do not break due to the milling procedure. Consequently, deformation, breakage or recombination of Al-hole centers in the surface disordered layers can lead decrease of red-TL from QXX.

According to Freund (2000, 2002), holes released from dissociated PHPs travel through the O 2p-dominated valence band of oxide and silicate minerals. Similarly, holes released from Al-hole centers may travel in the same way when they are generated during the formation of the surface disordered layers. Holes released

from Al-hole centers and PHPs are disturbed in surface disordered layers during the milling procedure. All minerals, including quartz, generally contain charge trapping centers (e.g. Kittel, 1953; Varotsos and Alexopoulos, 1986). Therefore, disturbances of charges in surface disordered layers of minerals can generally occur during formations of surface disordered layers due to the milling procedure. As well as milling, fracturing or frictional slipping can form surface disordered layers on fractured or frictionally slipped surfaces and on gouge grains (e.g. Dunn et al., 1973; Ohnaka, 1975; Moody and Hundley-Goff, 1980). Likewise, the disturbances of charges in surface disordered layers can also occur during stick-slip motions. Stick-slips of granite samples generate electrification on the surfaces thus formed (e.g. Lockner et al., 1986; Yoshida et al., 1997, 1998; Takeuchi and Nagahama, 2001, 2002a). Since charges released from charge trapping centers distribute on stick-slip surfaces during stick-slip motions, these charges are related to the surface electrification.

In addition to the formations of surface disordered layers, frictional heating during stick-slip motions cannot be neglected even if it may only lead to a very short and highly localized heat pulses. If the stick-slip surfaces reach several hundred degrees Celsius during stick-slip motion, the TL may have already occurred, which would otherwise be observed in our measurement system (Fig. 3). On the other hand, rocks generate not only luminescence when heated but also currents (charges) causing their conductivity to change, known as thermally stimulated current or conductivity (e.g. Chen and McKeever, 1997 and references therein). Dologlou-Revelioti and Vatotsos (1986) and Dologlon (1993) measured thermally stimulated currents in rocks such as granite and limestone within a narrow temperature range between 6 °C and 23 °C, and pointed out that these currents arise from the relaxation of dipoles due to impurities and piezoelectric inclusions in a non-random orientation. Freund et al. (1991, 1993) measured thermally generated charges in fused silica and MgO crystals above 500 °C, and pointed out that these charges are positive holes released from dissociated PHPs. Some of these stimulated charges may recombine with trapped charges and also generate luminescence. Thus, the mechanisms of TL and of thermally stimulated current/conductivity are fundamentally connected in each other. Further measurements will be necessary, using the same minerals as previous investigator such as Halperin et al. (1970) and Schloessin (1985) to clarify the complex behavior of released charges.

Enomoto et al. (1993) measured thermally stimulated exoelectron emission (TSEE) in a temperature range between 300 °C and 400 °C from granite, which is a kind of thermally stimulated currents mentioned above. They proposed that the possible source of TSEE was electrons released from E′ centers. In addition, they measured

fracture-induced transient electric signal (FTES) from the same granite. Based on less FTES from granite annealed at 400 °C, they proposed that the main source of FTES is electrons released from trapping centers due to frictional heating at clacking edges. Their proposition is very similar with ours. It can be said that our investigation supports their proposition also from the view point of TL measurements. However, generation of charges only is not enough to explain electrification on the fractured or frictionally slipped surface because simultaneous release of positive and negative charges from charge trapping centers means electronically neutral at the charge generation zone. To explain the surface electrification (uneven distribution of positive and negative charge), further mechanism is needed as followed.

Surface disordered layers in contact with stick-slip surfaces may become semiconducting even when the original minerals are insulators. State and density changes of disturbing charges cause the Fermi level of these layers to change (e.g. Guinier and Jullien, 1989). Therefore, contact electrification can occur at the interface between surface disordered layers by transferring charges from one layer to another. When there is approximately 0.1 eV difference between the Fermi levels at the contact surfaces, a surface charge of approximately 10^{-3} C/m^2 will appear (e.g. Harper, 1967; Guinier and Jullien, 1989). The 10^{-3} C/m^2 value is estimated from data of previous fracture or frictional slip tests (Takeuchi and Nagahama, 2002a). As the difference of Fermi levels between dissimilar minerals is believed to be approximately 1 eV (Ogawa et al., 1985), a value of 0.1 eV can be reasonably assumed at the contact between different layers of the same mineral such as quartz, formed during in the milling procedure. Thus, charges released from charge trapping centers in surface disordered layers can explain the electrification induced by fracturing or frictional slipping of rocks.

Deformations of fault zones involve fracturing and frictional slipping of rocks, and produce gouges. The minerals along the fault planes and in the gouges suffer mechanical and thermal damage. Therefore, a release of charges from various trapping centers in surface disordered layers is likely to occur during deformations or microfracturing along the fault zones. In other words, fault zones can generate electrification independent of the existence of piezoelectric minerals such as quartz and independent of water streaming through the gouges and neighboring rocks. Based on the electrification assumed occur along fault or in microcracks in the fault zones, scaling laws have been proposed between the electric/magnetic fields during earthquakes and the earthquake magnitude (e.g. Molchanov and Hayakawa, 1995, 1998; Takeuchi and Nagahama, 2002b). According to the generation mechanism of surface electrification proposed in the present paper, the amount of surface electrification depends on the states and the properties of

charges and charge trapping centers. Further investigations on these processes with surface disordered layers are required to elucidate the generation mechanisms of seismo-electromagnetic phenomena.

5. Conclusions

We measured TL from quartz grains with and without surface disordered layers formed during the milling procedure. The results indicate apparent changes in the state of Al-hole centers in the surface disordered layers. Broken Al-hole centers release holes, while newly formed E' centers release electrons. These holes and electrons are disturbed in surface disordered layers during the milling procedure. Some charges form surface electrification on grains and others generate TL due to recombination. Stick-slip motion of rocks is a process that similarly forms surface disordered layers along stick-slip surfaces and in the gouge. The charges thus activated, both hole and electrons, may be related to the generation of electromagnetic fields and/or electromagnetic signals during stick-slip motions. Therefore, seismo-electromagnetic phenomena may be intimately correlated with the activation of these charges before and during earthquakes.

Acknowledgements

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