eEarth Discuss., 1, S112–S122, 2006
www.electronic-earth-discuss.net/1/S112/2006/

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Interactive comment on “Stimulated infrared emission from rocks: assessing a stress indicator” *by* F. T. Freund et al.

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Received and published: 5 October 2006

Stimulated infrared emission from rocks: assessing a stress indicator

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eEarth Discuss., 1, 97-121, 2006 www.electronic-earth-discuss.net/1/97/2006/

Introduction: Both Reviewers pointedly draw attention to the fact that our paper on “Stimulated infrared emission from rocksĚ” describes only a laboratory experiment. Both suggest that the assertion, our findings may help understand pre-earthquake “thermal anomalies” as derived from satellite observations of the Earth’s surface, may be overreaching.

We are of course fully aware of the limitations, which come with a single (though wellprepared) laboratory experiment conducted with one particular rock sample, selected primarily because this rock, an anorthosite, is monomineralic consisting almost entirely of one mineral, a Ca-rich feldspar. We believe that we inserted enough caveats into the body of our text to alert the reader to the limitations of our experiment. We do not reject as Reviewer 1 suggests “more trivialĚ effects causing the slight detected variation of IR emission”, but we believe that none of the explanations offered so far in the literature can explain the appearance of large, rapidly changing areas of enhanced IR emission, which have been called “thermal anomalies”.

Spectroscopy versus Temperature: Both Reviewers did perhaps not recognize that our paper describes principally a spectroscopic phenomenon and that our conclusions rely much more on the spectroscopic information than on the (modest) brightness temperature increase. We show that a series of distinct narrow bands is emitted from the front face of the block of anorthosite as soon as we begin to apply stress some 40 cm away.

Spectroscopy is powerful and diagnostic. The observed narrow emission bands provide unique insight into the processes that take place at the atomic level at the rock surface. These bands are consistent with only one physical explanation: excitation of local oscillators in the rock surface that involve a few atoms or ions at any given time. Specifically, in our paper, we address three narrow emission bands below 1000 cm-1, which we assign to a sequence of O-O stretching vibrations.

The narrow bands evolve during loading as both the raw spectra (Figure 4) and the difference spectra (Figure 5) demonstrate. Their absolute intensity increases between beginning and end of the run. Their relative intensities increase and decrease, but the bands never loose their narrow character (Figure 6). The possibility of “a spurious shift” of the wavenumber positions due to small changes in the ambient temperature as invoked by Reviewer 1 in #2a can be ruled out with great confidence on the basis of fundamental physics. Under no circumstances can a conventional small temperature increase, due to an influx of Joule or “sensible” heat during loading, produce the narrow band spectroscopic signature that we can discern in the raw spectra (Figure 4)

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and more clearly in the difference spectra (Figure 5). Any Joule temperature increase would lead to a monotonous and uniform increase of the intensity (albeit asymmetric, according to Planck's law) across the entire region covered in Figure 3.

For the purpose of our paper it is important to note that the narrow IR emission bands are diagnostic and unique. They are different from the broad bands that dominate the emission spectrum (Figure 3). These broad bands arise from a large ensemble of vibrating atoms and ions that are strongly coupled. As Reviewer 1 correctly points out in #1 the broad maxima at 1020 cm-1, 1110 cm-1 and 1195 cm-1 are due to stretching modes of Si-O and Al-O modes, but they represent the thermal average of these Si-O and Al-O modes in a 3-dimensionally coupled system. By contrast, the narrow bands, most distinctly observed at the beginning of loading, are diagnostic of individual Si-O, Al-O and O-O oscillators that are selectively excited by a non-thermal process. These narrow bands indicate that their oscillating atoms or ions have not yet become part of the thermal bath. These bands are not caused by "heating".

Brightness Temperature Scale: The fact that we plot the intensity changes of the IR emission spectrum as changes in "temperature" has caused confusion in the reviewers' minds. We note: kT is an energy. The Boltzmann constant k has the units eV/T [Kelvin] and the numerical value ?8.6 10-5 eV per degree. At a temperature of 300 K kT corresponds to ?25 meV. Reviewer 1 points out in #2b that we plot the intensity in units of "brightness temperature", an energy scale widely used in remote sensing, where the intensity at the frequency ? is defined as I? = B?(TB) with B? in units [Joule sec-1 m-1 ster-1 Hz-1]. B? ? 2?2 kTB/c2, where k is again the Boltzmann constant, TB the absolute temperature, and c the speed of light. Expressing TB in terms of wavelength ?, we obtain TB = [?4/2kc] I?. This relation shows that, while the brightness temperature depends on the fourth power of the wavelength of the emitted light, changes in temperature will cause smooth intensity changes over the entire spectral range. However, our narrow bands are clearly non-thermal. We use the "brightness temperature" scale only because the satellite data, from which "thermal anomalies" are derived, are expressed in TB units. One of the reasons for TB is that thermal IR data from satellites are primarily used for the purpose of weather and climate, where temperature is an essential parameter. In addition, currently flying satellites lack the spectral resolution to “see” narrow band emissions. Therefore their sensors average the intensity of the IR emission over relatively broad frequency windows to calculate TB by means of temperature-calibrated gray body reference spectra.

Correlation between “Thermal Anomalies” and Meteorological Data: Both Reviewers express doubts as to the applicability of our basic process to “thermal anomalies”. Both Reviewers feel that the recombination of positive hole charge carriers (defect electrons on the O2- sublattice), formation of vibrationally excited peroxy links at the rock surface, and their radiative deactivation cannot account for the pre-earthquake increase in temperature derived from satellite data. Reviewer 2 points to reports in the literature about correlations between meteorological data such as the near-ground air temperature and “thermal anomalies”. He suggests that the cause for the “thermal anomalies” lies in the near-surface atmosphere and not, as we claim, in the surface of the solid Earth. Reviewer 2 also emphasizes, correctly so, that the surface of the Earth rarely consists of bare rock. More widely it consists of sand or clay and is often covered by vegetation or snow. Because “thermal anomalies” reportedly occur even under these conditions, he categorically states that “the IR emission produced by p-hole recombination is several orders of magnitude lower and absolutely insufficient to produce the air heating by 2-5 K”.

While these are valid points, we don’t think that the situation is anywhere close as bleak. When dealing with “thermal anomalies”, we need to also look at other reported pre-earthquake phenomena. There is a bewildering array ranging from ionospheric perturbations and low frequency electromagnetic emissions to “thermal anomalies” and atmospheric effects. Even the most contentious of the alleged pre-earthquake phenomena, unusual animal behavior, must not be left out. The signals are so disparate that it seemed impossible to ever find single physical process at the surface of

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the Earth.

Many who have dealt with pre-earthquake phenomena have tried to explain the type of signals with which they are familiar. However, even when those researchers were able to make a relatively strong case for their particular hypothesis, it is discomforting to note that the other phenomena, which seem to be also part of the family of pre-earthquake signals, could be not covered by the same explanation.

The discovery of the positive hole charge carriers, their activation by stress, their fast and seemingly facile propagation through the rocks, their capability to cross grain boundaries and even through layers of sand and soil, their accumulation at the rock-air interface with the concomitant positive ground potentials and microscopically very large electric fields (which are expected to cause changes in the near-ground atmosphere) seem to provide for the time a physically coherent, testable basis for most, if not all, phenomena that have been linked to impending seismic activity. The IR emission experiment that we describe in our paper is part of the broader project to develop a comprehensive theory of pre-earthquake signals. The IR emission experiment was specifically designed to test the predictions that (i) p-holes have an enhanced probability to recombine at the rock-air interface, (ii) recombination of p-holes is exothermal and should lead to vibrationally excited O-O bonds, (iii) de-excitation of the O-O bonds leads to characteristic narrow emission bands at distinct wavenumbers, which must agree with the theoretically calculated peroxy bond strength, (iv) the accumulative effect of the narrow-band emissions is the elevation of TB, the brightness temperature as measured by the broad-band thermal IR sensor onboard the satellite. The narrow emission bands and their evolution as a function of time and of increasing stress more than 40 cam away from the emitting rock surface unequivocally confirm these predictions and instills us with the confidence that we are on the right track.

The current status of this broader project to understand p-holes is described in a series of recent papers: Freund, F. (2002), Charge generation and propagation in rocks, J. Geodynamics, 33, 545-572. Freund, F. T., et al. (2004), Stress-Induced Changes in the Electrical Conductivity of Igneous Rocks and the Generation of Ground Currents, Terrestrial, Atmospheric Oceanic Sci. (TAO), 15, 437-467. Ouzounov, D., and F. T. Freund (2004), Mid-infrared emission prior to strong earthquakes analyzed by remote sensing data, Adv. Space Res., 33, 268-273. Freund, F. T. (2006), When the Earth speaks: Understanding pre-earthquake signals, paper #426 presented at Europ. Conf. Earthquake Eng. Seismology, Sept. 4-8, 2006, Geneva, Switzerland. Freund, F. T., A. Takeuchi, and B. W. S. Lau (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. St.-Laurent, F., J. S. Derr, and F. T. Freund (2006), Earthquake lights and the stress activation of positive hole charge carriers in rocks, Phys. Chem. Earth, 31, 305-312. Takeuchi, A., B. W. S. Lau, and F. T. Freund (2006), Current and surface potential induced by stress-activated positive holes in igneous rocks, Phys. Chem. Earth, 31, 240-247.

Because our physical model has been validated by the results of the IR emission experiment, we feel justified to be explicit in our statement that pre-earthquake “thermal anomalies” are most likely due either to direct p-hole recombination at the Earth’s surface or to secondary effects that are linked to the p-hole recombination or, more generally, to the influx of p-holes to the Earth’s surface.

The secondary effects will include extensive ionization of the near-surface air and a host of follow-on reactions that can conceivably lead to heating of the air by 3-5 K to which Reviewer 2 refers. We can say with some degree of confidence that the follow-on reactions will remain operational even when the ground is covered with vegetation and possibly snow.

Peroxy Links and Positive Holes Recombination Luminescence: Reviewer 1 raises questions about the peroxy link. Specifically he asks in #3.2-#3.7 about the paper by Ricci et al. (2001) and how we use the information contained therein to support our position.

The presence of peroxy links in fused silica has attracted a lot of attention. A large body of literature exists that we did not feel necessary to quote. The attention arises from the fact that, when fused silica optical fibers are used in nuclear reactors or space applications, energetic particles and x-ray or gamma irradiation split the peroxy link forming peroxy radicals, O3Si-OOŢ and E’ centers, ŢSiO3. The peroxy radicals produce a strong optical absorption in the visible and near-IR, causing losses in transparency. Beginning with Edwards and Fowler (“Theory of the peroxy-radical in a-SiO2, Phys. Rev. B 26, 6649-6660, 1982) several authors have characterized the peroxy link. The Ricci et al. 2001 paper offers the most advanced level of quantum-mechanical computation. It has yielded among others the vibrational ground state energy of the O-O bond, 930-950 cm-1, in different local environments of O3Si-OO-SiO3 in the structure of amorphous SiO2. Professor G. Pacchioni, the senior author of the Ricci et al. (2001) paper, has kindly performed a lower level quantum-mechanical calculation for the configuration in feldspars, O3Si-OO-AlO3 (unpublished). He confirmed that the vibrational energy of the O-O bond is relatively insensitive to the Al replacing Si in the peroxy link.

In #3.4 Reviewer 1 erroneously refers to the energy to photodissociate the peroxy link. In our paper we specifically refer to the energy required for the thermal break-up of the O-O bond, which is thought to split the peroxy link in the middle, O3Si/OŢŢO/SiO3 producing p-hole charge carriers as described in Freund and Masuda (“Highly mobile oxygen hole-type charge carriers in fused silica, J. Mater. Sci. 8, 1619-1622, 1991). The value for the energy required to thermally split the O-O bond and generate p-holes, 2.4 eV, comes from electrical conductivity measurements on single crystal MgO summarized in Freund, Freund and Batllo (“Critical review of electrical conductivity measurements and charge distribution analysis of magnesium oxide”, J. Geophys. Res. 98, 22,209-22,229, 1993). In MgO the vibrational frequency of the Raman-active O-O stretching mode of O22- lies at 880 cm-1, underlining the statement above that the O-O bond is relatively insensitive to the chemical and crystallographic surroundings and, hence, that the energy required for dissociation of this bond will not vary greatly in different solid matrices. This general knowledge provides the basis for our statement “We

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expect similar activation energies for the break-up of peroxy links in silicate minerals and, by extension, in rocks", which Reviewer 1 felt is not sufficiently supported.

In #3.5 Reviewer 1 requests clarification as to how the Ricci et al. (2001) paper connects to our description on p. 106, line 6, where we write with reference to Figure 7 "Ěthe two O- are shown to snap together to form the short O–O- bond characteristic of the peroxy linkĚ". The diameter of O2- anions in essentially all silicate structures is about 2.8 Å and in MgO almost 3 Å. By contrast the O-O bond length of the peroxy link is dramatically shorter, ˜1.5 Å in MgO and fused silica. We quote the Ricci et al. (2001) paper simply because it confirms the shortness of the peroxy bond. We did not want to add another reference to, for instance, an inorganic structural chemistry textbook where the shortness of the O-O bond in the peroxy entity is mentioned as a well-known fact.

In #3.6 Reviewer 1 misquotes us by saying that we stated on p. 106, line 8-12 that the dissipation of excess energy is mainly done by "a non-radiative decayĚ". In fact we don't say "mainly". We simply present the fact that, whenever a peroxy link is "born" in a vibrationally excited state, two channels exist to dissipate its excess energy, a radiative decay channel and a non-radiative decay channel.

Radiative decay means that the system emits photons at energies that reflect the difference between two levels involved in the transition, usually levels n and (n-1) where n is the quantum number of the excited state. A non-radiative decay means that the vibrationally excited system can "dump" energy into the vibrational manifold of a neighbor which thereby climbs from its ground state n0 to the first excited level n = 1 and subsequently de-excites by returning to the ground state and emitting a photon characteristic of the energy difference between these two levels. We were careful not to weigh the relative contributions from the radiative and non-radiative decay channels because they are not known.

In the same section, #3.6, Reviewer 1 seems to confuse the broad band emission features, which arise from the 3-dimensionally strongly coupled ensemble of Si-O and Al-O in the thermal bath at kT equivalent to 300 K, with the narrow band emission features that arise from local oscillators. Those local oscillators are largely decoupled from their surroundings by virtue of the fact that they are in a vibrationally excited state. Hence, their characteristic frequencies are more narrowly defined and different. The broad bands around 1020 cm-1 and 1190 cm-1 dominate the emission spectra before loading and during loading. The broad bands cancel when we subtract the pre-load spectra from the spectra recorded during loading. We do not see any fault in the simple subtraction used to derive the difference spectra nor any logical error in the cancellation of the broad emission bands. In fact, the difference spectra were obtained so that they render the narrow emission bands more clearly visible.

In #3.7 Reviewer faults us for not explaining well enough on p. 106 how we calculated the probability to populate the n1, n2, n3 and higher levels. If we assume a Boltzmann distribution, the probability of thermally populate any level ni above n0 is given by exp[-(En-E0)/kT], where (En-E0) refers is the energy of the nith level above n0, k the Boltzmann constant and T the absolute temperature. The energy of the levels that give rise to the IR emission in the 1000 cm-1 is about 100 meV, while kT at T = 300 K is 25 meV. From these values we straightforwardly obtain the probabilities given on p. 106, lines 19-20. At the same time we remind the reader that the term “hot band” describes any band that arises from a transition between higher levels that are not thermally populated. In the case of the O-O stretching modes any downward transition from levels n2 or higher qualifies as a “hot” band.

Earlier, in #2c, Reviewer 1 had called on us to explain why the narrow band positions recorded during some preliminary experiments with granite were slightly different from those reported here for anorthosite. Our remark as to the band positions referred specifically to the narrow bands around 930 cm-1, 870 cm-1 and 820 cm-1. We have assigned these bands to O-O stretching modes, specifically to the fundamental, first and second hot bands due, respectively, to the downward transitions from n1 to n0, from n2 to n1, and from n3 to n2. Granite is mineralogically more complex than the monomineralic anorthosite. Hence, differences in the band positions on the order of 10-20 cm-1 are not unexpected.

On p. 107, lines 2-3 we state that the “energies of hot transitions for the O-O bond, from n=2 to n=1 and from n=3 to n=2, are unknown.” Reviewer 1 derives great concern from this statement, asking how we can then be sure about the probabilities to thermally populate the higher levels. This is obviously a misunderstanding. The energy V as a function of interatomic distance r of the O-O oscillator can be described by a Morse potential, V(r) = Dc{1-exp[-?(r-r0)/r0]}, where Dc is the dissociation energy, r0 the equilibrium distance, and ? an adjustable constant. A Morse potential is a parabola that opens asymmetrically to one side. The eigenvalues can be obtained by solving the Schrödinger equation for the system. They show a ladder of discrete energy levels that become ever more narrowly spaced with increasing level of vibrational excitation. Our statement about the “unknown” hot transition energies was meant to alert the reader that we do not know yet the Morse potential of the O-O entity. Hence, we are uncertain where precisely these two hot bands should lie. Our level of uncertainty lies within 10-20 cm-1. The experimental values, 870 cm-1 and 820 cm-2, shifted by about 60 and 110 cm-1 relative to the fundamental at 930 cm-1 (Figure 8), appear very reasonable for n2-n1 and n3-n2 transitions respectively. This allows us to be confident that we correctly assigned these bands to the last two “hot” transitions of a larger de-excitation sequence, when a vibrationally highly excited initial state of O-O, formed during recombination of p-hole charge carriers, cascades down the quantum ladder.

Conclusions: Though Reviewer 1 has raised a number of critical questions and Reviewer 2 wants us to present “much more modest conclusions regarding the possibility of application of (our) laboratory results to the Ě interpretation of the satellite IR anomalies”, we think we can put to rest all major objections. The spectroscopic results presented here provide convincing evidence that a mechanism exists to deposit energy into the surface of a rock through the influx of positive hole charge carriers and their recombination. The fact that the energy is initially deposited non-thermally does not rule out that it will eventually turn into Joule heat once the locally excited O-O bonds thermalize and spread their excess energy onto more neighboring atoms. We respectfully submit that understanding the nature of p-hole charge carriers in the Earth's crust holds the key to understand pre-earthquake ”thermal anomalies”.

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