

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

Anonymous Referee #1

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The paper of Freund et al. “Stimulated infrared emission from rocks: assessing a stress indicator” presents the results of a laboratory experiment. Its aim is to propose an explanation to the observation of an enhanced IR emission seen in night-time satellite images of the land surface before major earthquakes. The laboratory experiment is based on a large block of rock subjected to a localized intense stress and the measurement of an InfraRed (IR) signal as detected by a sensitive spectrometer. The authors observed an increase of IR emission during mechanical loading. They propose an explanation of that phenomenon based on the “effect of stress-activated positive hole (p-hole) charge carriers on the infrared (IR) emission from rocks”.

The referee doubts that the actual laboratory experimental set-up allow the authors to definitely reject more trivial (and consequently spurious) effects causing the slight

detected variation of IR emission. The discussion about the experimental data, the involved hypothetic physical phenomena and their scientific interpretation have to be greatly improved in order to convince readers that the proposed scenario might be the explanation of atmospheric and meteorological anomalies observed by satellites. A special care will have to be taken in order not to over-interpret data -and references as well-. Strong improvements for that paper are thus required. Main points are now detailed (I will mainly focus my referee report on the discussion about the laboratory experiment)

1. The experiment can be resumed as following : An important stress is put at one end of the large block of rock and IR emission signal is measured as emitted by the limiting surface far away from the stressed zone. The experimental set-up is at room temperature (around 300K). IR spectra are measured thanks to a very sensitive spectrometer. Two types of data are presented in this paper: i) direct values of emission spectra (but plotted on a “temperature” scale) taken at regular time intervals during the first 6minutes (step 1) without stress on rock and during the following 30mn (step 2) when stress is gradually increased up to rupture and ii) “difference spectra” resulting from computed difference between spectra taken during step 2 minus the average value of those from step1. The authors observed then a regular increase of the intensity of IR bands at wavenumbers around 1020cm^{-1} , 1190cm^{-1} and 1110cm^{-1} . These emission bands are related to stretching modes of Si-O and Al-O bonds. On the opposite difference spectra reveal an important signal “concentrated at wavelengths that are different from those of the two emission maxima in the pre-load emission spectrum”.

2. Several questions arise when looking at experimental condition carefully.

2.a. Mean temperature of experiment is around 300K as measured by authors and as observed on spectrum in figure 3 where the maximum of intensity is around 10microns as predicted by Wien law (derived from Planck’s law describing the emission spectrum by a “black body”, valuable approximation for that piece of rock). Thus minute variations of temperature (few 100mK or less) i) during the whole duration of experiments

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(at least 36 minutes), ii) or along the large piece of rock (60cm long) could modify slightly the position in wavenumbers of the maximum of intensity of emitted light. Consequently that spurious shift could have a huge effect on difference spectra : spurious peaks could raise in intensity only because of these minute variations of temperature. Another important point is that the signal received by the spectrometer is the “convolution” of what is emitted by the piece of rock AND what is absorbed by the atmosphere present between the emitting surface of rock and the detector (distance between both : one meter). So variation of composition of atmosphere -such as content in CO2 (variation due to breathing of physicists around the experiments for instance!) or H2O (outgasing of apparatus due to slight increase of temperature, variation of composition of atmosphere) could cause variation of absorption of IR radiation. This spurious effect has to be quantified carefully by the authors before eventually being ruled out.

2.b The spectra are calibrated (along Y axis , the so-called by authors “intensity” axis) in temperature scale. This temperature is very likely what is called “brightness temperature” as it is discussed in technical notes available on web site of NASA (relatively to MODIS project as mentioned by the authors in page 100 line 24) http://oceancolor.gsfc.nasa.gov/DOCS/modis_sst/. As it is mentioned in that technical note “the brightness temperatures, TB, are derived from the observed radiances by inversion (in log space) of a the radiance versus blackbody temperature relationship”. That use is completely justified for analysis of satellites data but far less for this experiment as the corresponding law between TB, and the real intensity (in counts detected by spectrometer for a narrow bandwidth) depends on wavenumbers in a very nonlinear way. So the referee is wondering whether such choice of scale does not introduce artificial variations of signal giving weird peaks in difference spectra. The referee proposed that “intensities” are plotted in real intensity or a comment of authors on that would be greatly appreciated.

2.c The authors did most of their experiments with a block of anorthosite which structure is already complex (role of impurities, nature of grain boundaries etc..) and com-

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pleted them with experiments done with a piece of granite (with a “more complex mineralogy”). They do find that “the band positions were slightly different”. This comment has to be developed as the explanation proposed by the authors and presented as an universal explanation (via the concept of Positive Hole pairs) is based on a detailed discussion on the position of IR bands with wavenumbers.

3. About discussion and the proposed scenario

3.1 The authors ruled out a pure thermal effect to explain the increase of some IR bands when stress is applied mainly by arguing that the increase of intensity is very fast (almost concomitant with the increase of stress). The authors have in mind that this thermal effect could only be produced locally where the increase of stress occurs causing propagation of microcracks and generation of heat. From that remark the authors concluded that their preferred scenario (role of PHP) is only the right one able to explain their observations. Following explanation could not be completely ruled out: local increase of pressure could cause an increase of the internal pressure of residual gases or liquids the presence of which could not be completely ruled out as the rock is not monocrystalline or completely homogeneous. This could cause an increase of the temperature of that residual atmosphere through out the sample and that heat wave could propagate at the typical speed of a perturbation of pressure in air (around 300m/s) which is the mean speed of propagation of the so-called PHP as measured by authors (page 105 line 3). Nevertheless the explanation of the observed variation of IR emitted signal as proposed by the authors is based on a discussion about positive holes and related peroxy links.

3.2 In page 104 line 18 the reference Ricci et al. 2001 looks to be mentioned to enforce the idea of the “well-known” presence of peroxy-links in fused silica as claimed by the authors. But in that cited paper the only “effect of local and long-range disorder on the incorporation energy, optical, IR, and XPS spectra of a peroxy linkage defect in amorphous silica ($\alpha\text{-SiO}_2$)” ‘as mentioned in the abstract) is studied by means of quantum-mechanical modeling. Nothing else! No comment indeed was done by Ricci

et al. about the probability of occurrence of such a defect. Very similarly I am wondering why the same reference is called in page 106, line 6.

3.3 In page 105, line 5 it is written that “because the valence band forms an energetic continuum, the p-holes can jump grain boundaries”. This sentence looks very “strange” from a physical point of view. The referee is wondering whether the p-holes could “jump” so easily whatever the width and/or the height of potential barrier modeling the grain boundary! The authors reinforced their faith in that weird idea in their interactive comment (<http://www.cosis.net/copernicus/EGU/eed/1/S54/eed-1-S54.pdf>) where they claimed that “these electronic charge carriers (p hole charge carriers can even cross 1-2 cm thick layers of liquid water (though the direction of the current changes)”. Thus by following that new physical concept developed by the authors the referee is wondering why the p-holes could not be collected directly by an electrode put few millimeters in front of the surface of the sample from where IR emission is gathered instead of working with a very expensive spectrometer?

3.4. In last paragraph in page 105 a comparison of different energies is done : energy to photodissociate a peroxy link, activation energy, etc? The definitions of these important notions have to be carefully mentioned by the authors as experiments or calculation give mainly variation of energies in a process and thus the final energy drastically depends on the chosen initial state (a nice example is given in one of the favorite reference of the authors Ricci et al. 2001 page 2241104-2. If that is not rigorously precised all the values of energies given by the authors have very few scientific meaning. The referee would like very much that the authors precise too the (scientific) meaning of such sentence “We expect similar activation energies for the break-up of peroxy links in silicate minerals and, by extension, in rocks (Freund, 2003)”. Does an “expectation” means a scientific proof?

3.5. In page 106 line 6: the referee does not fully understand the link between the sentence of authors and the cited reference (Ricci, 2001).

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3.6 In page 106 lines 8-12 and following (p. 107 lines 15-19) it is sentenced that the dissipation of excess energy is mainly done by “a non-radiative decay by channeling energy into neighboring Si-O and Al-O bonds, which in turn become excited and emit at their characteristic vibrational frequencies”. It was mentioned by authors that these bands were observed mainly on raw spectra (not on difference spectra) around 1020 and 1190 cm^{-1} (p. 101 lines 11-17) and NOT on difference spectra. So the referee do not understand why the stress was put by authors in part “3 Results” on difference spectra and why main conclusions are apparently drawn from raw spectra (which reveal opposite conclusion s as minima in spectra for one type of data are maxima for the other type of spectra. More explanation is needed.

3.7. In page 106 lines 13-24 a discussion of probability of occupation of energy levels is done. It needs -as seen in formula in line 15- the knowledge of the energy of these levels, En. In page 107 lines 2-3 the authors said 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”. In these conditions the authors have to explain how their calculations of probability of occupation of levels were done. Furthermore as the energy of these levels and transitions are unknown how can the authors be sure that the proposed process can explain the position of the narrow bands and claim that “The two narrow bands at 870 cm^{-1} (11.5 microns), and 810 cm^{-1} (12.35 microns) are consistent with O-O “hot” bands arising from the $n=2$ to $n=1$ and $n=3$ to $n=2$ transitions respectively”?

3.8 A technical comment : in page 12 the words “p-holes” are missing and it should be written “equivalent to 10(13) p holes m^{-2} ”.

3.9; In figure 2 the color code has to be mentioned.

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