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# What we Know and don't Know about Positive Hole Charge Carriers and their Role in Generating Pre-Earthquake Phenomena

Friedemann T. Freund [1,2,3] and Minoru M. Freund [1]*

1) *NASA Ames Research Center, Moffett Field, Mountain View, CA, 94035, USA*

2) *SETI Institute, 189 Bernardo Ave., Mountain View, CA, 94043, USA*

3) *Physics Dept. San Jose State University, San Jose, CA 95192-0106, USA*

There are, in principle, two ways in science to approach complex issues such as pre-earthquake signals: (i) collect as many data as possible, for instance through extensive field observation campaigns, trying to find statistically significant trends that would allow us to establish believable and reliable correlations, or (ii) work on a theoretical concept, based on insight gained through fundamental research, and try to apply such insight to different facets of the observational evidence that Nature presents to us.

Much of the controversy surrounding pre-earthquake signals arises from the fact that the geoscience community interested in earthquakes has traditionally emphasized approach (i), collecting field data and building up a library of past events. Laboratory experiments to support the field observations have been primarily designed to mimic plausible conditions in the field and to derive plausible correlations. Many types of pre-earthquake signals, however, point to some electrical processes, which are often not deeply understood. The causative relations between mechanical and electrical processes are often obscure. This makes it difficult to look through the maze of correlations in a multi-parameter space. An alternative is to try approach (ii), using deductive reasoning to derive insight from fundamental aspects of the solid state.

Having come to pre-earthquake science as an outsider, I was uninhibited by the traditional approach (i). Prior work had alerted me to the presence of a family of defects in oxide materials and then minerals, which had never before been properly identified. While studying these defects in single crystals, I found them to exhibit unexpected properties, specifically with respect to electrical behavior. I started to wonder whether these "new" defects could help us better understand the diversity of pre-earthquake phenomena. If so, I hoped, this might help overcome some of the divisions within the scientific community.

The name "positive holes" has been given to defect electrons in the oxygen anion sublattice of oxide and silicate materials, chemically equivalent to $O^-$ in a matrix of $O^{2-}$ [1,2]. $O^-$ can be readily produced by ionizing radiation, ripping electrons off $O^{2-}$ anions, and can be studied at cryogenic temperatures [3] – conditions that are not of much interest to earthquake science. However, I found another geophysically much more relevant process, by which positive holes can be introduced into materials: through a little known redox conversion involving pairs of hydroxyls, typically $O_3Si\text{-}OH$, which are present in every mineral that ever crystallizes from a $H_2O$–laden magma. These minerals incorporate traces of $H_2O$ into their matrices, even though – crystallographically – they should nominally be anhydrous. Feldspars, pyroxenes, olivines etc. fall into this category. Upon cooling below 600-400°C, when thermodynamic equilibrium can no longer be maintained, hydroxyl pairs, $O_3Si\text{-}OH$ $HO\text{-}SiO_3$, rearrange electronically in by transferring an electron from their oxygens to their protons, forming peroxy defects and molecular hydrogen, $O_3Si\text{-}OO\text{-}SiO_3 + H_2$ [4,5]. This is a basic solid state reaction, by which peroxy defects are introduced into every igneous and high-grade metamorphic rocks in the upper regions of the Earth crust.

Peroxy are thermodynamically allowed, though metastable. They are ubiquitous. They are everywhere.

I started out studying what happens, when peroxy bonds break, releasing $h^\bullet$ charge carriers. At first, I focused on the temperature-induced break- up of peroxy bonds and found that this is fully reversible within the range of metastability.

A major step forward (with respect to earthquake science) was achieved when I serendipitously discovered that mechanical stress also leads to the activation of positive hole charge carriers [6,7].

In this report I'll discuss:

1) why peroxy defects in rocks are thermodynamically allowed;
2) how peroxy defects are activated by stress;
3) what happens when peroxy defects release positive holes $h^\bullet$, highly mobile electronic charge carriers, and inject them into an otherwise insulating medium (like most rocks);
4) why the $h^\bullet$ have the ability to spread out of the stressed rock volume;
5) how long the $h^\bullet$ remain active before returning to their dormant peroxy state;
6) how the $h^\bullet$ travel fast and far, potentially forming powerful electric currents deep in the Earth crust;
7) what happens when the $h^\bullet$ arrive at the Earth surface;
8) how the $h^\bullet$ can recombine at the surface, returning to the peroxy state and emitting in the process infrared radiation with a characteristic spectroscopic signature;
9) how the $h^\bullet$ set up microscopic electric fields at rock surfaces, steep enough to field-ionize air molecules far from where the rocks are stressed, and even trigger corona discharges;
10) that there is observational evidence suggesting that air ionization takes place episodically and on a regional scale around the epicenters of impending earthquakes;
11) how the flow of $h^\bullet$ through the rocks is <u>not</u> inhibited by the presence of water in the rock pores.

Completing this journey through the maze of correlations in a multi-parameter world, I'll discuss how the $h^{\bullet}$ change from behaving as electronic charge carriers (their physical nature) to being highly oxidizing •O radicals (their chemical nature) when they arrive at rock-water interfaces.

A crucial part of this whole story is the concept of the rock battery, i.e. the recognition that, when rocks are stressed, they turn into a source of $h^{\bullet}$ charge carriers. Flowing out along the self-generated "battery" potential gradient, the $h^{\bullet}$ generate electric currents, which generate EM signals. However, sustained currents are possible only when the battery circuit is closed. Circuit closure requires special conditions, which we still hardly understand. Circuit closure in the Earth crust is difficult but not impossible.

The battery concept gives us an opportunity to look at pre-earthquake signals from a new perspective. It also provides insight into how to conduct – and how not to conduct – laboratory experiments aimed at learning as much as we can about those elusive and controversial positive hole charge carriers in rocks.

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* Minoru M. Freund died early this year.