Electronic Charge Carriers in Igneous Rocks and their Activation through Tectonic Processes

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OUTLINE

Most rocks, in particular igneous rocks of the continental crust are fairly good insulators. Whenever their electrical conductivity increases, locally or with depth along the geotherm, the increase is thought to be caused by (1) pore water, (2) intergranular carbon films, or (3) incipient partial melting.

However, there is mounting evidence that igneous rocks contain an elusive type of electronic charge carriers, totally overlooked in the past. These charge carriers are defect electrons in the O^{2-} sublattice, O^-, also known as positive holes. Normally they lie dormant in form of spin-coupled positive hole pairs, PHP, where two O^- are linked in a peroxy bond, O^-–O^-. In this paired state they are electrically inactive and undetectable. Yet, when activated, PHPs release positive hole charge carriers, which are highly mobile and turn the rocks momentarily into pure p-type semiconductors. Hence, whenever PHPs are activated, positive holes will appear. They have the potential of affecting not only the electrical conductivity of rocks but also other properties of geophysical and geochemical interest.

My contribution to the EarthScope workshop will center on the role which the elusive PHPs and positive hole charge carriers may play in large-scale tectonic and magmatic processes in the crust.

HOW DO PHPS AND POSITIVE HOLES FORM?

All magmatic and high-grade metamorphic environments on Earth are H_2O–laden. Consequently, all minerals, even those that are nominally anhydrous, dissolve small amounts of H_2O when they crystallize in such environments. At first the dissolved H_2O forms hydroxyl, OH^- or O_3Si-OH. However, during cooling, a redox conversion takes place by which OH^- pairs rearrange their electrons in such a way as to form peroxy links, O^-–O^- or $O_3Si/^{OO}\backslash SiO_3$, and molecular H_2. The H_2 molecules are diffusively mobile and can escape, leaving the rocks “doped” with PHPs, i.e. with dormant positive hole charge carriers.

There is evidence that this sequence of solid state reactions leading to PHPs – the dissolution of small amounts of H_2O and the conversion of hydroxyl pairs to peroxy links plus H_2 – takes place somewhere along the cooling path from high temperatures, probably around 400-500°C. As a result, PHPs may be present in most, if not all igneous and high-grade metamorphic rocks.

HOW ARE PHPS ACTIVATED?

There are at least three ways to activate PHPs and to generate positive hole charge carriers: (1) by heating, (2) by stress leading to dislocation movements, and (3) by acoustic or seismic waves.

(1) The effect of heating has been most extensively studied, mostly on structurally and compositionally simple model minerals like periclase, MgO, though minerals ranging from olivine to feldspars show closely similar behavior. Upon heating the spin pairing breaks down first around 200-300°C, leading to a delocalization of the electron wave function associated with the hole state. This is followed around 400–500°C by full dissociation and the generation of a free positive hole charge carrier. Above 600-700°C the positive holes are irreversibly lost in secondary reactions.

(2) High levels of stress act on PHPs through plastic deformation, i.e. through dislocations that sweep through the minerals and dislodge, on an atomic scale, the peroxy bond. This instantly breaks the bond and causes positive holes to be generated as free charge carriers.

(3) Acoustic or seismic waves act on the PHPs through the same elementary process, by the passing wave transiently straining and destabilizing the peroxy bond, leading to generation of positive holes.

WHAT ARE POSITIVE HOLES?

Being defect electrons in the O^{2-} sublattice, positive holes have the remarkable property that they travel through the O 2p-dominated valence band of oxide and silicate minerals. They can cross grain boundaries nearly unimpeded. Therefore, they can carry currents through otherwise insulating rocks. Being electronic charge carriers, positive holes travel fast, at velocities in the 100-300 m/sec range. Thus, even if the charge carrier density is low, the high velocity of positive hole charge carriers combined with the enormous cross section of rocks raise the possibility of large currents in the crust.

Another remarkable property of positive holes is that, when activated, they turn the rocks into pure p-type semiconductors. Because of their like charge, positive holes repel each other maximally in the dielectric bulk and tend to flow outward from their source of origin.

GEO-ELECTROCHEMISTRY

An outward flux of positive holes necessarily leads to an opposing electric field. Such a field invites a flux of positive charges in the opposite direction. This counterflux can be carried by different cationic species, depending on the conditions. In hot rocks, where positive holes are thermally activatged, the counterflux will be carried by cations, most likely by those of highest mobility, H^+, Li^+, Na^+ and K^+.

From the perspective of petrogenesis, the postulated outflow of positive holes draws our attention to electrochemically driven ion transport in the crust. As a result, magmas in seemingly closed magma chambers would evolve non-isochemically. Understanding these processes – and understanding positive holes – may help us understand why many magmas tend to become peralkaline with time.

GEO-ELECTROPHYSICS

If positive holes are generated at a high rate in a cool rock, for instance in a rock volume compressed to the point of plastic deformation and massive microfracturing, the outward flux of positive holes would translate into very large currents. This will result in very high counterfields, causing water to electrolyze and generate a large number of H^+. These H^+ would then be the likely counterions, set to flow massively inward into the stressed rock volume to compensate for the outflow of positive holes.

Systems of two fluxes in opposite directions that are coupled through some physical parameter such as the electric field often tend to go into oscillations. Such current oscillations can be inferred from the remarkable magnetic field pulses that have been observed over a period of several weeks prior to the Sept. 22, 1999 M=7.7 Chi-Chi earthquake, Taiwan. The pulses lasted a few hours and reached amplitudes up to nearly 10% of the Earth's magnetic dipole field. Each of these pulses must have been accompanied by low frequency electromagnetic emissions which, however, were not recorded.

From extreme situations encountered prior to large earthquakes we can learn not about non-seismic earthquake precursors. We can also learn, more generally, about electric currents that may be generated in the Earth's crust in response to tectonic stress and possibly about electrochemical transport processes that should occur as a result of electric field gradients.

TIME-RESOLVED IMPACT EXPERIMENTS

In order to learn more about positive holes and their activation and propagation in rocks, impact experiments have been conducted with a range of igneous rocks, both quartz-free rocks and quartz-bearing granite. It was found that PHPs are activated in a small volume near the impact point when the rocks were impacted at a relatively low velocity of 90 m/sec. At higher impact velocities, around 1.5 km/sec, the sound waves apparently created enough transient stress to activate positive holes in the entire rock volume. The positive holes thus activated propagated through the rock as a charge cloud, causing the rock to become momentarily semiconducting. As a moving charge cloud the positive holes caused electromagnetic emission. When the charge carriers reached the surface they gave rise to positive surface potentials of the order of a few hundred mV. These surface potentials gave rise to very high electric fields across the surface-to-air interface and, hence, to corona discharges. These corona discharges may be the laboratory equivalent of earthquake lights. Where the rock was in contact with grounded metal, the electric field causes electrons to be injected. This injection can lead to resonant oscillations.

What has not yet been done is to extend these experiments to water-impregnated rocks in order to determine, how and in what way water films interact with the propagation of positive holes.

IONOSPHERIC PERTURBATIONS

A few days prior to the 21 Sept. 1999 M=7.7 Chi-Chi earthquake in Taiwan the ionospheric plasma density above the island changed noticeably. A review of over 140 earthquakes in Taiwan of M≥5 and of 12 earthquakes in central Japan during the past 10 years revealed similar ionospheric perturbations to nearly all earthquakes with a focal depth ≤35 km. Ionospheric perturbations affecting radio transmission had also been noted earlier, prior to the 1964 Alaskan Good Friday earthquake and the great 1961 Chilean earthquake. Ionosonde data available from Taiwan indicate that the ionospheric perturbation is consistent with a vertical positive electric field that arose from the ground.

These observations suggest that the ground potential may be an important physical parameter that undergoes large variations on a regional scale prior to large earthquakes. The ground potential may also undergo more subtle variations as a result of tectonically induced activation of positive holes. Ground potential changes seem to have never been measured systematically.

MAGNETIC FIELD ANOMALIES

In the weeks prior to the M=7.7 Chi-Chi earthquake and its Chia-Yi aftershock, the 8-station Taiwan magnetometer network recorded anomalous magnetic field pulses, each lasting for a few hours and reaching intensities up to 10% of the Earth's magnetic field.

The magnetic field pulses are consistent with large underground currents flowing out of a rock volume that is tectonically stressed prior to the earthquake. The magnetic field pulsations indicate that the currents do not flow out steadily but in an oscillatory manner. This points at a coupled system whereby the electric field built up by outflowing charges induces some form of countercurrents.

ELECTROMAGNETIC EMISSIONS

If currents flow in pulses, they necessarily emit electromagnetic (EM) radiation. Such EM signals have long been reported. However, because no explanation was available of how large currents can be generated in the crust, the very existence of such EM signals was considered doubtful.

OUTLOOK

Catastrophic ruptures that cause earthquakes mark the final stage of a long process during which rock volumes are subjected to progressively higher compressive stresses. The stressed rocks go through various stages of elastic deformation, plastic flow, microfracturing, and culminating in brittle failure.

During plastic flow, dislocations sweep through the minerals, activating PHPs. During micro-fracturing, billions of tiny cracks open and close explosively, each emitting a packet of acoustic wavelets. Both processes can activate PHPs and momentarily generate positive hole charge carriers.

This raises the tantalizing prospect that rock volumes subjected to increasing compressive stress generate large numbers of highly mobile positive holes. These charge carriers would flow out of the stressed rock volume, causing transient currents and a wealth of other physical phenomena.

Likewise, if the stress levels are more moderate, slow plastic deformation of rocks due to tectonic forces may still generate positive hole charge carriers in the Earth's crust. Increasing temperatures in the crust, for instance in the vicinity of a magma chamber that shows signs of inflation, may also activate positive holes in a rock halo. Understanding the behavior of positive holes may help to set up stations that can detect the transient electric currents and cationic countercurrents thus generated.

The ideas about positive holes presented here are expected to be most pronounced in situations where large rocks volumes are under compressive stress. They may also apply to other situations where the tectonic forces cause some level of PHP activation in the rocks but where the stresses are not so extreme as to lead to catastrophic rupture and earthquakes. How liquid water interferes with the generation and propagation of positive holes will require further studies.