

Charge Distribution Analysis: Studying Defects in Minerals under Minimum Perturbation Conditions.

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Important knowledge is derived from electric conductivity measurements of minerals as a function of temperature, pressure and gas fugacities. Laboratory determinations have provided pivotal information. However, natural minerals represent very complex systems and the nature of the charge carriers responsible for a given conductivity mechanism cannot be unambiguously determined by conventional measurements. The reason is that charge carrier injection/extraction across the sample/metal electrode interfaces introduce uncertainties that are sources of potential error, especially in minerals which often contain a host of defects and impurities. At the same time these defects and impurities are important for understanding the genesis of a mineral.

We developed a new method, Charge Distribution Analysis, which performs measurements without contact electrodes and thus alleviates many of the above difficulties¹). The CDA technique is highly sensitive, capable of detecting charge carrier concentrations that give rise to d.c. conductivities of the order of $<10^{-16} \Omega^{-1}\text{cm}^{-1}$. CDA provides for minimum perturbation of the sample under study. It relies on measuring the dielectric polarization in an electric field gradient ∇E_{ext} . The measurements are performed by suspending a dielectric sample (6 mm \varnothing , 1-2 mm thick) inside an inhomogeneous capacitor consisting of a cylindrical Au electrode (10 mm \varnothing , 20 mm high) at ground potential and a disk-shaped Au bias electrode (4 mm \varnothing), separated from the sample by a gap of ≈ 0.2 mm. Both the ground and bias electrodes sit in a small cup-shaped furnace (20-1000°C) with bifilar Pt windings. The force acting on the sample under \pm bias voltages (0-1000 V) is measured with a microbalance (10^{-7} g sensitivity). This force F_z^{\pm} in the z direction is:

$$F_z^{\pm} = - \int_V (\mathbf{P} \cdot \nabla) E_{\text{ext}} dV$$

where the integral over the volume V includes the sample but not the sources of the field. The polarization \mathbf{P} is given as $\mathbf{P} = \frac{\epsilon_0(\epsilon-1)}{4\pi} \mathbf{E}_{\text{ext}}$ where ϵ_0 is the permittivity and ϵ the static dielectric constant. \mathbf{P} contains four contributions, $\mathbf{P}_0 + \mathbf{P}_1 + \mathbf{P}_2 + \mathbf{P}_3$, from

- (a) the ideal dielectric consisting of polarizable atoms and bonds,
- (b) local dipoles associated with defects which may rotate but not diffuse,
- (c) mobile charges which can diffuse,
- (d) surface charges.

For a dielectric that has only \mathbf{P}_0 , \mathbf{P}_1 and \mathbf{P}_2 contributions the relation holds: $F^+ = F^-$. Because E_{ext} is proportional to the potential difference U between the electrodes, we have: $F^{\pm} \propto U^2$, meaning that, if we plot F^+ and F^- as a function of U^2 , we shall obtain straight lines passing through the origin. By contrast, when surface charges are present that make a \mathbf{P}_3 contribution, the dielectric will be either attracted to or repelled from the region of higher electric field density, depending upon the sign of the surface charge and polarity of the bias electrode. To separate the bulk contribution due to $(\mathbf{P}_0 + \mathbf{P}_1 + \mathbf{P}_2)$ from the surface contributions \mathbf{P}_3 we form the linear combinations:

$$F_{\Sigma} \equiv \frac{1}{2} (F^- + F^+) = - \frac{\epsilon_0(\epsilon-1)}{4\pi} \int_V \nabla \cdot E_{\text{ext}}^2 dV$$

$$F_{\Delta} \equiv \frac{1}{2} (F^- - F^+) = - \int_V (P_3 \cdot \nabla) E_{\text{ext}} dV$$

The advantage of the CDA over conventional conductivity techniques is that it relies solely on to-and-fro movements of charges inside the sample, avoiding complications that arise at the sample/electrode contacts through interfacial reactions and the need to inject or extract charge carriers. In addition, CDA provides information that is otherwise available only through Hall effect and Seebeck coefficient measurements, in particular about the drift mobility and sign of the majority charge carriers. Through its unique capability to measure surface/subsurface space charge layers CDA can distinguish between conductivity, due to surface contamination, and surface charge layers that build up from within a sample, due to the presence of highly mobile charge carriers with a propensity for the surface. It can even determine the internal field by which the charge layers are “glued” to the surface. Such internal fields are important in the discrimination between contaminants and charged defects that originate in the bulk.

With the help of CDA a new family of defects has been discovered in minerals from a variety of geological settings. These defects are characterized by an unusually high mobility and a strong tendency to form surface charge layers. As a consequence they give rise to a high surface conductivity which may be mistaken for contamination. At the same time these defects are reactive at the surface when reduced gases are being offered. Though often observed in prior studies that used conventional techniques for measuring the conductivity, these defects have indeed been misinterpreted as caused by surface contamination. With the advent of CDA this can be corrected and new insight may be gained in the complex history of minerals from different terrestrial and extraterrestrial environments.

This Poster presentation is intended to introduce CDA as a powerful new technique, to discuss its physical basis and demonstrate its capabilities for the study of difficult geological samples under conditions of minimum perturbation. Application of CDA to olivine, illustrating the way these new defects express themselves in conductivity measurements, will be presented elsewhere at this Conference.

- 1) Freund, M. M., F. Freund and F. Baillo. (1989) Phys. Rev. Lett. **63**: 2096-2099.