O^- in Olivine: Cause for a Pronounced Electric Anomaly around 600°C

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Electric conductivity measurements are of fundamental interest because they provide information about defects in minerals and allow to draw conclusions about the conditions prevailing during formation. In addition, electric conductivity measurements of upper mantle minerals and rocks provide much needed clues for the interpretation of geotherms and associated electric conductivity layers in the Earth or in other planets. One of the most important minerals in this context is olivine, ideally $(Mg,Fe)_2SiO_4$. A large body of laboratory studies exists that aims at correlating the electric conductivity of olivine with the formation of defects under controlled temperature, pressure and gas fugacity, simulating upper mantle conditions [1, 2, 3]. During these studies strange enhancements of the electric conductivity, often by several orders of magnitude, have been observed above 500°C [4, 5]. These anomalies are reduced and eventually disappear upon prolonged heating above 700°C in reducing CO/CO_2 atmospheres. This disappearance has led to the belief that the whole phenomenon is an artefact caused either by an unspecified surface contamination in the laboratory or by a thin carbon layer precipitated on the sample surface during measurement from the CO/CO_2 gas mixture under non-equilibrium conditions [6, 7].

We have used Charge Distribution Analysis to study the generation of charge carriers in olivine in the temperature region below 800°C. CDA is a new contact-free technique which relies on measuring the dielectric polarization of mobile charge carriers within the sample and its surface [8]. It does away with many complications and difficulties that are inherent to conventional electric conductivity techniques. CDA allows not only to determine the sign of charge carriers but also to identify surface charge layer that may develop through mobile charge carriers diffusing from the bulk of the sample to its surface.

In **Fig. 1** we show CDA data collected for a sample of olivine from San Carlos, AZ, (≈ 9 mole-% fayalite) which has been studied intensely by conventional conductivity techniques. The CDA measurements were performed in high purity Ar at 1 bar total pressure during stepwise heating to the indicated temperatures. F_Σ shown in **Fig. 1** represents the bulk contribution to the dielectric polarization which, in essence, depends on the concentration of mobile charge carrier. During cooling at rates as high as 10°C/min the depicted curves are fully reversible, at least up to 600°C. Above 600°C the reversibility degrades slightly, due to incipient oxidation in the non-buffered Ar atmosphere. **Fig. 1** clearly indicates that there is a sudden surge in the number of charge carriers which is reversible upon cooling.

The sign of the charges is positive and they build up a surface/subsurface charge layer that is depicted in **Fig. 2** by means of F^+ measured under positive bias. Each F^+ curve deconvolutes into a parabolic component which represents the ideal dielectric and a linear component which gives the surface charge. The only one type of charge carriers that can account for this particular behavior are O^- states, internally generated by the dissociation of peroxy defects. O^- are electronic charge carriers that owe their high mobility to the fact that they delocalize as positive holes on acceptor levels near the O2p-dominated valence band. The inferred presence of peroxy parent defects in olivine is probably linked to interactions during crystallization in the fluid-rich, reduced upper mantle environment. Recognizing the presence of these defects has potentially far-reaching implications for the electric conductivity of the upper mantle.

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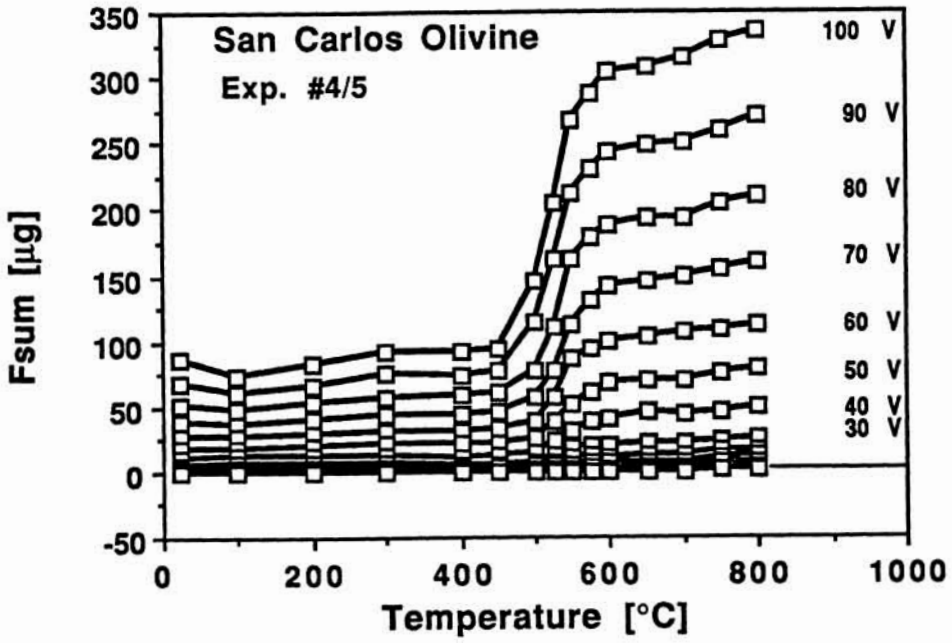

Fig. 1: Evidence of highly mobile charge carriers generated in San Carlos olivine around 600°C.
Fig. 2: Deconvolution of the F^+ signal to illustrate the formation of a positive surface charge layer.