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The effect of A-site cations on charge-carrier mobility in Fe-rich amphiboles

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Abstract

Elucidating the high-temperature behavior of rock-forming minerals such as amphiboles ($AB_2C_5T_8O_{22}W_2$) is critical for the understanding of large-scale geological processes in the lithosphere and, in particular, the development of high conductivity in the Earth's interior. Recently, we have shown that at elevated temperatures, ^{C}Fe-bearing amphiboles with a vacant *A* site develop two types of charge carriers: (1) small polarons and (2) delocalized H^+ ions.

To elucidate the effect of *A*-site cations on the formation and stability of charge carriers within the amphibole structure, here we analyzed synthetic potassic-ferro-richterite as a model Fe-rich amphibole with a fully occupied *A* site via in situ temperature-dependent Raman spectroscopy. We further compare the results from in situ time-dependent Raman-scattering experiments on pre-heated and rapidly quenched potassic-ferro-richterite and riebeckite as a model Fe-rich amphibole with a vacant *A* site.

We show that the presence of *A*-site cations (1) reduces the activation temperature of mobile polarons and delocalized H^+ cations; (2) decreases the magnitude of the polaron dipole moment; (3) slows down the process of re-localization of electrons on cooling; and (4) makes the electrons inert to rapid change in external conditions, supporting the persistence of a metastable state of pre-activated delocalized electrons even at room temperature.

Our results have important geological implications demonstrating that the *A*-site cations may control the depth of development of high conductivity in subducted amphibole-bearing rocks. Moreover, from the viewpoint of mineral-inspired materials science, our results suggest that the amphibole-structure type has great potential for designing functional materials with tunable anisotropic-conductivity properties.

Keywords: Iron-rich amphiboles, riebeckite, synthetic potassic-ferro-richterite, in situ high-temperature Raman spectroscopy, polaron conductivity, hydrogen diffusion