

Cordierite I: The coordination of Fe²⁺

CHARLES A. GEIGER,^{1,*} THOMAS ARMBRUSTER,² VLADIMIR KHOMENKO,³ AND SIMONA QUARTIERI⁴

¹Institut für Geowissenschaften, Universität Kiel, Olshausenstrasse 40, 24098 Kiel, Germany

²Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3
CH-3012 Bern, Switzerland

³Institute of Geochemistry, Mineralogy and Ore Formation, Ukrainian Academy of Science, pr. Palladina 34, 252142 Kyiv, Ukraine

⁴Dipartimento di Scienze della Terra, Università di Messina, Salita Sperone 31, 98166 S. Agata di Messina, Italy

ABSTRACT

The incorporation of Fe²⁺ was investigated in four natural cordierite samples. ⁵⁷Fe Mössbauer, single-crystal UV-VIS optical absorption, and X-ray absorption spectroscopies, as well as X-ray single-crystal diffraction were used. Mössbauer, optical, and XAS spectroscopy show that Fe²⁺ is incorporated on two different structural sites in two Mg-rich samples. Mössbauer measurements give the best quantitative measure of the amounts of Fe²⁺, but the optical spectra are the most sensitive for determinations at low concentrations and at high-bulk Fe²⁺ concentrations in cordierite. The spectroscopic data are most consistent with small amounts of Fe²⁺ (i.e., 0.02 of Fe²⁺ per formula unit) being located on a tetrahedral site rather than in the center (or off center) of the six-membered tetrahedral rings or in channel cavities. X-ray single-crystal refinements on two Mg-rich cordierites show a very small excess electron density on T₁1 and not in the channels. A third refinement on a slightly more iron-rich sample shows, in contrast, no excess electron density on T₁1. We interpret these data as indicating that small amounts of Fe²⁺ (0.01 to 0.02 atoms per formula unit) replace tetrahedral Al₁1 in cordierite, where charge balance is achieved by placing Na in the center of the six-membered rings. This substitution is consistent with the known chemistry of natural cordierites and with simple structural energetics. The identification and assignment of small amounts of Fe²⁺ on T₁1 requires spectroscopic determination or careful X-ray single-crystal refinements and cannot be achieved from composition data and structural formula calculations.