

Calcium $L_{2,3}$ -edge XANES of carbonates, carbonate apatite, and oldhamite (CaS)

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ABSTRACT

The local electronic structure and stereochemistry of calcite, aragonite, dolomite, ferroan dolomite, manganoan calcite, synthetic carbonate hydroxylapatite (CHAP), and CaS (synthetic oldhamite) have been studied using Ca $L_{2,3}$ -edge X-ray absorption near-edge structure (XANES) spectroscopy. The XANES spectra of the calcite- and dolomite-structure carbonates are identical within error of measurement, confirming the local nature of X-ray absorption at the $L_{2,3}$ edge of Ca^{2+} . The Ca $L_{2,3}$ -edge XANES spectrum of aragonite is distinct and indicates a weak crystal-field splitting of positive $10Dq$. Separate Ca1 and Ca2 sites are resolved in the XANES of hydroxylapatite and CHAP: Ca1 appears to have a very weak crystal field of negative $10Dq$, and Ca2 has a weak crystal field of positive $10Dq$. The Ca $L_{2,3}$ -edge XANES spectrum of CaS reflects both Ca and S unoccupied $3d$ states, and is used to show progressive oxidation of the sulfide on exposure to air. The $L_{2,3}$ X-ray absorption edge of $3d^0$ cations is associated with the $2p^33d^1$ excited electronic state. It is, therefore, a novel technique for studying the crystal field of K^+ , Ca^{2+} , Sc^{3+} , and Ti^{4+} , which do not have populated $3d$ orbitals in their ground state.

Keywords: XANES, calcite, aragonite, dolomite, carbonate hydroxylapatite, oldhamite