**Calcium L\textsubscript{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, andaragonite and dolomite, and synthetic carbonate hydroxylapatite (CHAP), and CaS (synthetic oldhamite) have been studied using Ca L\textsubscript{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\textsubscript{2,3} edge of Ca\textsuperscript{2+}. The Ca L\textsubscript{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\textsubscript{2,3}-edge XANES spectrum of CaS reflects both Ca and S unoccupied 3p states, and is used to show progressive oxidation of the sulfide on exposure to air. The L\textsubscript{2,3} X-ray absorption edge of 3p cations is associated with the 2p\textsuperscript{3}3d\textsuperscript{0} excited electronic state. It is, therefore, a novel technique for studying the crystal field of K\textsuperscript{+}, Ca\textsuperscript{2+}, Sc\textsuperscript{3+}, and Ti\textsuperscript{4+}, which do not have populated 3d orbitals in their ground state.

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

**Introduction**

Calcium is a major element in the Earth’s crust and mantle and an essential cation in biosystems. Carbonate hydroxylapatite (CHAP) is the dominant biomineral of vertebrates, and calcite and aragonite are similarly dominant in invertebrates. Calcium is also an essential component of leaves, and plays an important role in the biochemistry of living organisms, particularly in binding with proteins (Spirito 1983). Calcium phosphate biomaterials are extensively researched in connection with applications in dentistry (Elliott 2002) and orthopaedic medicine (Gross and Berndt 2002). Also, calcium carbonate in the crust is an important reservoir for the carbon cycle, and it may have a future role in the sequestration of atmospheric CO\textsubscript{2} (e.g., Oelkers et al. 2002; Kravtsova et al. 2004). Although the stereochemical environment of calcium in crystalline materials can be determined with some confidence using diffraction methods, there remains the challenge to develop techniques for studying the local structural environment of calcium in amorphous materials like silicate and phosphate glasses and simulated biological systems. Calcium K-edge X-ray absorption spectroscopy (XAS) has already been applied to this problem (e.g., Quartieri et al. 1995; Neuvile et al. 2004), but earlier study of the Ca L\textsubscript{2,3}-edge was hindered by limitations in instrumentation and theoretical understanding. The information on local geometry and electronic structure obtained from study of the Ca L\textsubscript{2,3}-edge complements that from the Ca K-edge. Moreover, the L\textsubscript{2,3} edge directly probes the crystal field of Ca cations, and of K and 3d transition-metal cations as well (e.g., De Groot et al. 1990).

This study presents the local electronic structure and stereochemistry of some Ca-bearing carbonate minerals (calcite, aragonite, dolomite, ferroan dolomite, andmanganoan calcite), synthetic carbonate hydroxylapatite (CHAP), and CaS (synthetic oldhamite) using Ca L\textsubscript{2,3}-edge X-ray absorption near-edge structure (XANES) spectroscopy. The Ca L\textsubscript{2,3}-edge of calcite and basic calcium phosphate (hydroxylapatite) reagent have been studied by Nafel et al. (2001) using XANES and of calcite by Garvie et al. (1995) using electron-loss near-edge structure (ELNES) spectroscopy. More recently, Ca L\textsubscript{2,3}-edge XANES has been used to study the electronic structure of CaO (Ko et al. 2007) and the transformation of amorphous CaCO\textsubscript{3} to calcite in sea urchin larval spicules (Politi et al. 2008). The present synthetic CHAP samples were from studies on the structural locations of the carbonate ion in hydroxylapatite (Fleet et al. 2004; Fleet 2009). Oldhamite is commonly associated with enstatite chondrites and enstatite acondrites (e.g., Floss and Crozaz 1990), and also occurs terrestrially as an alteration product of anhydrite. Synthetic CaS has been investigated by S K- and L\textsubscript{2,3}-edge XANES and shown to have an interesting electronic structure (Farrell et al. 2002; Kravtsova et al. 2004).

**Experimental methods**

Samples of calcium carbonate minerals were obtained from the Dana Mineral Collection of the University of Western Ontario, and included calcite from an unknown locality (collection no. 2852), aragonite from Tsunebe, Namibia (no. 1249), dolomite from Ottawa County, Colorado (no. 1730), ferroan dolomite from Charlemont, Massachusetts (no. 403), and manganoan calcite from Ouray, Colorado (no. 2651). We also investigated analytical grade CaCO\textsubscript{3} (Alfa Aesar Co.). All carbonates were characterized by X-ray powder diffraction; compositions of complex carbonates estimated from unit-cell parameters are given in the footnote to Table 1. Carbonate hydroxylapatite (CHAP) was synthesized at 2-4 GPa and 1400 °C in a piston-cylinder apparatus (Fleet et al. 2004), and characterized by powder X-ray diffraction and Fourier transform infrared spectroscopy (FTIR). CHAP samples PC16, PC17, and PC18 were also investigated by X-ray structure...