

Evaluation of Europium Oxidation State and Anomalous Partitioning Behavior in Intrasectorally Zoned Apatite Using Wavelength Dispersive Micro-XANES

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Introduction

Heterogeneities in crystal surface structure can strongly influence trace element incorporation during apatite growth.^{1,2,3} Rakovan and Reeder^{1,2} found that rare earth elements (REEs) were segregated during growth between symmetrically nonequivalent steps on the {100} crystal face of apatite, leading to intrasectoral zoning (Fig. 1). The partitioning behavior between subsectors associated with the nonequivalent growth steps was found to be correlated with the size of the REE ion relative to Ca²⁺, for which it substitutes in the structure. Rare earth elements with an ionic radius larger than Ca²⁺ (e.g., La³⁺) are enriched in the [001] subsector relative to the <011> subsectors. All of the REEs analyzed, except Eu, with ionic radii smaller than Ca²⁺ (e.g., Sm³⁺) are depleted in the [001] subsector relative to the <011> subsectors (Fig. 2). Europium is the only REE that was not found to show a differential distribution between subsectors. This anomalous behavior was pos-tulated to be the result of roughly equivalent proportions of Eu²⁺ and Eu³⁺ in the crystals, assuming that the distribution coefficients for Eu²⁺ and Eu³⁺ are approximately the inverse of one another.² In apatite, the ionic radii of Eu²⁺ is larger than Ca²⁺, whereas Eu³⁺ is smaller. If Eu²⁺ follows the same partitioning behavior as the trivalent REEs that are larger than Ca, it will be enriched in the [001] subsector; the opposite is true of Eu³⁺. To determine the presence and relative concentration of Eu²⁺ and Eu³⁺, Eu x-ray absorption near-edge structure (XANES) spectroscopy was conducted by Rakovan et al.⁴ In that study a bulk powder was analyzed. To better understand the role of crystal surface structure in trace-element incorporation into apatite, we have conducted spatially resolved Eu micro-XANES measurements between structurally different regions of the surface (vicinal faces of hillocks) and their associated subsectors of single crystals studied by Rakovan and Reeder.²

Experimental Methods

To determine the concentration and distribution of Eu²⁺ and Eu³⁺ between compositionally distinct subsectors in apatites from Llallagua, Bolivia, Eu micro-XANES line scans were conducted over symmetrically nonequivalent vicinal faces of growth hillocks on the (100) surface (e.g., Fig. 1). A total of 10 points were collected within each of the subsectors under the two vicinal faces, for a total of 20 points per line scan. X-ray absorption measurements were made at station 13-ID of the Advanced Photon Source at Argonne National Lab. A water-cooled Si(220) channel-cut monochromator was used to select incident x-rays of the desired energy from an undulator source. A 250 x 250 μm monochromatic beam was focused to 6x6 μm at the sample position using Kirkpatrick-Baez mirrors coated with rhodium. These mirrors were pitched to 6 μrad, and so also served to reject harmonics from the monochromator. Because of interference from

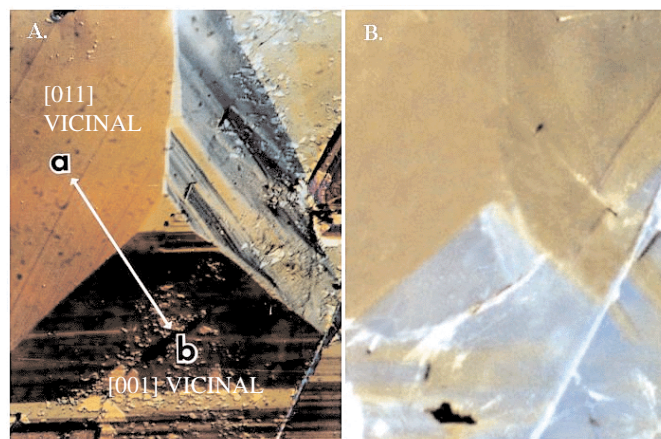


FIG. 1. A) Differential interference contrast photomicrograph of a three-sided growth hillock on the (100) face of a Llallagua apatite. The line a-b indicates the position of a XANES line scan. B) Cathodoluminescence photomicrograph of the area shown in A. Differential luminescence correlated with the different vicinal faces of the growth hillock indicates intrasectoral zoning.

the high concentration of Mn, which is almost ubiquitous in natural REE-containing apatites, conventional XANES detection of Eu is not possible. To overcome this problem, fluorescence x-rays from the apatite sample were detected using a wavelength dispersive spectrometer (Microspec WDX600) from Oxford Instruments, Inc. The maximum energy resolution of this spectrometer is about 6 eV at 6000 eV. XANES scans were taken from 6932 to 7034 eV with a 0.25 eV step. Data were collected at 5 seconds per step, and the integrated fluorescence was normalized to the incident intensity.

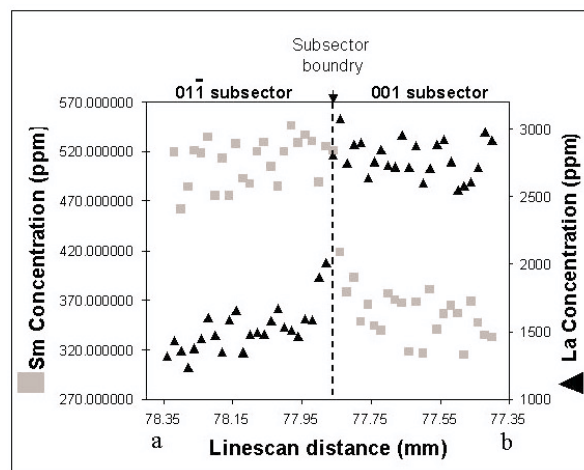


FIG. 2. Concentration of La and Sm determined by xynchrotron x-ray fluorescence microanalysis in a line scan (indicated in Fig. 1A) between structurally different vicinal faces of a growth hillock on the (100) face of a Llallagua apatite. Data from Rakovan and Reeder.²

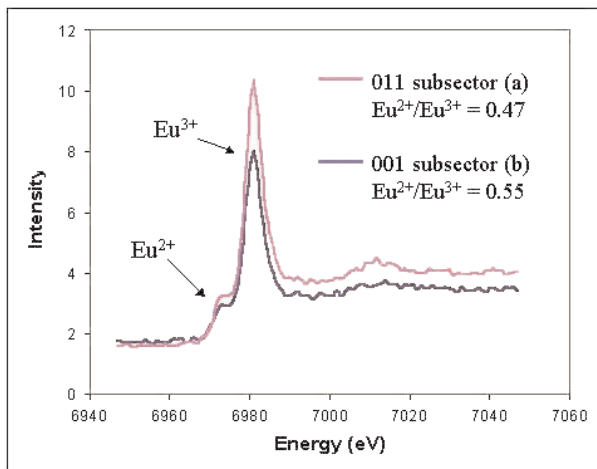


FIG. 3. XANES spectra of the Eu L3-edge taken from the [011] and [001] subsectors of the Llaguna apatite.

Results

A total of 6 line scans over 3 individual growth hillocks from two different [100] faces were made. Figure 3 shows XANES spectra of the Eu L3-edge taken from the [011] and [001] subsectors, regions under vicinal faces a and b, respectively, of the growth hillock in Fig. 1. Each spectra is the sum of six individual spectra from each subsector taken along the line indicated in Fig. 1. The $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios calculated from peak heights and corrected for transition probabilities⁵ are 0.55 in the [001] subsector and 0.47 in the [011] subsector. X-ray absorption near-edge structure measurements were made both parallel to and perpendicular to the c crystallographic axis of the apatite to assess possible polarization differences.

Discussion

The XANES data in Fig. 3 show that the total concentration of Eu is larger in the [011] subsector relative to the 001 subsector; however, this difference is smaller than the variation found with-

in a single subsector and thus is not indicative of intrasectoral zoning. The $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios are very similar in the two sectors which would not be expected if differential incorporation with opposite partitioning trends occurred for the two states during crystal growth. The anomalous lack of intrasectoral zoning of Eu^{2+} and Eu^{3+} is difficult to explain given that the Llaguna apatites exhibit intrasectoral zoning of all of the other REE.² One possibility that is being investigated is that Eu^{2+} and Eu^{3+} were differentially incorporated during growth, but post growth processes changed the oxidation state of Eu throughout the crystal to an equilibrium ratio measured here.

XANES spectra collected both parallel to and perpendicular to the c crystallographic axis of the apatite showed no differences indicating a lack of polarization effects.

Acknowledgments

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