

XAFS study of the coordination and local relaxation around Co^{2+} , Zn^{2+} , Pb^{2+} , and Ba^{2+} trace elements in calcite

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ABSTRACT

Analysis of divalent Co, Zn, Pb, and Ba XAFS spectra of synthetic and natural calcite samples containing trace concentrations of these heavy metals confirms their substitution in the unique Ca site in octahedral coordination with varying degrees of local distortion. The existence of each trace metal at the single site in the bulk crystal is significant in view of previous studies showing that these trace elements are incorporated differentially at multiple, structurally distinct surface sites occurring in nonequivalent growth steps on calcite surfaces. The octahedral coordination for Ba is particularly noteworthy because of its large size (35% larger than host Ca) and the fact that it rarely exists as a major constituent with such a low coordination number.

Analysis of the local distortion and relaxation around the impurities shows a nearly complete contraction of the structure around Co^{2+} and Zn^{2+} . The Co-O and Zn-O first-shell distances are only slightly longer than in CoCO_3 and ZnCO_3 , with a site compliance of ~80–90%. Displacements of higher shells relative to those in calcite decrease rapidly, but irregularly, over a short distance, and the relaxation may be largely confined within 6–7 Å of the impurity. The dilation around the large Pb^{2+} and Ba^{2+} ions in calcite also shows a high degree of site compliance (85–90%). Relaxation around Pb and Ba also appears to be restricted, but extending further for Ba than for Pb. The limited observations suggest that compliance of the octahedral site in calcite is larger than for the cation site in the rocksalt structure. The high compliance for the metal site in calcite may reflect the corner-sharing topology of the structure and is also probably the reason that calcite shows such a wide range of isovalent substitutions in nature. The findings also provide a direct indication of the local strain associated with a dilute substitutional solid solution.