Carbonate in igneous and metamorphic fluorapatite: Two type A and two type B substitutions

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ABSTRACT

Fourier transform infrared (FTIR) microspectroscopy of igneous and metamorphic fluorapatites shows measurable carbonate in all specimens. All specimens show the presence of the type A1 and A2 (carbonate for columnar anion, Fleet et al. 2004) and the type B (carbonate for phosphate) substitutions in the carbonate ν3 domain (1400–1600 cm−1). This is the first report of the type A2 substitution in naturally occurring apatites. Spectra also show ν2 carbonate peaks that have not been unambiguously assigned. In some spectra, two doublets can be resolved, indicating two different B-type substitutions. The presence of multiple B-type substitutions in infrared spectra is in accord with the recognition of different mechanisms of substitution of the carbonate for the phosphate tetrahedron and explains the scatter observed in published data.

Consideration of crystal structural details shows site symmetry of the carbonate group to be C3v rather than C5v, as has been previously assumed. Decent of C3v symmetry from D2h through C5v lifts degeneracy and preserves orthogonality of ν2 doublets. Extra type B peaks are not due to lower site symmetry, and Davydov splitting can be ruled out.

Results demonstrate that carbonate contents of apatites from pegmatites and cumulate mafic magmas are well within analytical capability, opening another line of inquiry into CO2 behavior in igneous and metamorphic rocks. The type A1 substitution shows the most promise for thermodynamic calculations that would allow extraction of CO2 activities. Analyses show similar ratios of water to carbon dioxide activities recorded in pegmatite apatites.

Keywords: IR spectroscopy, pegmatites, analysis, chemical (mineral), thermodynamics, crystal structure

INTRODUCTION

Carbon dioxide (CO2) is the most elusive of magmatic, hydrothermal, and metamorphic gases. Measurement of CO2 in igneous rocks is presently limited to analysis of melt inclusions or fresh volcanic glass. Fluid inclusions in quartz from metamorphic or hydrothermal environments may also contain CO2. Few magmatic and metamorphic minerals can incorporate CO2 as carbonate (CO32−), and none are as ubiquitous as apatite.

Apatite, Ca5(PO4)3(F,Cl,OH), might provide a mineralogical recorder of carbon dioxide fugacities (or activities) in environments where melt inclusions or fluid inclusions are absent, or complement inclusion data. Biogenic apatites and apatites from phosphorite deposits have been long known to incorporate carbonate (CO32−), and none are as ubiquitous as apatite.

The details of carbonate substitution into the apatite structure are one of the more persistent problems in the study of organic and inorganic apatite. The study of carbonate in large, well-crystallized specimens of apatite illuminates several of the problems involved with interpretation of this substitution.

SPECTROSCOPY AND CRYSTALLOGRAPHY OF CARBONATE IN APATITE

Point symmetry for the unperturbed carbonate ion is D2h, and shows six normal modes: a symmetric stretch (ν1, Raman active), an out-of-plane bend (ν3, infrared active), an antisymmetric stretch (ν2, Raman and infrared active), and in-plane bend (ν4, Raman and infrared active). The ν1 and ν2 modes are doubly degenerate. If symmetry is reduced to C3v, by the presence of a single non-equivalent O atom (Adler and Kerr 1963; Elliott 1965, 1994) degeneracy is lifted and the ν1 and ν2 modes appear as doublets. All bending and stretching modes in C3v symmetry are Raman and infrared active. If all three O atoms in the carbonate group are non-equivalent, symmetry is further reduced to C3. The assumption of C3v symmetry for the carbonate was initially made for convenience (Elliott 1965). New data require a re-examination of the substitution mechanisms and the site symmetry of the carbonate group.

The type A site is identified as a substitution for a columnar anion, (F, Cl, or OH) (Elliott 1965; Suetsugu et al. 2000; Fleet and Liu 2003, 2005; Fleet et al. 2004), charge balanced by a variety of means including vacancies on an adjacent columnar anion site (Schramm et al. 2001). Recent studies have shown that there are two configurations of carbonate ions in the columnar site (Fleet and Liu 2003, 2005; Fleet et al. 2004). The more commonly recognized type A (A1 of Fleet and Liu 2003, 2005;