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Radiation-induced defects in apophyllites. I. The NH_2 free radical in fluorapophyllite

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Abstract: The NH_2 free radical, which is one of the most studied triatomic molecules and is widely used as spin labels in biophysical and biomedical research, has not been reported in mineral lattices. Fourier-transform infrared (FTIR) spectrum supports electron-microprobe analyses that fluorapophyllite on the cavity walls in a phonolite (North Bohemia, Czech Republic) contains ammonium NH_4^+. Powder and single-crystal electron paramagnetic resonance (EPR) spectra of this fluorapophyllite, with and without γ irradiation, disclose at least four paramagnetic defects, including two previously reported VO^{2+} centers, the NH_2 free radical and an oxygen-associated center. The spin-Hamiltonian parameters of the NH_2 free radical have been determined from single-crystal EPR data and show that this molecule is oriented parallel to (and rapidly rotated about) the crystallographic **c** axis. The NH_2 free radical in fluorapophyllite, most likely formed from radiolysis of the NH_4^+ ion, remains stable after annealing at 300 °C, but is bleached at 340 °C.

Key-words: fluorapophyllite, layer silicates, single-crystal EPR, radiation-induced defects, NH_2 free radical, motional effects.

Introduction

Radiation-induced defects in layer silicates (*e.g.*, kaolinite, dickite, illite, and montmorillonite) have received considerable interests, because they are sensitive dosimeters for determining and monitoring the migration of radionuclides in the Earth's surface environments and have direct relevance to long-term nuclear waste disposal (*e.g.*, Clozel *et al.*, 1994; Allard & Muller, 1998; Götze *et al.*, 2002; Allard *et al.*, 2003, 2007; Sorieul *et al.*, 2005; Morichon *et al.*, 2008). For example, Clozel *et al.* (1994), on the basis of a detailed powder electron paramagnetic resonance (EPR) spectroscopic study, distinguished three radiation-induced defects in kaolinite: Centers A and A′ are trapped holes on apical oxygen from Si–O bonds, and Center B is a hole trapped on an oxygen shared by two Al octahedra. Clozel *et al.* (1994) used EPR spectra measured on oriented films to demonstrate that Centers A and A′ have orthogonal orientations. They also showed that the hyperfine structure of Center B arises from interaction with two equivalent ^{27}Al nuclei ($I = 5/2$ and natural isotope abundance = 100 %). Confirmation of these structural models requires additional data: *e.g.*, (1) localization of the unpaired spin on a single oxygen atom, (2) characteristic hyperfine structures arising from interaction with a ^{29}Si nucleus (*i.e.*, Centers A and A′), and (3) defect orientations and their relationships to specific bond and other symmetrical directions in the ideal structures. All of these data can be obtained by analysis of single-crystal EPR spectra but are missing for radiation-induced defects in layer silicates, because of the fact that these minerals invariably occur in "clay" sizes.

Apophyllites [$(K,Na)Ca_4Si_8O_{20}(F,OH)\cdot 8H_2O$, *P*4/*mnc*] consist of tetrahedral SiO_4 sheets alternating with layers of K, Ca, F and H_2O (Colville *et al.*, 1971; Rouse *et al.*, 1978; Pechar, 1987) and are analogues of layer silicates (Aldushin *et al.*, 2004; Chen *et al.*, 2007). Apophyllites usually occur as large crystals that are amenable to single-crystal EPR studies. Therefore, detailed structural information for radiation-induced defects in apophyllites obtainable from single-crystal EPR studies can be used for better understanding of similar defects in other layer silicates. Accordingly, we initiated a single-crystal EPR study on a suite of natural apophyllites with or without γ irradiation. Results reported herein show that a specimen of ammonian fluorapophyllite contains at least four paramagnetic centers. These centers correspond to two previously reported VO^{2+} centers (Bershov & Marfunin, 1965; Vassilikou-Dova & Lehmann, 1988), a new NH_2 free radical and a new oxygen-associated center. This contribution focuses on the quantitative characterization, formation, and thermal stability of the NH_2 free radical, which has never been reported to occur in mineral lattices. The oxygen-associated center, which is particularly relevant to radiation-induced defects in layer silicates (Clozel *et al.*, 1994; Allard *et al.*, 2003), is better resolved in a sample of hydroxylapophyllite and will be dealt with in a subsequent contribution.

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