

Mechanism of CO_3^{2-} substitution in carbonate-fluorapatite: Evidence from FTIR spectroscopy, ^{13}C NMR, and quantum mechanical calculations—Discussion

Y. NATHAN

Geological Survey of Israel, 95501 Jerusalem, Israel

The carbonate substitution in apatite continues to provoke controversies. In a recent paper, Regnier et al. (1994) challenged the existence of the hypothetical CO_3F^{3-} ion in carbonate-fluorapatite (francolite) and concluded that it has reached its demise approximately 55 yr after it was first proposed (Borneman-Starinkevitch and Belov 1938). Nevertheless, it is necessary to clarify some points before agreeing with all of the paper's conclusions.

The two samples used in the study are not very appropriate for the purpose. The formula of the synthetic sample is given as $\text{Ca}_{10}(\text{PO}_4)_{5.64}(\text{CO}_3)_{0.244}(\text{F},\text{OH})_{2.587}(\text{H}_2\text{O})_{4.18}$.

OH, determined from charge-balance considerations, is claimed to account for 27% of the monovalent positions. This sample has low carbonate substitution because of the low pH of the experiment; it is also different from most natural samples because of the relatively high OH content. Furthermore, if indeed 27% of the monovalent positions are occupied by OH, it is incorrect to calculate the carbonate content from the $\Delta 2\theta$ difference. Both the equations of Gulbrandsen (1970) and Schuffert et al. (1990) break down with OH substitution for F because OH substitution increases the value of the *a* axis, whereas carbonate substitution decreases its value. Therefore, either the OH or the CO_3^{2-} content (or both) is wrong in the formula of the synthetic sample.

The formula of the natural sample is given as $(\text{Ca}_{4.50}\text{Mg}_{0.06}\text{Na}_{0.20}\text{Sr}_{0.01})(\text{PO}_4)_{2.17}(\text{CO}_3)_{0.57}(\text{SO}_4)_{0.18}\text{F}_{0.97}$. This sample, too, has no nonstoichiometric F, again not exactly the best type of sample for demonstrating the presence of CO_3F^{3-} . The formula as given is not balanced, and there is a possibility that OH is present (up to 0.36 pfu, again some 27% of the monovalent positions). If the OH content is correct, the question arises, How was the CO_2 content determined? Furthermore, it should be proved for both samples that OH^- is actually replacing F^- in the structure (along the *c* axis). The only evidence given in the paper is the presence of "a very weak band at 740 cm^{-1} " and "a faint absorption band at 3570 cm^{-1} " (p. 812). Both bands were reported for the synthetic sample only; nothing was reported for the natural sample. It should be noted that 3570 cm^{-1} is too high for an OH band in a fluor-hydroxy-carbonate-apatite if there are fewer OH^- than F^- ions; in this environment the band is near 3540 cm^{-1} (Baumer et al. 1985; Elliot 1994, p. 175–177). Furthermore, it is almost impossible to detect this band without heating the sample because of the presence of a strong, wide H_2O absorption band in this region.

In the classical study of natural carbonate-fluorapatite

by McClellan and Lehr (1969), 98 of the 110 samples studied contained more F^- ions per unit cell than the theoretical two for fluorapatite, showing clearly that the samples examined by Regnier et al. (1994) are not representative of most natural carbonate-fluorapatite.

The paper of Regnier et al. (1994) also implies that nonstoichiometric F is not the main factor determining the preservation of electroneutrality in carbonate-fluorapatite: "However, these results seem to be ambiguous. Okazaki (1983) and Jahnke (1984) found no clear positive relationship between the F^- content and the amount of CO_3^{2-} incorporated during apatite precipitation" (p. 809). In this respect, the facts are not ambiguous. There is a clear correlation in natural carbonate-fluorapatite between nonstoichiometric F and structural CO_3 ; see Figure 1, which shows an excellent correlation ($R^2 = 0.996$). The values in Figure 1 were taken from Table 4 of McClellan (1980), and the F content above that needed to fill the monovalent sites along the *c* axis was considered nonstoichiometric. The reason for the choice of samples is that several duplicate analyses were performed for each of these samples, and these analyses were used as internal standards at the Tennessee Valley Authority (TVA) and the International Fertilizer Development Center (IFDC). Furthermore, heating experiments (Lehr et al. 1968; Mathews and Nathan 1977) clearly indicate that the nonstoichiometric F is expelled together with structural CO_2 , proving their interrelationship (at least in regard to charge).

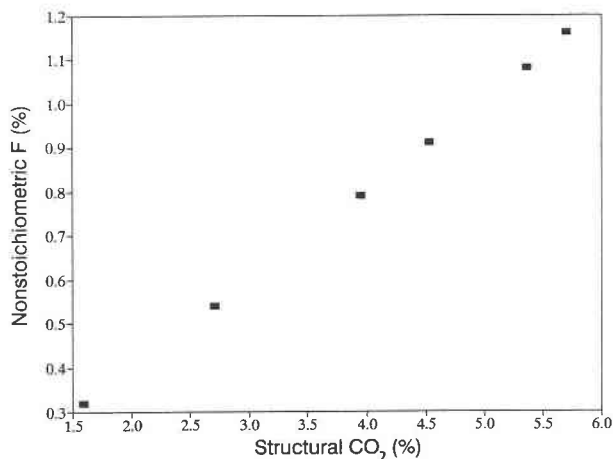


FIGURE 1. Relationship between nonstoichiometric F and structural CO_2 in carbonate-fluorapatite.

Although nonstoichiometric F is the primary means of maintaining electroneutrality after the occurrence of the CO₃ substitution, it accounts for only about 40% of this value (McClellan and Lehr 1969); other substitutions (or vacancies) account for the remaining 60%.

All of the above arguments should not be understood to mean that the CO₃F³⁻ ion exists. The existence of this ion has been thought improbable because the close proximity of CO₃²⁻ and F⁻ ions, both with negative charges, violates Pauling's rule (Elliot 1994, p. 199). Finally, there is no contradiction between the correlation of nonstoichiometric F and structural CO₃²⁻ and the nonexistence of the CO₃F³⁻ ion.

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