

## Mechanism of $\text{CO}_3^{2-}$ substitution in carbonate-fluorapatite: Evidence from FTIR spectroscopy, $^{13}\text{C}$ NMR, and quantum mechanical calculations—Reply to Nathan

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In the critical comment by Nathan (1996), the author essentially claims that the samples used in our study (Regnier et al. 1994) were not very appropriate to demonstrate the absence of  $\text{CO}_3\text{F}^{3-}$ . Furthermore, Nathan argues that we challenged the hypothesis of excess nonstoichiometric F as the main factor for preserving electroneutrality in natural fluorapatite.

We fully disagree with the first statement. The chemical composition of the synthetic sample is very pure and exhibits definite nonstoichiometric amounts of excess monovalent anions. The composition calculated from the stoichiometry of carbonate-fluorapatite, charge balance, and our chemical analyses is  $\text{Ca}_5(\text{PO}_4)_{2.82}(\text{CO}_3)_{0.18}(\text{F} + \text{OH})_{1.18}$ . Therefore, even though the sample has low carbonate substitution (to prevent precipitation of calcite, our syntheses were conducted at comparatively low pH), to obtain charge balance there must be an excess of nonstoichiometric F + OH ions. We do recognize that both our  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  contents were determined only roughly. Nevertheless, the calculated composition of the synthetic material given above results in a  $\text{CO}_3$  content (2.2%) that agrees rather well with our direct measurements on the basis of  $\Delta 2\theta$  differences (1.4%). Also, it is unreasonable to assume that all the excess of monovalent anions is represented by  $\text{OH}^-$  alone, with no excess  $\text{F}^-$ . Finally, our sample exhibits all the spectral characteristics of the substitution of carbonate for phosphate in apatite.

The natural sample also has appreciable nonstoichiometric monovalent anions. The chemical composition given in our paper is independent of any charge-balance requirement, and if one considers that electroneutrality is essentially maintained by (nondetermined)  $\text{OH}^-$ , the stoichiometric formula of the natural sample is given as

$\text{Ca}_{4.5}\text{Mg}_{0.06}\text{Na}_{0.2}\text{Sr}_{0.01}(\text{PO}_4)_{2.17}(\text{CO}_3)_{0.57}(\text{SO}_4)_{0.18}(\text{F} + \text{OH})_{1.33}$ , which has sufficient amounts of  $\text{CO}_3^{2-}$  and excess  $\text{F}^- + \text{OH}^-$  to be appropriate for this study.

The second statement must be clarified. Nathan argues that we disagreed with the idea that nonstoichiometric F is the main factor that preserves electroneutrality in carbonate-fluorapatite, referring to our paper's introduction. In that section, however, the main argument we wanted to stress was the fact that, from the physico-chemical point of view, the formation of  $\text{CO}_3\text{F}^{3-}$  as a structural ion is certainly not a likely mechanism to maintain charge balance. Furthermore, if we used a conditional form in the last section of our paper where we discussed the excess nonstoichiometric F hypothesis, it was because (as stated in Nathan's comment), other substitution mechanisms could also maintain electroneutrality.

In conclusion, we agree with the many observations showing a clear correlation between nonstoichiometric F and structural  $\text{CO}_3^{2-}$  in carbonate-fluorapatite, but we challenge the existence of a  $\text{CO}_3\text{F}^{3-}$  ion (or a  $\text{CO}_3\text{OH}^{3-}$  ion) in natural apatites. As clearly demonstrated in our paper, these statements are not contradictory.

### REFERENCES CITED

- Nathan, Y. (1996) Mechanism of  $\text{CO}_3^{2-}$  substitution in carbonate-fluorapatite: Evidence from FTIR spectroscopy,  $^{13}\text{C}$  NMR, and quantum mechanical calculations—Discussion. *American Mineralogist*, 81, 513–514.
- Regnier, P., Lasaga, A.C., Berner, R.A., Han, O.H., and Zilm, K.W. (1994) Mechanism of  $\text{CO}_3^{2-}$  substitution in carbonate-fluorapatite: Evidence from FTIR spectroscopy,  $^{13}\text{C}$  NMR, and quantum mechanical calculations. *American Mineralogist*, 79, 809–818.

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