Aspects of Quantitative Determination by Ion Probe of Fluorine Concentrations in Apatites

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In studies of F concentrations in apatite crystals by means of secondary ion micro-analysis, it is found that even in a sample with a known and constant F/Ca ratio the recorded ratios of the F and Ca secondary ion currents can vary widely, depending on the experimental conditions of primary bombardment. An attempt has been to explain this behaviour and to devise a way to obtain quantitative atomic F to Ca ratios independent on measuring conditions. Simultaneous recording of the mass peaks of F^+, Ca^+ and another matrix ion (P^+ or C^{++}) appears to offer a solution of the reproducibility problem. This is demonstrated by ion probe measurements under varied conditions in three groups of materials where the F concentrations had previously been determined by macroscopic methods: apatite crystals with about 3% F, whale teeth of about 10^{-1} % F, and human enamel ob about 10^{-2} % F.

For the study of dilute elements in solids, the secondary ion microanalyzer ("ion probe") is an attractive instrument. As regards the analysis of fluorine in geo- and biological ceramics, the concentrations are often so small that the sensitivity of other methods, such as electron microprobe[1], is only just sufficient for detection. With the ion probe, the detection limits for F in apatite are very low; using a commercial Cameca IMS 300 instrument under standard analytical conditions[2], one could readily detect concentrations of the order of 1 ppm. When attempting quantitative interpretation of the observed data, however, specific problems are encountered. The proportionality factors between the observed secondary ion currents and the element concentrations depend on the ionization efficiencies. These are different for each observed element, and moreover are functions of the nature and energy of the bombarding species as well as of the nature and surface conditions of the matrix. Although certain internal-calibration methods of quantitative evaluation have been proposed[3], the use of external standards appears unavoidable for practical purposes at today's stage. Even with good standards, care has to be taken to ensure reproducible conditions of bombardment, vacuum, sample orientation, surface roughness, etc. In the ion probe analysis of trace elements in metals[4], such precautions yielded good results, especially when continuously comparing the ion current of the impurity with that of a matrix element.

In a project intended to explore the applicability of ion microanalysis to studies of fluorine in apatites[2] we decided to use negative oxygen ions as primaries, and to record ion current peaks in the mass spectrum of the positive secondaries. The first task comprising the subject of the present report was to compare the peaks of $^{19}F^+$ with those of $^{20}Ca^{++}$ from three groups of well-defined and chemically analyzed apatite standards, and to observe the reproducibility of the ion current ratios under variable intensities of primary beam and variable locations on and depths in the matrix, maintaining other experimental parameters under the normal analyzing conditions of the IMS 300 instrument.

The standards utilized were the following:

a) A homogeneous apatite crystal with a measured content of 38.6 weight % Ca and 3.17% F; the F/Ca ratio guaranteed to be $(8.2 \pm 0.2) \times 10^{-2}$.

b) Fragments of dentine and cement of a whale tooth; the dentine has average concentrations of about 23.5% Ca and 780 ppm F, the cement roughly 18% Ca and 1000 ppm F. The F/Ca ratios were measured to, respectively, $(3.0 \pm 0.4) \times 10^{-3}$ and $(5.2 \pm 0.7) \times 10^{-3}$.

c) Two sections of human tooth enamel, sufficiently far from the front surface to ensure only slow variations in F content. The Ca content of the enamel is about 35% and chemical analysis yielded about 90 ppm F. The F/Ca ratio was measured to 1.9×10^{-4}, respectively to 2.8×10^{-4}, with an accuracy of the order of 20%.

The results can be seen in Figure 1. In the left half of the diagram one shows also the ion current ratios obtained from the matrix elements P and Ca; the weight ratio of these elements is about the same in all apatites, $P/Ca \cong 0.46$. The ratios of the ion currents are, however, seen to vary quite considerably for a given sample, dependent on the prevailing experimental conditions of analysis. In the right half of the diagram the $^{19}F^+/^{20}Ca^{++}$ ratios are, instead, plotted against the ratio of two calcium peaks, $^{43}Ca^+/^{20}Ca^{++}$. Here, too, a very considerable scatter can be seen. The observed fluorine-to-calcium ratios in Fig. 1 range from about 0.17 to 1.0 for the crystal, from 0.019 to 0.06 in the whale tooth. Obviously, to establish a quantitative conversion from ion ratios to atom ratios it is by no means sufficient to possess calibrated external standards.

A way out of the difficulties is, however, suggested by the interdependence, clearly seen in Fig. 1, between the impurity-to-matrix ion ratios (F^+/Ca^{++}) and the matrix-to-matrix ion ratios (P^+/Ca^{++}, resp. Ca^+/Ca^{++}). All the points lie, with fair approximation, on straight lines, each line corresponding to the particular F concentration in the respective sample. Thus, if one knows not only the chemical composition of the standard, but also the slope of the F^+/Ca^{++} vs P^+/Ca^{++} resp. Ca^+/Ca^{++} line at that particular composition, a quantitative calibration is possible. Different F/Ca weight ratios then correspond to different calibration lines rather than to distinct values of ion current ratios.

Within experimental accuracy limits the three lines in each half of the diagram can be said to be parallel. The scale of F/Ca weight ratios is perpendicular to these lines, and its values for points between the lines can be obtained by interpolation. The scatter of the F/Ca ratios determined in this way may be considered as acceptable in this exploratory study. E. g. for the apatite crystal, the points in the left half of the diagram show a 55% deviation from the arithmetic mean of F^+/Ca^{++}, but only about 20% deviation of F/Ca from "best line".

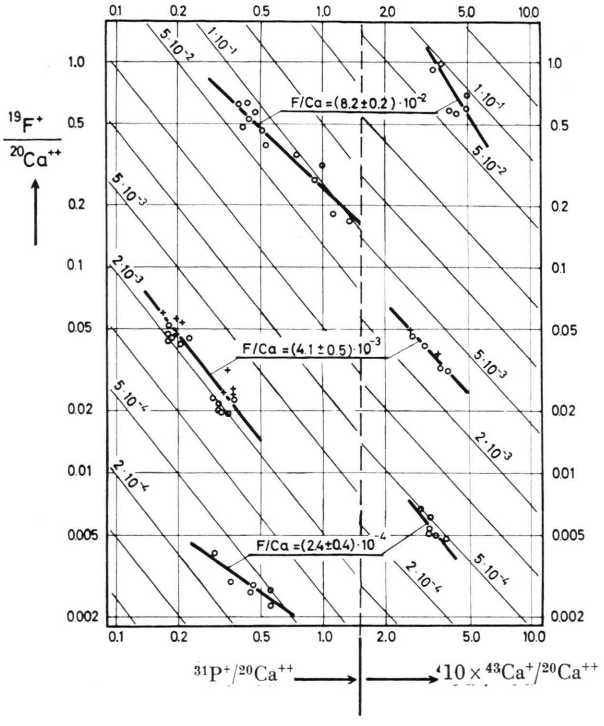

Fig. 1. Variation of the ion current ratios F^+/Ca^{++} vs the ratios P^+/Ca^{++} (left) and Ca^+/Ca^{++} (right). The weight ratios, quoted with error margins, denote, from high to low, an apatite crystal, whale tooth standards, and human enamel. The points marked by crosses in the whale groups denote cement, the rest dentine.

The interpolating values in the figure (parallel sloping lines), calibrating the whole range of F concentrations, were constructed in such a way that the composition of the chemically most reliably known standard (i. e. the apatite crystal) was taken as concentration reference, while the slope was accepted from the set where the greatest number of points was available (i. e. the whale standards). With this calibration the computed F/Ca weight ratio for the whale samples turns out to be on an average 2.5×10^{-3} according to the left half of the diagram, about 3.5×10^{-3} according to the right half. This is to be compared with the quoted ratio of $(4.1 \pm 0.5) \times 10^{-3}$ obtained by macroscopic chemical analysis. As expected, the cement points lie somewhat higher than the dentine points. For the human enamel samples one finds 3.5×10^{-4} and 4.5×10^{-4}, to compare with $(2.4 \pm 0.4) \times 10^{-4}$ of macroscopic analysis. Good order-of-magnitude agreement may thus be seen, but the whale results appear low by about 30%, those from human enamel high by about 60%.

The mutual agreement between the results of the right half and those of the left half of the diagram is quite good. The slight discrepancies may be due to the circumstance that teeth probably have a somewhat lower P/Ca ratio than the crystal. A correction for this would shift the two sets of points on lower left a little towards the right.

In the points with the lowest F concentration an error may possibly have been introduced by the absence of a counting dead-time correction. At high F/Ca ratios the pulse rates due to F and to Ca are of about the same magnitude and the dead-time losses approximately cancel out in the ratio. For the human enamel points, however, only the Ca current (about 300 times that of F) is affected by dead-time, and so the recorded ratio appears too high. A correction would bring the computed F/Ca ratios nearer to the given values of the enamel standards.

An attempt shall be made to discuss the observed near-linear interdependence of F^+/Ca^{++} on one hand, P^+/Ca^{++} or Ca^+/Ca^{++} on the other. This appears possible in terms of a plasma model, reminiscent of that proposed by Andersen and Hinthorne[3], avoiding, however, far-reaching employment of tabled thermodynamic data. At the bombarded spot, the ejected material is thought to exist partly as ions, partly as atoms, this "plasma" approximately obeying the laws of equilibrium thermodynamics. The chemical composition of the plasma is assumed the same as that of the bombarded species, i. e. matter is ejected quantitatively. The ratio of singly ionized to neutral atoms of a species per unit volume in the plasma, A^+/A, is given by a Saha-Eggert type equation[5]

$$\ln(A^+/A) = K_A(T) + \ln(T^{1.5}/n) - (I - \Delta E)_A/R\,T\,, \qquad (1)$$

where $K(T)$ is a term, only slightly temperature dependent, containing the ratio of the internal partition functions of the charged and neutral states, n is the density of electrons in the plasma, I the ionization potential, and ΔE the coulomb-interaction correction to I. Putting $I - \Delta E = E$, one may write for the present problem

$$\ln(F^+/F) = K_F(T) + \ln(T^{1.5}/n) - E_F/R\,T\,, \quad (2\text{ a, b, c})$$

and similar expressions replacing F with P and Ca. Subtracting 2 b from 2 a, one gets

$$\ln(F^+/P^+) = \ln(F/P) + \Delta K_{F,P}(T) - (E_F - E_P)/R\,T\,. \qquad (3)$$

One can now see that, especially on account of the last term in Eq. (3), a sample with a given weight ratio F/P may well exhibit a scatter in the ion ratio F^+/P^+, if differences in bombardment intensity and surface conditions make the effective plasma temperature T vary. It is hardly surprising that this effect should be particularly noticable on insulators, with small tendency to lead away locally developed heat.

In Eq. (3) one may replace P with Ca, obtaining $\ln(F^+/Ca^+)$, and similarly one may formulate $\ln(P^+/Ca^+)$. Differentiating with respect to T, and treating $K(T)$ as constants within the relatively small variations of T caused by only moderately differing experimental conditions,

$$d\ln(F^+/Ca^+) = (E_F - E_{Ca})\,T^{-2}\,dT\,, \quad (4\text{ a, b})$$

and similarly for P replacing F.

Dividing 4 a with 4 b,

$$d\ln(F^+/Ca^+)/d\ln(P^+/Ca^+) = (E_F - E_{Ca})/(E_P - E_{Ca})\,. \qquad (5)$$

If for our diagram we had registered the ratios of the F and P ions with respect to singly ionized Ca (such as the mass 43), Eq. (5) would have given us the slope of the calibration lines. However, with the apparatus used in these exploratory measurements, it was not experimentally possible to view simultaneously three peaks as far apart as 19, 31 and 43. A modification of the apparatus is under way. Meanwhile one had to be content with the comparison with doubly ionized calcium, $^{20}Ca^{++}$, a more than sufficiently large mass peak. The biggest peaks by far in the spectrum were the singly ionized Ca isotopes, with the lowest ionization potential[6] of all relevant elements, 6.11 eV, as compared with 17.42 for F, 10.48 for P and 11.87 for Ca^{++}. With the doubly ionized Ca as reference, the counterpart of Eq. (5) becomes somewhat more complicated and loses its usefulness for the present problem. It will be only quoted here:

$$\frac{d\ln(F^+/\sqrt{Ca^{++}})}{d\ln(P^+/\sqrt{Ca^{++}})} = \frac{E_F - \frac{1}{2}(E_{Ca} + E_{Ca^+})}{E_P - \frac{1}{2}(E_{Ca} + E_{Ca^+})}\,, \qquad (6)$$

where E_{Ca^+} is connected with the second ionization of Ca. As we only record relative ion currents, this formula cannot be used without the substitution of conjectural parameters. However, as Ca is not only the most easily ionized but also (except oxygen) the most abundant element in the apatite, one may roughly approximate that practically all the electrons in the plasma originate from the single ionization of Ca, i. e.

$$\mathrm{Ca}^+ \cong n\,. \tag{7}$$

For doubly ionized ions one then has, according to Eq. (1),

$$\begin{aligned}\ln(\mathrm{Ca}^{++}/\mathrm{Ca}) &= \ln(\mathrm{Ca}^{++}/\mathrm{Ca}^{+}) + \ln(\mathrm{Ca}^{+}/\mathrm{Ca}) \qquad (8)\\ &= K_{\mathrm{Ca}^+} + 1.5\ln T - E_{\mathrm{Ca}^+}/R\,T - \ln \mathrm{Ca}\,.\end{aligned}$$

Subtracting this from Eq. (2 a),

$$\begin{aligned}\ln(\mathrm{F}^+/\mathrm{Ca}^{++}) &= \ln(\mathrm{F}/\mathrm{Ca}) + (K_{\mathrm{F}} - K_{\mathrm{Ca}})\\ &\quad - \ln(\mathrm{Ca}^+/\mathrm{Ca}) - (E_{\mathrm{F}} - E_{\mathrm{Ca}^+})/R\,T\,.\end{aligned} \tag{9}$$

Further, via Eq. (2 c),

$$\ln(\mathrm{Ca}^+/\mathrm{Ca}) = \tfrac{1}{2}\,(K_{\mathrm{Ca}^+} + 1.5\ln T - E_{\mathrm{Ca}}/R\,T)\,. \tag{10}$$

Substituting into Eq. (9), one obtains

$$\begin{aligned}\ln(\mathrm{F}^+/\mathrm{Ca}^{++}) &= \ln(\mathrm{F}/\mathrm{Ca}) + (K_{\mathrm{F}} - K_{\mathrm{Ca}^+} - \tfrac{1}{2}K_{\mathrm{Ca}})\\ &\quad - 0.75\ln T - \frac{E_{\mathrm{F}} - E_{\mathrm{Ca}^+} - \frac{1}{2}E_{\mathrm{Ca}}}{R\,T}\,.\end{aligned} \tag{11}$$

Differentiating, treating the K − s as constants, and dividing with the corresponding expression with P replacing F,

$$\frac{\mathrm{d}\ln(\mathrm{F}^+/\mathrm{Ca}^{++})}{\mathrm{d}\ln(\mathrm{P}^+/\mathrm{Ca}^{++})} = \frac{(E_{\mathrm{F}} - E_{\mathrm{Ca}^+}) - \frac{1}{2}E_{\mathrm{Ca}} + 0.75\,R\,T}{(E_{\mathrm{P}} - E_{\mathrm{Ca}^+}) - \frac{1}{2}E_{\mathrm{Ca}} + 0.75\,R\,T}\,. \tag{12}$$

This would give calibration lines with a slight curvature. However, at the likely plasma temperatures [3] of at most a few tens of thousands °K, *RT* would not be a dominating term, and the curvature would be moderate. If one substitutes the respective ionization potentials into Eq. (12) (the ΔE − s being of secondary importance), and uses the experimentally obtained slopes from Fig. 1, one may get an order-of-magnitude notion of the mean plasma temperatures under the analytical conditions of this apatite study. Performing this calculation one finds plasma temperatures of the order of 3×10^4 °K, comparable with the temperatures quoted in Ref. [3] for the sputtering of insulators (some 10^4 °K). Thus the plasma model, albeit crudely approximated in the above treatment, appears reasonably well supported.

One may summarize: 1) the method of comparing the fluorine peak with two matrix peaks (i. e. not only a Ca peak) affords a nearly quantitative determination of F/Ca weight ratios in apatites, reducing the importance of the fact that reproducible ion current ratios are difficult to maintain; and 2) the interrelations between the ion currents of different elements appear compatible with a plasma model.

In this paper two of us (G.F. and L.G.P.) have the main responsibility for the odontological aspects, one of us (A.L.) for the final model discussion.

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[1] C. A. Baud and S. Bang, Caries Res. **4**, 1 [1970].

[2] L. G. Petersson, G. Frostell, and A. Lodding, Z. Naturforsch. in press.

[3] C. A. Andersen and J. R. Hinthorne, Anal. Chem. **45**, 1421 [1973].

[4] V. Leroy, J. P. Servais, and L. Habraken, CRM Rep. (Liège) nr **35**, 69 [1973].

[5] M. N. Saha, Phil. Mag. **40**, 472 [1920]; J. Eggert, Z. Physik **20**, 570 [1919].

[6] Handbook of Chemistry and Physics, 53rd ed., Chemical Rubber Co. Press, Cleveland 1973, p. E 56.