

## Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis

JOHN C. STORMER, JR., MILTON L. PIERSON, ROBERT C. TACKER

Department of Geology and Geophysics, Rice University, P.O. Box 1892, Houston, Texas 77251, U.S.A.

### ABSTRACT

Under conditions routinely used for electron microprobe analyses (15 kV, sample current of 0.015  $\mu\text{A}$ , beam diameter of 5–50  $\mu\text{m}$ )  $\text{FK}\alpha$  X-ray intensities of Durango fluorapatite sections with the surface perpendicular to the *c* axis increase up to 100% during the first 60 s of exposure to the beam. After longer periods of exposure to an electron beam the intensity falls to values below the initial intensity. This effect is strongly anisotropic. Sections parallel to the *c* axis show a similar behavior but on a time scale approximately 20 times longer. There appears to be no relaxation or decay of the effect when the same spot is reanalyzed after periods of up to several weeks. Under similar microprobe operating conditions, topaz shows no change in  $\text{FK}\alpha$  intensity, and fluorite shows a decline in intensity with increasing duration of beam exposure.

The intensity variation and its anisotropy can be explained by diffusion of F to the surface driven by the electrical field produced by primary beam electrons implanted at a depth below the analyzed region. The increase in intensity is believed to be due to the diffusion of F ions to sites near the surface where their X-rays are subject to much less absorption than in the apatite matrix. The anisotropy of the effect is explained by the known, structurally controlled anisotropy of diffusion in apatite. Cl appears to behave in a similar manner except that the initial enhancement of X-ray intensity is less pronounced, since Cl X-rays are not so strongly absorbed in the apatite matrix.

Accurate analysis of apatite will require a series of analyses on the same spot extrapolated to a value at the initiation of beam exposure. Because of permanent long-term changes in X-ray intensity with cumulative beam exposure, apatite should not be used as a primary standard. Samples exposed to an electron beam for cathodoluminescence studies should not be analyzed without removing the altered surface layer ( $\sim 5 \mu\text{m}$ ).

### INTRODUCTION

It has been known for many years that in glasses and certain minerals some elements are mobile under the influence of electron bombardment. The X-ray intensities of the mobile elements are often significantly reduced over a period of time (Sweatman and Long, 1969). The alkali elements in glasses are particularly mobile, and the very large effect on their X-ray intensities during microprobe analysis has been quantified by Neilson and Sigurdsson (1981). This effect has often been incorrectly termed "volatilization." Lineweaver (1963) deduced that the alkali ions move deeper toward the region of excess negative charge created by implanted primary beam electrons and are depleted in the shallower zone from which the X-rays are generated. Mobile anions would, of course, move away from the region of excess negative charge toward the surface, and Lineweaver's (1963) work was, in fact, directed toward the problem of O outgassing from the glass in cathode ray tubes. Cazaux (1986) made a theoretical analysis of the electric field that would be induced in nonconductive materials by electron bombardment and applied his model to several experimental stud-

ies showing Auger and X-ray signal variation for various anions and cations.

Although the effects of Na and K mobility on microprobe analyses are now well understood and procedures to avoid the problem have been developed (Neilson and Sigurdsson, 1981), there is no similar study of the complementary problem of anion mobility. For cations in minerals and natural glasses, the effect generally results in a reduction of X-ray intensity with time (under conditions of practical interest). However, in the course of detailed microprobe calibration, we recently observed large, time-dependent increases in the X-ray intensity for F in apatite. We also noticed significantly increased F X-ray intensities on samples that had previously been exposed to electron bombardment in a cathodoluminescence stage on an optical microscope. The magnitude of these increases was strongly dependent on the crystallographic orientation of the section. The anisotropy of F diffusion in apatite subject to an applied electrical field has been described by Royce (1974), but the large effect this has on the X-ray intensity during microprobe analysis has not previously been noted. In view of the unusual nature of these effects and their obvious importance for

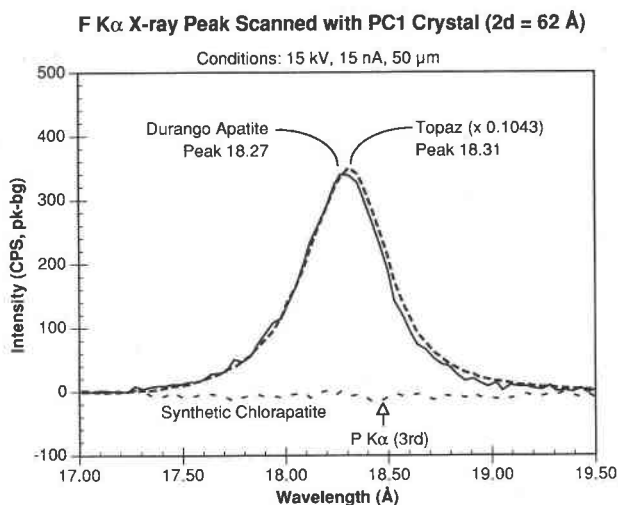


Fig. 1. Wavelength scans across the  $FK\alpha$  X-ray peak with the W-Si multilayer pseudocrystal. The data were obtained in 10-s counting intervals at wavelength steps of 0.03 Å. Total beam exposure time was approximately 850 s. A very large spot and (100) sections were used to minimize alteration or contamination. Background, calculated as the average of 10 steps at 17.00 Å and 10 steps at 19.50 Å, has been subtracted from all data. The topaz data have been multiplied by 0.1043, a factor that adjusts for the difference in F concentrations and matrix corrections. The  $FK\alpha$  peak is slightly shifted from apatite to topaz, and peak shape on apatite is slightly asymmetric in comparison with topaz. However, the ratio of apatite to topaz peak heights is 0.971, and the ratio of apatite to topaz integrated peak areas is 0.961. These ratios are not significantly different from 1.000, given the uncertainty in the F concentrations for our samples. The scan on F-free synthetic chlorapatite (USNM no. 136739) demonstrates the complete suppression of the third-order  $PK\alpha$  peak, which would appear at about 18.47 Å.

microprobe analysis of apatite, we have attempted to quantify them.

## METHODS

The results reported here were obtained using a Cameca SX-50 microprobe with SUN computer-based control and data reduction package employing the Cameca PAP correction procedure. A vertical spectrometer with a standard Cameca PC1 crystal, (W-Si multilayer,  $2d = 62$  Å) and light element detector was used. The analytical characteristics of a similar W-Si pseudocrystal have been described in detail by Potts and Tindle (1989). As shown in Figure 1, this crystal gives a relatively broad and symmetrical  $FK\alpha$  peak that differs only slightly between apatite and topaz (unlike the higher resolution but much weaker diffraction from TAP crystals). The W-Si pseudocrystals also suppress the third-order peak of  $PK\alpha$ . In apatite analysis the potential interferences from Fe and Mg are not significant. The analyses of Cl and Ca were made using a standard PET crystal supplied by Cameca with the same type of spectrometer.

Our preliminary report of this phenomenon (Stormer et al., 1991) was based largely on measurements that were

made using an ETEC Autoprobe with a Tracor TN-2000 X-ray analysis system and a W-Si multilayer pseudocrystal with  $2d = 49.8$  Å. Although the ETEC uses a beam inclined at  $27^\circ$  from the specimen perpendicular, the data were qualitatively identical, but lower count rate, spectrometer positioning errors, and beam instability yielded data that were much less precise.

A euhedral, columnar crystal of fluorapatite from Durango, Mexico, measuring approximately 20 mm in length and 10 mm across, was oriented manually, with sections cut parallel to (001) and (100) using a slow speed diamond wafering saw. These sections were mounted together on a glass slide and ground as a standard petrographic thin section. Final polishing was with 1- and 0.3- $\mu$ m alumina. The accuracy of the orientation was checked by measurement of the optic axis using universal stage microscopy, and [001] is within  $1^\circ$  of perpendicular and parallel to the respective sections. Although apatite from Durango may be variable in composition, this crystal appears to be identical to that described by Young et al. (1969; F = 3.53 wt%). Several quantitative step scans across both of our sections showed no significant zoning in major elements.

The chlorapatite used in this study is reported to be from Bamle, Norway, and our analysis gives 2.9 wt% Cl and 0.8 wt% F. The fragments available to us were mounted on glass slides as above, but precise orientation was difficult. The best-oriented (100) section, for which results are reported here, had [001] approximately  $6^\circ$  from the perpendicular, as measured by universal stage microscopy.

A portion of a euhedral topaz crystal was similarly mounted. The section parallel to (100) was accurately oriented using the {001} cleavage. The other section is in the zone [001] but is only approximately located with respect to (100). This specimen from the Thomas Range is apparently identical to that described by Barton et al. (1982) and by Penfield and Minor (1894, F = 20.33 wt%).

The specimen of fluorite (Wards, assumed stoichiometric F = 48.67 wt%) consisted of several fragments of unknown orientation mounted with epoxy in 2-mm holes in a brass disk, ground and polished by the same method as the thin sections.

All specimens were coated with 200 Å of C using procedures described by Kerrick et al. (1973).

## RESULTS

Under conditions routinely used for mineral analysis (15 kV, beam current of 15 nA at specimen, beam diameter of 5  $\mu$ m) the  $FK\alpha$  X-ray intensity doubles during the first 60–120 s on sections of apatite oriented perpendicular to the c axis (Fig. 2A). The intensity then peaks and diminishes over the next 10 min, gradually approaching a constant value below the initial value. Although not shown, the gradual decline continues for at least 4 h without any other significant change. On sections cut parallel to (100), the intensity increases only about 20% over a period of 300 s under the same analytical

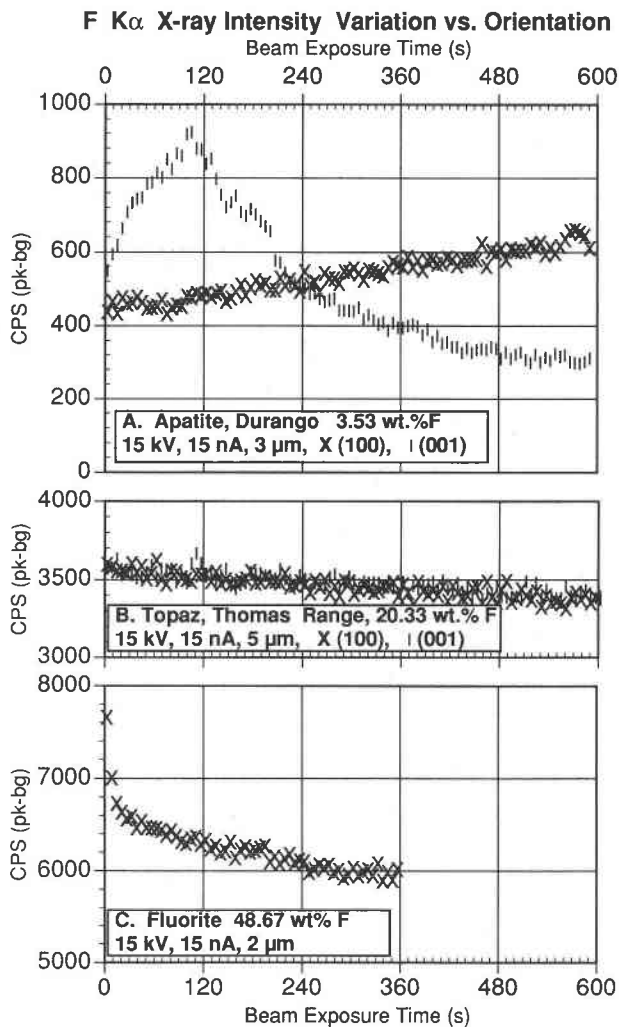


Fig. 2.  $FK\alpha$  X-ray intensity plotted against total cumulative beam exposure time for (A) (001) and (100) sections of fluorapatite, (B) (001) and (100) sections of topaz, and (C) a section of fluorite of unknown orientation. Data were obtained in 6-s counting intervals separated by 3 s of beam blanking. Background was determined by separate measurement at wavelengths above and below the peak on immediately adjacent spots.

conditions. This behavior was found to be very consistent, given the same specimen and operating conditions. No significant differences in this pattern were noted in the same experiments using an ETEC Autoprobe (inclined beam), although the intensity ultimately declined to a value closer to the initial intensity.

The behavior of  $FK\alpha$  X-ray intensity on topaz and fluorite over long periods of exposure to an electron beam were investigated for comparison with apatite. In contrast to that of the fluorapatite, the  $FK\alpha$  intensity of topaz remains nearly constant for both orientations (Fig. 2B). There is a linear decline of about 5% in intensity over a period of 10 min of beam exposure, probably caused by the increasing carbonaceous contamination of the surface where the beam impinges. Contamination probably af-

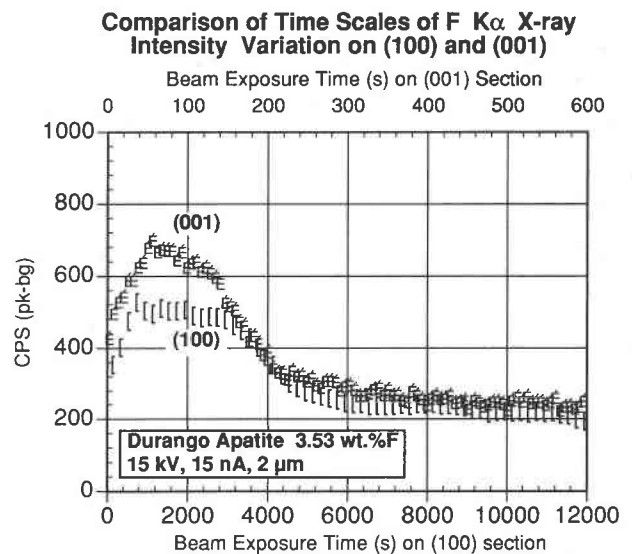


Fig. 3.  $FK\alpha$  X-ray intensity plotted against total cumulative beam exposure time for (001) and (100) sections of Durango fluorapatite. The time scale for the (100) section (lower x axis) has been compressed by a factor of 20 to emphasize the similarity. The data for the (001) section were obtained in 6-s counting intervals and for (100) in 200-s counting intervals, both separated by 3-s intervals of beam blocking.

fects apatite similarly but is insignificant with respect to the other effects seen. The  $FK\alpha$  intensity on fluorite decreases rapidly, at least 20% over the first 60 s (Fig. 2C). Comparisons with topaz and with the extrapolation of the first few points both suggest a 10% loss, even during the first 6-s counting interval. There is no evidence for an increase in intensity as seen in apatite. Reconnaissance experiments on F-bearing amphiboles and micas from our standard collection did not reveal any significant increase in intensity, nor anisotropy for  $FK\alpha$  X-rays, though crystallographic orientation was not controlled.

The slow rise in  $FK\alpha$  intensity on the (100) section contrasts with the slow linear decline seen for topaz. This suggested that the behavior of the (100) section was similar to that of the (001) section, but on a much longer time scale. Figure 3 shows that the patterns for both sections are at least qualitatively similar but develop approximately 20 times more slowly on the (100) section.

Beam diameter and voltage are often varied in microprobe analyses to minimize element migration. In the case of apatite, increasing the beam diameter (Fig. 4) reduces the rate of the intensity rise and the subsequent intensity decrease. However, the height of the peak increases with increasing beam diameter, although it takes longer to reach the peak intensity. Even a beam as large as 10  $\mu$ m shows an intensity rise of about 10% in the first 60 s of beam exposure. Varying the beam current has a similar effect, indicating that the important variable is the current flux per unit area.

Varying the accelerating voltage appears to have a negligible effect on the rate of the initial intensity rise and

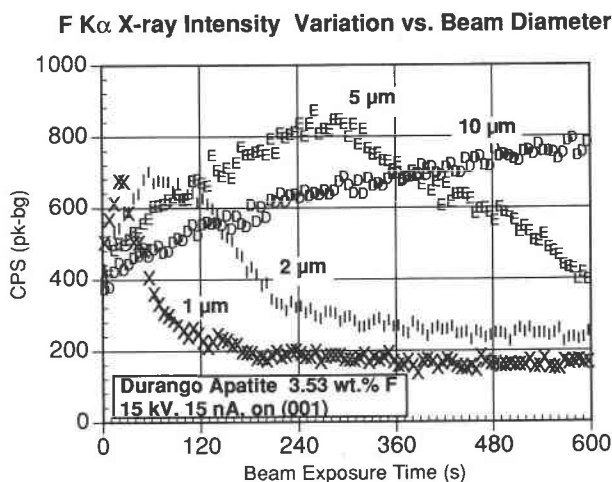


Fig. 4.  $FK\alpha$  X-ray intensity plotted against total cumulative beam exposure time for various beam diameters on (001) sections of Durango fluorapatite. Data collection routine the same as in Fig. 2.

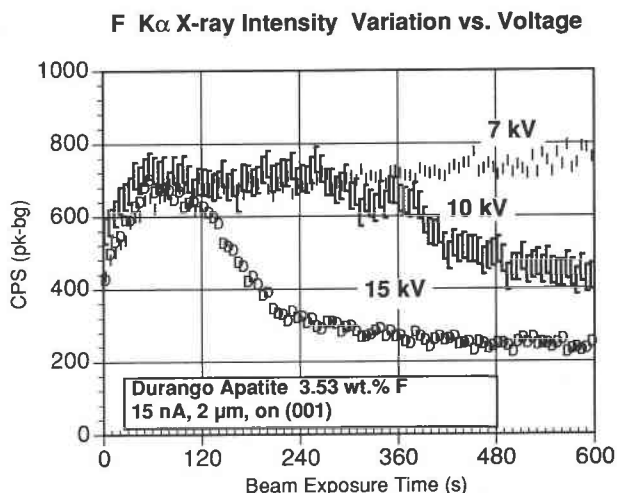


Fig. 5.  $FK\alpha$  X-ray intensity plotted against total cumulative beam exposure time for various accelerating voltages on (001) sections of Durango fluorapatite. Data collection routine the same as in Fig. 2.

the height of the peak reached (Fig. 5). However, the voltage seems to have a strong effect on the subsequent decrease in intensity. At 7 kV there is no decrease over at least 10 min. In fact, after the rapid initial rise the data show a much more gradual rise, continuing for at least 10 min. However, given the long exposure time involved, we cannot be sure that the phenomenon is not caused by beam contamination or the destruction of the C coat, rather than an intrinsic property of the voltage used.

It also appears that there is no relaxation of the intensity variation over periods from a few seconds to several days. The intensity variation is quantitatively similar for equivalent cumulative beam exposure times whether the beam remains continuously on the specimen or whether it is blocked for a period between each count interval. Most of the data presented here were obtained with 6-s exposures separated by 3-s blocked periods, as this represented the most efficient data collection scheme, given the nature of the standard automation routines on the Cameca. However, in experiments using various combinations of beam exposure time and blocked intervals, there was no difference in the curves when they were plotted against cumulative beam exposure. Interrupting the experiment for periods of nearly a day produces results identical to continuous experiments. Figure 6 shows the results for two spots where the usual analysis routine was interrupted for 16 h just after reaching the intensity peak. The curves appear to be continuous when plotted against beam exposure time and are comparable to the continuous analysis shown in Figure 2A. We also noted that our measured F contents of apatite in a polished thin section of rhyolite tuff were systematically higher several weeks after observing zoning patterns using the diffuse electron beam of a cathodoluminescence stage on an optical microscope. In this case, the duration of beam ex-

posure was longer, approximately  $\frac{1}{2}$  h, but specimen current per unit area was much lower than in the microprobe, though not precisely controllable. There is no evidence in our data for any tendency of the intensity to return to the initial value or any previous value during a hiatus in beam exposure. The alteration observed is apparently cumulative and permanent.

The variation of  $CaK\alpha$  X-ray intensity has an inverse relationship with  $FK\alpha$  intensity during the same experiment, as shown in Figure 7. The Ca intensity decreases slightly during the rapid rise in  $FK\alpha$  intensity.  $CaK\alpha$  intensity then increases as that of F decreases. The maximum variation in Ca intensity is only a few percent of the initial value. This slight variation might not be noticed during routine microprobe analyses of a few seconds' duration. Although not illustrated,  $PK\alpha$  X-ray intensity was found to follow the same pattern as that of Ca.

The results on the chlorapatite are shown in Figure 8. On the section nearly perpendicular to the c axis, Cl X-ray intensity appears to increase slightly over the first 60 s and then declines. F shows a pattern very similar to that of the fluorapatite, although at a lower intensity, consistent with its lower F content.

## DISCUSSION

We believe that the variation of X-ray intensities shown by our data is a result of the diffusion of the halogens, OH, and vacancies in the electric field created by beam electrons implanted in the specimen. The affinity of F ions for the apatite surface and the extreme absorption of  $FK\alpha$  X-rays in an apatite matrix are responsible for the unique features of  $FK\alpha$  variation. Diffusion in the [001] direction of apatite is known to be faster than diffusion perpendicular to [001] (den Hartog et al., 1972; Farver and Giletti, 1989; Royce, 1974; Tse et al., 1973;

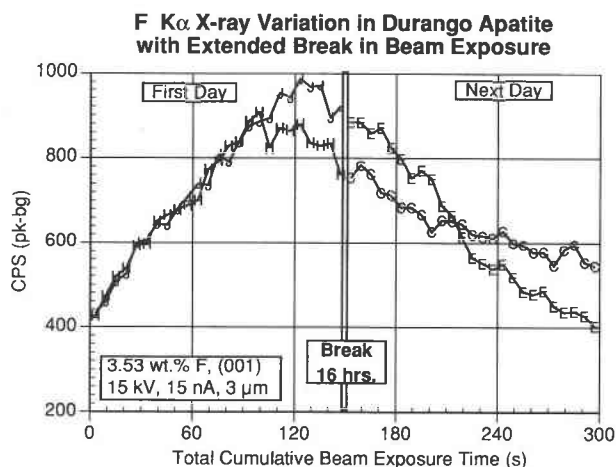


Fig. 6.  $FK\alpha$  X-ray intensity plotted against total cumulative beam exposure time on (001) section of Durango fluorapatite. Compare with Fig. 2, but note expanded time scale. Data collection routine the same as in Fig. 2, except that the analyses and beam exposure were suspended after 150 s of cumulative exposure and resumed 16 h later.

Watson et al., 1985; Welch and Royce, 1972), and halogen diffusion is essentially limited to the c-axis direction. The hexagonal  $P6_3/m$  apatite structure (Beever and McIntyre, 1946) contains a zeolitic channel along the six-fold axes, which contains the halogens and OH (Montel, 1968). It is difficult for the anions to jump past one another within the confines of this channel. Hence diffusion occurs when a halogen ion jumps to an adjacent vacancy, but the relative positions of the anions is unchanged. Therefore, in a mixed F-Cl apatite the ratio of F and Cl reaching the surface should be equal to their ratio in the bulk. Although the slightly different position of Cl in end-member chlorapatite results in a reduction in symmetry to  $P2_1/b$  (Mackie et al., 1972) and doubles the size of the unit cell, the essential nature of the channel is unchanged in chlorapatite. Royce (1974) demonstrated that a net flux of halogens resulted when the motion of vacancies was influenced by a dc electric field. This diffusion is structurally limited to the sixfold c axis, i.e., along [001].

During electron microprobe analysis, vacancies and halogens diffuse as a result of the electrical field generated by the implanted electrons of the incident beam. The work of Cazaux (1986) suggested that this electric field develops to a steady state in  $<0.1$  s and decays on the same time scale. The electrical field gradient in the region from the surface to the depth of electron implantation, below the depth of X-ray generation, would tend to drive halogens to the surface. This occurs most readily if the c axis is perpendicular to the surface. Vacancies would become concentrated at the electron implantation depth, and diffusion of the halogens should slow as the vacancies are removed from the excited region.

The increase in  $FK\alpha$  X-ray intensity may be explained in terms of the bonding characteristics of the halogens

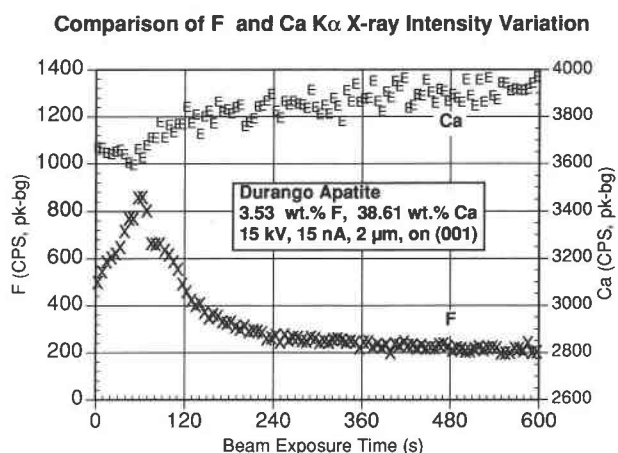


Fig. 7.  $FK\alpha$  and  $CaK\alpha$  X-ray intensity collected simultaneously, plotted against total cumulative beam exposure time on (001) section of Durango fluorapatite. Data collection routine the same as in Fig. 2, but a smaller beam diameter was used.

and the absorption of these light X-rays by the apatite matrix. F is very electronegative and reacts quite readily with the apatite surface. Although that has long been understood as the basis for the topical fluoride dental treatment, it is surprising to us that it apparently has such a strong effect in the vacuum of the microprobe. After diffusing from the excited region, the F ions must bond to the surface of the apatite until they absorb enough energy to break those bonds and escape into the vacuum.

The rise in  $FK\alpha$  intensity is the result of an increasing concentration of F at the surface of the apatite, where the X-rays generated suffer little or no absorption.  $FK\alpha$  X-rays are heavily absorbed in apatite, as reflected in the Bence-Albee correction factor for  $FK\alpha$  X-rays in apatite of about 6.2 (Albee and Ray, 1970). A modest increase in F at the surface would, therefore, be expected to increase the intensity approximately six times as much as the same amount dispersed in the apatite matrix.

The return of the  $FK\alpha$  intensity to values below the initial value can be explained if both processes have a negatively sloped exponential dependence on time. If, then, the desorption process has a longer time constant than the process of diffusion and surface bonding, the surface concentration will first rise, then decline, asymptotically approaching zero. The X-ray signal from the F remaining in the apatite matrix would, of course, continue. The 200-Å C coat must have some effect on the desorption, and in fact the shape of the curve as desorption becomes dominant (the trailing edge of the intensity peak) is more variable from spot to spot than the initial increase (see Fig. 6). But the results for fluorite, where the F is immediately lost to the vacuum, suggest that the influence of the C coat is relatively minor.

The rises in temperature caused by the beam are  $<30$  K under any of the analytical conditions used here, as calculated using the equations of Friskney and Haworth (1967) and thermal conductivities of 0.01–0.02

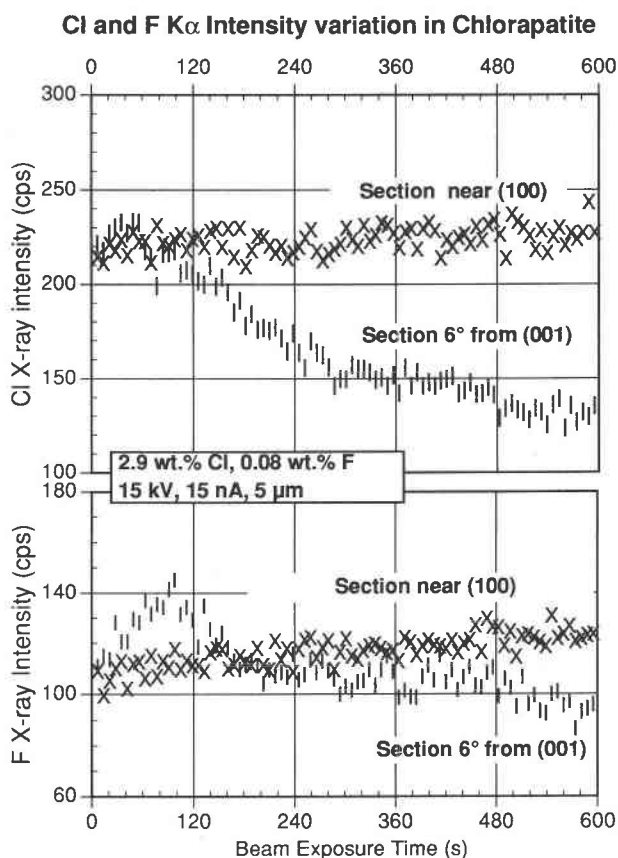


Fig. 8.  $FK\alpha$  and  $ClK\alpha$  X-ray intensity obtained simultaneously, plotted against total cumulative beam exposure time on sections nearly parallel and perpendicular to (001) from natural chlorapatite. Data collection routine the same as in Fig. 2.

$W \cdot cm^{-1}/K$  for apatite (Hopkins et al., 1971; Kijima and Tsutsumi, 1979). This temperature rise by itself is probably insufficient to induce diffusion and is not truly a requirement for vacancy diffusion to occur. The temperature rise is also probably too little to greatly influence the desorption process.

A higher electron flux per unit area (beam current, spot size) produces a stronger electrical gradient in the sample and would be expected to produce the variation in the rate of rise seen in Figure 4. The effect of variable accelerating voltage is more complicated. Since higher voltage increases the depth of electron penetration, it should decrease the electrical gradient and tend to slow the rate of diffusion. However, it would also increase the volume from which the F could be brought to the surface and increase X-ray production at depth. Figure 5 suggests that varying voltage has a relatively limited effect on the rate and magnitude of the X-ray intensity rise or on the initial intensity. However, voltage does appear to have a very strong effect on the hypothesized desorption process. In fact, at 7 kV the electrons must not contribute enough energy to stimulate desorption significantly. That suggests to us that the effects seen in the X-ray intensity do in fact involve absorption and desorption at the apatite surface.

There probably is some anisotropy in the surface properties of apatite affecting absorption-desorption, but the strong anisotropy in diffusion referred to above would be sufficient to explain the differences we see with respect to crystallographic orientation.

Cl is less electronegative than F. It should diffuse in the field created by the electron beam, but apparently it does not react with the apatite surface. It is well known that synthetic chlorapatite is very unstable in the electron beam. Cl simply diffuses and escapes into the vacuum, a process that is often visible as the escaping gas creates bubbles in the C coat. Unfortunately, we do not have at present crystals of synthetic chlorapatite large enough to provide well-oriented sections to test for anisotropy or a possible initial rise in intensity. The results for the Cl-rich natural apatite (Fig. 8) suggest that Cl behaves much like F. The initial rise takes place on approximately the same time scale.  $ClK\alpha$  X-rays, however, are not nearly so strongly absorbed by the apatite matrix (the Bence-Albee factor is only slightly greater than 1). As Cl is brought nearer the surface by diffusion, the intensity of X-rays emerging from the sample is not significantly increased. As Cl escapes into the vacuum, however, the intensity would decrease, as it does for F. In Figure 8, the modest rise but large subsequent decrease is to be expected, given the relatively slight absorption of  $ClK\alpha$  X-rays in the matrix and probable low affinity of Cl ions for the apatite surface.

In contrast to apatite, F must diffuse to the surface in fluorite but not bond as it does to the apatite surface. Topaz appears to be very stable under an electron beam, and the structure apparently has no channels for preferential diffusion of F.

If our hypotheses discussed above are correct, the rate of  $FK\alpha$  intensity rises, and the amount of F and Cl remaining in the matrix at any point in time is determined at least in part by the halogen site vacancies and other defects in the apatite. The vacancy concentration is variable from one specimen to another, and not easily determined. Apatite samples could not simply be "cooked" to a steady-state value in an electron beam prior to analysis.

Until the latest generation of microprobes with metallic multilayer pseudocrystals became available, the low precision and instability of F X-ray analysis probably masked the effects we have observed. In the past, the effects of the anisotropic variation of  $FK\alpha$  intensity in apatite have probably been attributed to sample heterogeneity, or sample preparation difficulties. However, in order to achieve the high accuracy that state-of-the-art instrumentation now promises, special procedures will have to be used to mitigate the problem of variation of exposure-dependent intensity resulting from the anisotropic beam.

The influence of these effects on the accuracy of microprobe analysis is complex. During the course of routine microprobe analyses taking 20–100 s, an increase in the intensity of  $FK\alpha$  X-rays and a high apparent F content should be expected. If we assume that this rise in intensity

is largely controlled by a diffusion rate that is (very roughly) 20 times larger in the [001] direction than in the [100] direction, we can calculate the curves in Figure 9. At an angle of only  $10^\circ$  from the perpendicular to [001], the magnitude of the effect would be only about 25% of the maximum. At  $20^\circ$  the effect would be only about 10%. If the analyzed apatite grains were in a random distribution of orientations, there would be only about a 10% probability that any given analyzed grain would be in error by more than 7%. The rare occurrence of a highly anomalous F value in an analysis probably would be rejected without comment by most analysts. Inclusion of a few moderately high values in a large number of analyses would shift the average only slightly. However, a sufficiently large number of analyses of different grains may not be possible, or the orientations of the analyzed grains may not be random. For instance, the hexagonal outline of apatite grains cut perpendicular to the c axis, the worst case, are more readily identified in thin section. A more serious problem may arise from the use of apatite as a microprobe standard. In most labs the standards are not newly polished for each use. Even on sections parallel to the c axis there is significant alteration over the long period of cumulative beam exposure such a standard may endure. Figure 3 shows that analyses using such a standard could be systematically in error by as much as 50%.

### CONCLUSIONS

The variation in F and  $ClK\alpha$  X-ray intensity during microprobe analysis of apatite is sufficiently large to cause significant analytical errors. The anisotropic nature of the effect is particularly problematic for analysis of apatite grains in rock thin sections where orientation will not be controlled. Mitigation of this effect through control of instrumental conditions is difficult. Reduced beam current diminishes the rate of intensity variation but also reduces the overall  $FK\alpha$  intensity and degrades analytical precision without eliminating the problem. Increasing the beam diameter is limited by the fact that apatite grains in many samples are small or zoned. We would certainly recommend the use of the lowest beam current that will yield adequate count rates and the largest spot size that the sample permits. However, other special procedures will be necessary to achieve the best results.

We believe that the most promising procedure for the analysis of the halogens in apatite is to make timed multiple analyses on the same spot and, using cumulative beam exposure time, to extrapolate back to the initial count rate (or apparent concentration). In practice this would probably consist of several short analyses rather than a single analysis of 50–100 s. The variable intervals of beam blanking and beam exposure during computer-controlled multielement analyses would, of course, have to be accounted for in the extrapolation.

Apatite should not be used as a microprobe standard in a general-purpose mount whose beam exposure history is not controlled. Topaz does not show significant variability from beam exposure and might be preferable as a

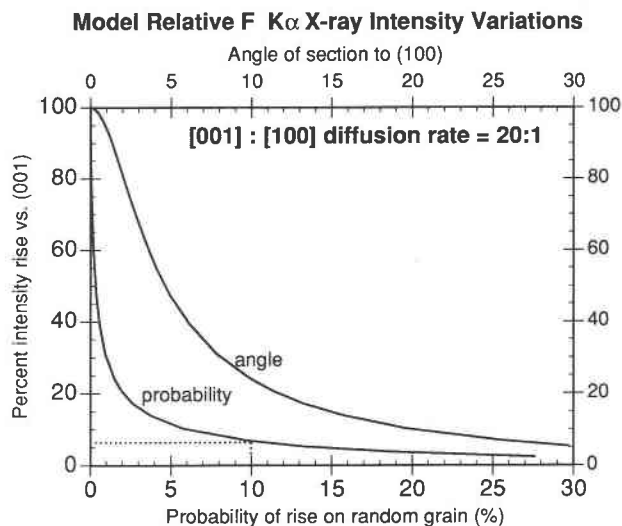


Fig. 9. Calculated percent of maximum intensity rise vs. angle of section to (001) and cumulative probability of encountering a rise as great or greater among a set of randomly oriented grains. Calculations assume that diffusion is the controlling factor, that it is 20 times faster in the [001] than the [100] direction, and that it can be represented as a uniaxial ellipsoid. Probability of encountering a grain of a given orientation was calculated as the area of a spherical surface within a given angular radius of the c axis normalized to the area of an equivalent hemisphere. Although inexact, this calculation suggests that the probability of encountering an obviously anomalous value in routine analysis is on the order of one in ten.

general-purpose standard. Variations in peak shape and wavelength shifts, as well as the very large matrix corrections for  $FK\alpha$  X-rays, generally make it desirable to use standards of similar composition and structure. However, the lower wavelength resolution W-Si crystals do not show as large a variation in peak shape as is seen with TAP crystals, and the use of full integrated peak area or of area peak factors (APF) and improved matrix corrections, as recommended for ultralight elements (Bastin and Heijligers, 1991), would permit the use of topaz as a standard for F. We suggest as a practical solution that topaz or another Mg- and Fe-free mineral of demonstrated stability be used as the standard for F calibration. Measurements with a well-characterized apatite standard, freshly polished and coated, should then be made with unknowns, using the same procedure (multiple counts), and the unknown analyses adjusted accordingly.

### ACKNOWLEDGMENTS

R. Guillemette provided an opportunity to use the Cameca SX-50 at Texas A&M University for some of the early analyses and helped a great deal in developing the procedures used in the analyses. H. Avé Lallemant made the universal stage measurements to check grain orientation. Unusually careful and thought-provoking reviews by J. Farver and J. McGee stimulated a much improved version. Colleagues R. Donelick, who also provided the natural chlorapatite, V. Sisson, and W. Protheroe made many useful suggestions.

This work was supported by NSF grants EAR-8803839 and EAR-

8719760. Matching funds for the purchase of the Cameca SX-50 at Rice University were provided by NSF grant EAR-9104930.

### REFERENCES CITED

- Albee, A.L., and Ray, L. (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulfates. *Analytical Chemistry*, 42, 1408–1414.
- Barton, M.D., Haselton, H.T., Jr., Hemingway, B.S., Kleppa, O.J., and Robie, R.A. (1982) The thermodynamic properties of fluor-topaz. *American Mineralogist*, 67, 350–355.
- Bastin, G.F., and Heijligers, H.J.M. (1991) Quantitative electron probe microanalysis of nitrogen. *Scanning*, 13, 325–342.
- Beevers, C.A., and McIntyre, D.B. (1946) The atomic structure of fluorapatite and its relation to that of tooth and bone material. *Mineralogical Magazine*, 27, 254–257.
- Cazaux, J. (1986) Some considerations on the electric field induced in insulators by electron bombardment. *Journal of Applied Physics*, 59, 1418–1430.
- den Hartog, H., Welch, D.O., and Royce, B.S.H. (1972) The diffusion of calcium and phosphate ions in fluorapatite. *Physica Status Solidi B*, 53, 203–212.
- Farver, J.R., and Giletti, B.J. (1989) Oxygen and strontium diffusion kinetics in apatite and potential applications to thermal history determinations. *Geochimica et Cosmochimica Acta*, 53, 1621–1631.
- Friskney, C.A., and Haworth, C.W. (1967) Heat flow problems in electron-probe microanalysis. *Journal of Applied Physics*, 38, 3796–3798.
- Hopkins, R.H., Damon, D.H., Piotrowski, P., Walker, M.S., and Uphoff, J.H. (1971) Thermal properties of synthetic fluorapatite crystals. *Journal of Applied Physics*, 42, 272–275.
- Kerrick, D.M., Eminhizer, L.B., and Villaume, J.F. (1973) The role of carbon film thickness in electron microprobe analysis. *American Mineralogist*, 58, 920–925.
- Kijima, T., and Tsutsumi, M. (1979) Preparation and thermal properties of dense polycrystalline oxyhydroxyapatite. *Journal of the American Ceramic Society*, 62, 455–460.
- Lineweaver, J.L. (1963) Oxygen outgassing caused by electron bombardment of glass. *Journal of Applied Physics*, 34, 1786–1791.
- Mackie, P.E., Elliot, J.C., and Young, R.A. (1972) Monoclinic structure of synthetic  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ , chlorapatite. *Acta Crystallographica*, B28, 1840–1848.
- Montel, G. (1968) Conceptions nouvelles sur la physico-chimie des phosphates de structure apatitique. *Bulletin de la Société Chimique de France*, 1693–1700.
- Neilson, C.H., and Sigurdsson, S. (1981) Quantitative methods for electron microprobe analysis of sodium in natural and synthetic glasses. *American Mineralogist*, 66, 547–552.
- Penfield, S.L., and Minor, J.C., Jr. (1894) On the chemical composition and related physical properties of topaz. *American Journal of Science*, 3rd Series, 47, 387–396.
- Potts, P.J., and Tindle, A.G. (1989) Analytical characteristics of a multilayer dispersion element ( $2d=60\text{\AA}$ ) in the determination of fluorine in minerals by electron microprobe. *Mineralogical Magazine*, 53, 357–362.
- Royce, B.S.H. (1974) Field-induced transport mechanisms in hydroxyapatite. *New York Academy of Sciences Annals*, 238, 131–138.
- Stormer, J.C., Jr., Pierson, M.L., and Tacker, R.C. (1991) Anisotropic variation of F and Cl X-ray intensity in apatite due to crystallographically controlled diffusion during electron microprobe analysis. *Geological Society of America Abstracts with Programs*, 23, A220.
- Sweatman, T.R., and Long, J.V.P. (1969) Quantitative electron-probe microanalysis of rock-forming minerals. *Journal of Petrology*, 10, 332–379.
- Tse, C., Welch, D.O., and Royce, B.S.H. (1973) The migration of  $\text{F}^-$ ,  $\text{OH}^-$ , and  $\text{O}^{2-}$  ions in apatites. *Calcified Tissue Research*, 13, 47–52.
- Watson, E.B., Harrison, T.M., and Ryerson, F.J. (1985) Diffusion of Sm, Sr, and Pb in fluorapatite. *Geochimica et Cosmochimica Acta*, 49, 1813–1823.
- Welch, D.O., and Royce, B.S.H. (1972) One-dimensional anion vacancy diffusion in the calcium apatites. *Physica Status Solidi B*, 57, 193–202.
- Young, E.J., Myers, A.T., Munson, W.L., and Conklin, N.M. (1969) Mineralogy and geochemistry of fluorapatite from Cero de Mercado, Durango, Mexico. U.S. Geological Survey of Professional Paper 650-D, D84–D93.

MANUSCRIPT RECEIVED SEPTEMBER 26, 1992

MANUSCRIPT ACCEPTED JANUARY 9, 1993