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Author

Perry, D.L.

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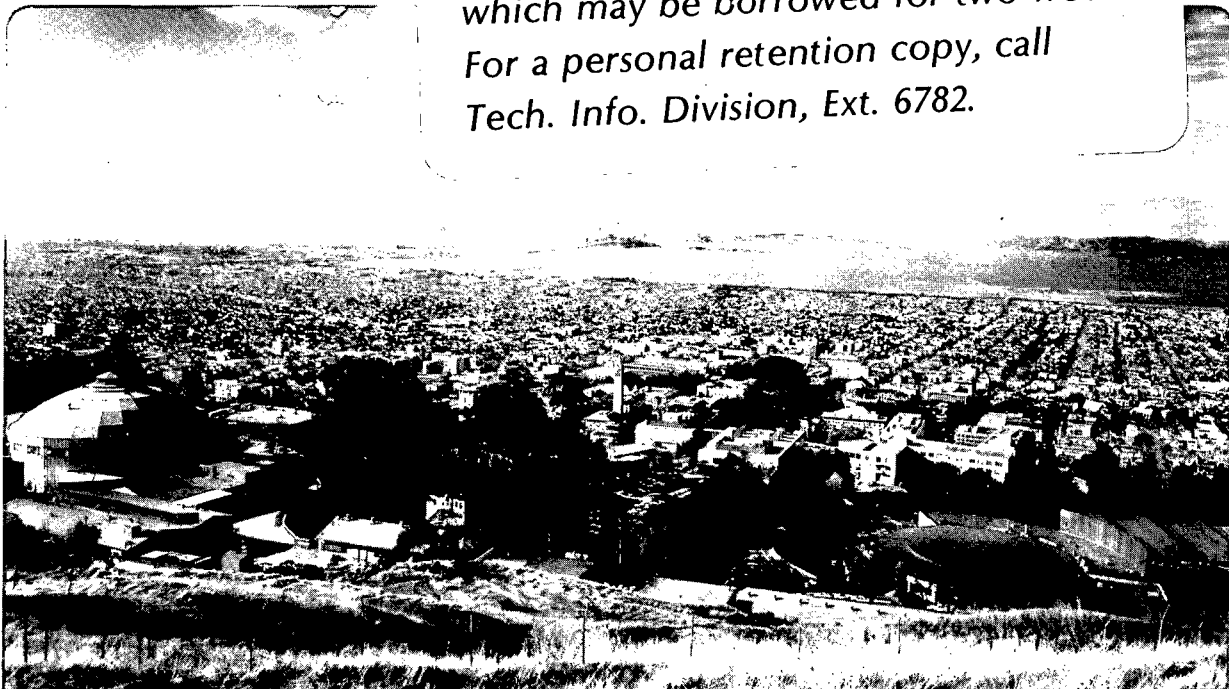
SURFACE STUDY OF HF- AND HF/H₂SO₄-TREATED
FELDSPAR USING AUGER ELECTRON SPECTROSCOPY

Dale L. Perry, Art F. White, Leon Tsao,
and Kenneth A. Gaugler

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Surface Study of HF- and HF/H₂SO₄-Treated
Feldspar Using Auger Electron Spectroscopy

by

Dale L. Perry*, Art F. White, and Leon Tsao

Earth Sciences Division

and

Kenneth A. Gaugler

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

ABSTRACT

Auger electron spectroscopy has been used to study K-feldspar that has been reacted with both aqueous 10% HF and a 50% mixture of a 10% HF/0.1 N H₂SO₄ solution. In the feldspar/HF system, the resulting feldspar surface was shown to have been fluorinated; depth profiling, using argon ion sputtering, showed the fluorination to have occurred substantially into the mineral bulk. In the feldspar/HF/H₂SO₄ system, the resulting surface contained both fluorine and sulfur. The fluorination had again penetrated into the bulk, but the sulfur could be removed with mild argon ion sputtering. The Al/F signal ratio was much lower on the feldspar surface treated with the 10% HF/0.1 N H₂SO₄ solution than the feldspar surface treated with the weaker 10% HF acid solution.

INTRODUCTION

A considerable interest has been expressed recently in experimental studies simulating dissolution kinetics and mass transfer rates of silicate mineral weathering. One problem which has arisen in such experiments has been the preparation and characterization of silicate surfaces which are representative of natural weathering processes. The work of HOLDREN and BERNER (1979), GRANDSTAFF (1980), and HOLDREN (1981) has shown that a distortion of the surface structure and the creation of fine particles during grinding and crushing of silicates have lead to anomalous experimental results. Previous studies citing parabolic dissolution rates for crystalline silicates may have resulted from such sample preparation effects. One recent approach to solving this problem has been to leach the crushed silicate with hydrofluoric acid (HF) to remove both the distorted surface layer of particles and the adhering microparticulate matter on the surface (HOLDREN and BERNER, 1979). Leaching with HF has also been used by WHITE (1982) to depth profile the surface layers of glassy silicates and by BERNER et al. (1979) to simulate natural dissolution features in pyroxenes and amphiboles.

In an ongoing study of the effects of weathering reactions on silicate surface chemistry, a significant decrease has been noticed in the sorption capacity of minerals treated with HF relative to untreated samples. The question therefore arises as to the possible effects of HF treatment on silicate surfaces, in particular irreversible surface reactions between silicate and fluoride which may influence experimental kinetic studies. The present report describes a preliminary Auger surface study of the potential influence of the HF and HF/H₂SO₄ reactions with new K-feldspar surface layers that result from this chemical interaction. The Auger

technique has been coupled with argon ion etching in an attempt to determine the depth of migration of the fluoride ion into the mineral bulk.

EXPERIMENTAL

K-feldspar samples were obtained commercially (Wards Natural History Establishment) and gave the following bulk analysis (percent by weight): FeO, 0.010 ± 0.001 ; Al_2O_3 , 21.2 ± 0.2 ; CaO, 0.48 ± 0.05 ; Na_2O , 3.7 ± 0.2 ; K_2O , 9.0 ± 0.2 ; MgO, 0.010 ± 0.001 ; SiO_2 , 65.0 ± 0.2 ; H_2O , 0.13 ± 0.01 ; total carbon 0.026 ± 0.005 ; total sulfur, 0.003 ± 0.001 ; inorganic carbon, 0.005 ± 0.005 . The samples were then chemically treated in the following two ways that are similar to that of HOLDREN and BERNER (1979). The first sample was reacted with an aqueous 10% HF solution for 20 min with mild stirring. It was removed from the reaction solution and washed several times with jets of distilled, deionized water. It was then dried in air overnight at approximately $100^\circ C$. The second sample was prepared in the same manner except that the original reaction solution was a 50% mixture of aqueous 10% HF and 0.1 N H_2SO_4 .

Auger spectra were recorded using a working vacuum chamber pressure of approximately 10^{-9} torr on a Physical Electronics Industries Model 590 scanning Auger microprobe. Samples were studied using a primary beam energy of 3 keV and a primary beam current of 0.12 μA ; these experimental parameters were found to minimize charging and specimen damage while yielding an acceptable signal-to-noise ratio. The peak-to-peak modulation in the lock-in amplifier was 6 eV throughout.

RESULTS AND DISCUSSION

The Auger spectra of K-feldspar "as received", treated with 10% HF, and treated with a 50% mixture of 10% HF/0.1 N H_2SO_4 are shown in Fig. 1 and 2.

Figure 1 shows the resulting Auger spectra of the feldspar sample that was treated with only the 10% HF solution. Figure 1a is a survey Auger spectrum (0-1000 eV) of the untreated, "as received," feldspar sample. After treatment with hydrofluoric acid, however, several major changes appeared in the spectrum (Fig. 1b). The surface concentration of potassium decreased dramatically (see Table 1) as shown by the O/K ratio. Sodium, which was not detectable on the original surface layer, was then quite visible. (It should be remembered that this chemical treatment removes layers of the feldspar sample; what is being observed spectroscopically, then, is the chemical state of the remaining surface). Additionally, the fluoride ion could also be detected on the new surface. Argon ion sputter etching, performed at the rate of 600 Å/min. relative to Ta₂O₅, was then used to depth profile the sample. After 15 sec of sputtering (Fig. 1c), the concentration of fluorine had diminished; after 30 sec (Fig. 1d), the fluorine concentration was even lower. The sodium content, on the initially HF-etched sample and on the subsequently argon ion-sputtered surface, remained fairly constant.

Similar results were also observed for the sample subjected to the HF/H₂SO₄ (Fig. 2). The major difference was the lack of sodium observed on the subsequent spectra of the acid-etched surface, presumably due to exchange in the much stronger acid solution. The fluoride was very evident on this treated surface, too, but the concentration of the fluoride ion, which was initially much greater on the surface of this sample than the feldspar sample treated with 10% HF alone, diminished as the ion-sputtering proceeded into the mineral bulk. In addition to the fluoride ion, sulfur could also be detected (Fig. 2b). The sulfur, however, had not migrated into the bulk of the feldspar to as great an extent as the fluorine and

was completely removed with only light ion-sputtering (Fig. 2c); after 30 sec of sputtering, there was no remaining trace of the initially observed sulfur (Fig. 2d). The Al/F intensity ratio for the surface of this sample was also markedly lower than it was for the surface of feldspar treated with HF alone; the Si/F ratio was somewhat similar in going from the feldspar/HF to the feldspar/HF-H₂SO₄ system. Thus, it appeared that in the stronger HF/H₂SO₄ acid, more aluminum was lost from the surface than silicon. This is in agreement with those results reported for dissolution of glassy silicates (WHITE, 1982).

The sample depths being observed in the spectra of the argon ion sputtered samples in this study could not be determined accurately, since sputter-etch profiling rate data for feldspars are not available. The profiling rate for quartz, however, is approximately 30% of the rate of Ta₂O₅ (TAYLOR, private communication), or 180 Å/min for the sputtering rate used here. Assuming a similar rate for feldspars, a 30 sec argon ion bombardment would be equivalent to a penetration of about 90 Å into the mineral bulk. While it should be emphasized that the feldspar value will probably vary somewhat from that of quartz, it would still represent a 45 Å/30 sec value at even half the rate of quartz. When one then considers the 10-15 Å mean free path of the emitted electrons for the 300-800 eV range (ALLEN, 1978), a 30 sec sputtering period would represent a roughly 60 Å depth that is being observed with respect to the fluorine Auger signal. It must also be remembered that elemental sputtering yields are different; this can result in altered surface layers enriched in elements that exhibit low sputtering yields (HOFMAN, 1980). In any case, however, the sputtering rate for feldspar will have to be known with certainty

before the depth of penetration for the fluoride ion in this reaction system can be accurately determined.

Clearly such HF treatments complex the surface in a manner that might be difficult to reverse; the extent of this chemical alteration is a function of the time of surface treatment and the concentration of the acid system being used. It is therefore suggested that such a treatment either not be applied to studies involving sorption measurements on silicate mineral surfaces or that this chemical treatment be extensively studied in order to thoroughly understand its effect on silicate mineral dissolution kinetics.

Current research in this laboratory is extending the present investigation of feldspar/acid interactions to include the use of x-ray photoelectron spectroscopy in conjunction with the Auger technique in order to attempt to identify the surface species involving sulfur and fluorine. The identification of potential complex anionic species such as SiF_6^{2-} and AlF_6^{3-} will also be facilitated using combined binding energies/Auger kinetic energies (Auger parameters) (TAYLOR, 1981). Additionally, other surface approaches such as secondary ion mass spectrometry will be used in order to attempt to partition the contributions of various species to the total elemental contributions in the spectra (for example, what are the relative contributions of lattice oxides and surface hydroxides to the Auger oxygen spectra?, of F^- or SiF_6^{2-} to the Auger fluorine spectra?)

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Table 1. Elemental Auger line intensity ratios for feldspar and acid-treated feldspar

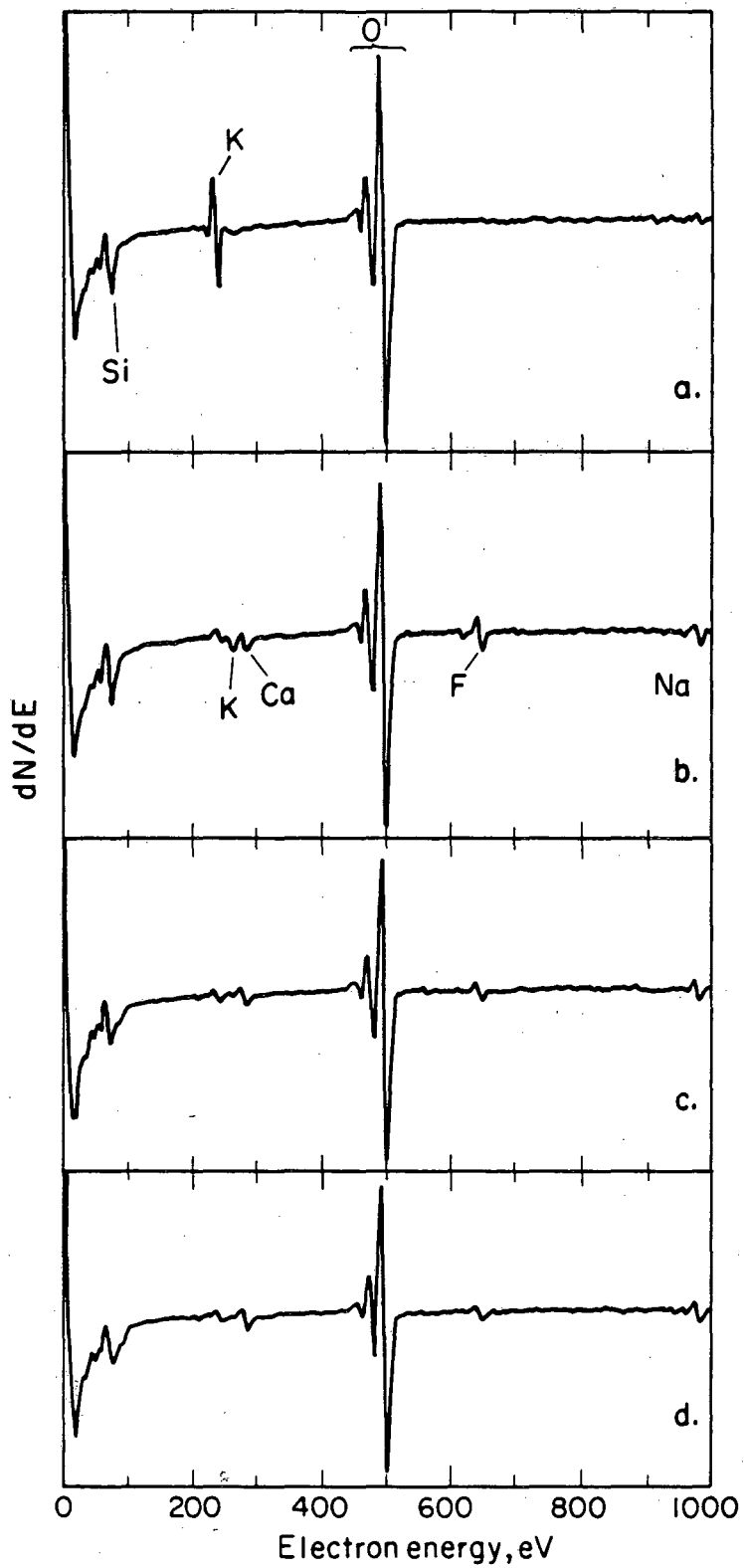
Feldspar Sample	O/Si	O/K	O/Na	Si/Na	Si/F	Al/F	Si/Al
I Untreated	6.4	3.5	*	*	*	*	1.8
II Treated with 10% HF	5.5	23.4	15.6	2.8	1.8	1.1	1.6
III Treated with 10% HF, ion sputtered for 15 sec	6.5	30.9	14.5	2.2	2.2	1.5	1.5
IV Treated with 10% HF, ion sputtered for 30 sec	4.3	29.9	14.1	3.2	3.9	1.6	2.4
V Treated with 10% HF/ 0.1 N H ₂ SO ₄	5.4	14.3	*	*	1.0	0.4	2.5
VI Treated with 10% HF/ 0.1 N H ₂ SO ₄ , ion sputtered for 15 sec	4.7	14.0	*	*	2.1	1.1	1.9
VII Treated with 10% HF/ 0.1 N H ₂ SO ₄ , ion sputtered for 30 sec	5.2	7.9	*	*	2.6	1.8	1.5

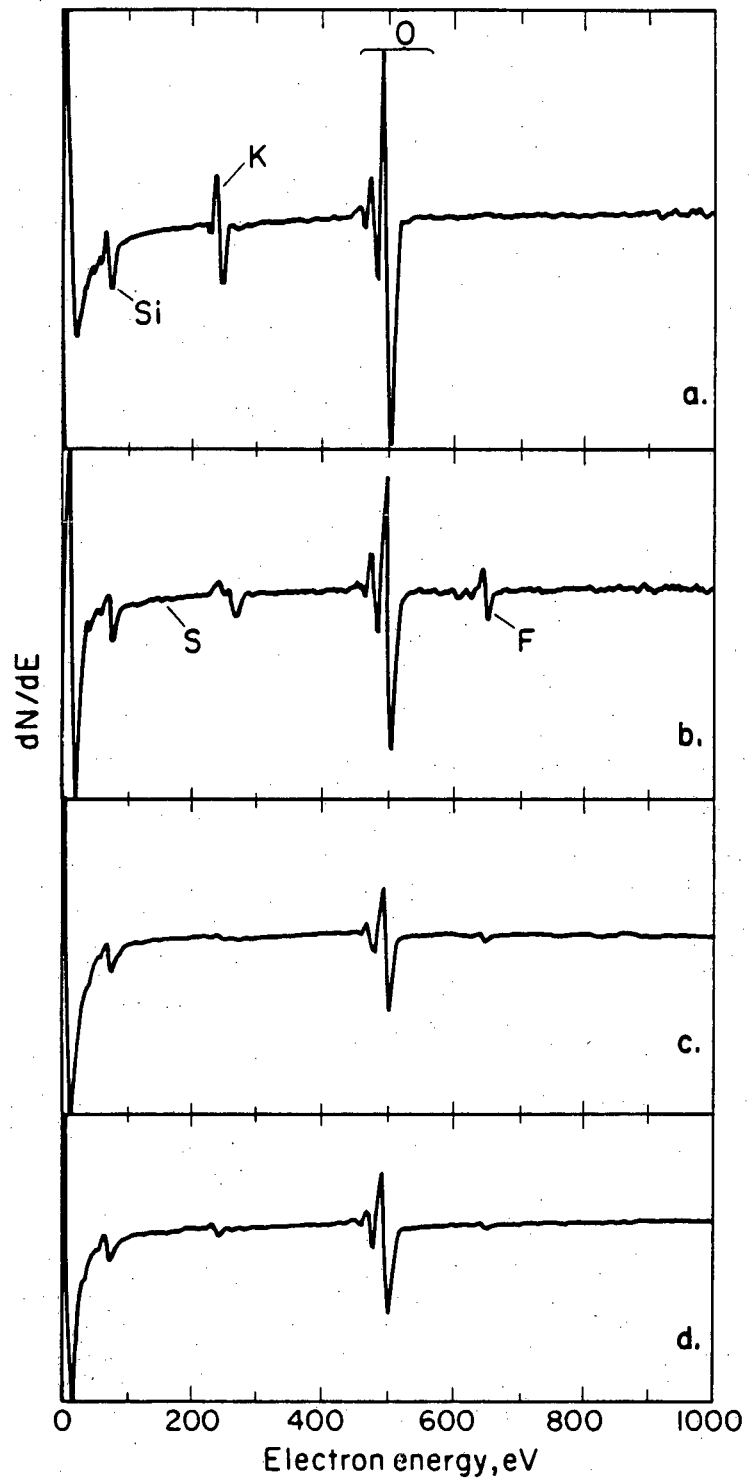
*One of the elements not detected

FIGURE CAPTIONS

Figure 1. Auger spectra of HF-treated K-feldspar. a) untreated, "as received," b) treated with 10% aqueous HF for 20 min., then washed with distilled, de-ionized water, c) HF-treated sample after 15 sec argon ion sputtering, and d) HF-treated sample after 30 sec argon ion sputtering.

Figure 2. Auger spectra of HF/H₂SO₄-treated K-feldspar. a) untreated, "as received," b) treated with a 50% aqueous mixture of 10% HF and 0.1 N H₂SO₄ for 20 min., then washed with distilled, de-ionized water, c) HF/H₂SO₄-treated sample after 15 sec argon ion sputtering, and d) HF/H₂SO₄-treated sample after 30 sec argon ion sputtering.





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