esters below −40 °C, the temperature at which the oxidation usually is carried out.[27]

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(8) Moreover, the most labile alkylpotassium compounds decompose at temperatures about −45 °C. Organometallics of the dienyl type are generally much more stable, but, at room temperature or higher, they may eliminate metal hydride or react with the solvent. Spectroscopic signals from secondary products can easily be confused with those from related organometallic intermediates.
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(12) In contrst, the branched product, which no longer delivers a stereochemical message, was found to predominate when electrophiles such as chloromethyl methyl ether were chosen as the reagent.
(13) Under somewhat modified reaction conditions typical product compositions were 50–52% (*Z*)-**4**, 20–22% (*Z*)-**5**, and 5–9% (*E*)-**4** + (*E*)-**5**.
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(21) At present, no definitive decision can be made whether the true structure is a symmetrical π complex or an unsymmetrical, "fluctuating" σ compound undergoing rapid [1,3]-sigmatropic metal shifts through a π-bonded *transition state*. In the latter case, however, the barrier to 1,3-potassium shifts can hardly be higher than 5 kcal/mol. When 2-isopropylallyl potassium in tetrahydrofuran-d_8/dimethyl ether-d_6 was cooled to −155 °C, the ^{1}H and ^{13}C NMR peaks broadened only slightly, probably owing to a viscosity effect. The methyl signals, however, did not reveal any indication of diastereotopicity. (M. Stähle, J. M. F. Oth, and M. Schlosser, unpublished results, 1976.)
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(26) 1,4-Pentadiene and 3-methyl-1,4-pentadiene produced *Z* and *E* derivatives, when the metalaction was performed with trimethylsilylmethylpotassium in tetrahydrofuran over a 15-min period at −80 °C and the mixture was immediately treated with fluorodimethoxyborane and peroxide. After the mixture was kept for 30 min at −60 °C, however, only (*E*)-2,4-pentadien-1-ol and (*Z*)-3-methyl-2,4-pentadien-1-ol, respectively, were obtained.
(27) We do not yet know whether allylic and dienylic boronic esters are π complexes or σ compounds. Currently we favor the less symmetric σ structure. In this case we assume the boron atom to be mainly linked to the unsubstituted allyl terminus, since boranes having primary alkyl ligands are thermodynamically more stable than those having secondary or tertiary alkyl ligands (H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **88**, 1433 (1966)). Small stationary concentrations of secondary boronic esters may still coexist owing to rapid [1,3]-sigmatropic shifts of the dialkoxyboron group. (For the fluxional behavior of allyl boranes, see B. M. Mikhailov, V. S. Bogdanov, G. V. Lagodzinskaya, and V. F. Pozdnev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 386; (1966); *Chem Abstr.*, **55**, 595c (1966); V. S. Bogdanov and B. M. Milhailov, *Dokl. Akad. Nauk SSSR*, **193**, 586 (1970); *Chem. Abstr.*, **74**, 12494e (1971).) However, we wish to emphasize that the conclusions drawn in the present communication do not depend on a particular structure postulate for dieneboronic esters. We have simply to worry about their torsional dynamics. The stereochemical information will be faithfully delivered only if cis/trans (endo/exo) isomerizations of the allylic (dienylic) system are slow at temperatures below −40 °C. This has been confirmed again in another way. The metalaction of cyclododecene (cis/trans mixture), followed by treatment with fluorodimethoxyborane and alkaline hydrogen peroxide, furnished only *cis*-cyclododecen-3-ol (mp 64–65 °C; configuration assignment based on ^{1}H NMR in the presence of varying amounts of tris(dipivalomethanato)europium)). If rotation around a carbon–carbon bond of the allylic system were feasible under the reaction conditions, the (*Z*)-cyclododeceneboronic ester would at least partially have been converted to the *E* isomer, trans-double bonds being generally favored in twelve-membered-ring systems.

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X-Ray Photoelectron Diffraction: A New Technique for Structural Studies of Complex Solids

Sir:

Whenever a guest species is substitutionally incorporated within a host solid the precise location of the dopant atoms is seldom capable of being determined directly. So far as isomorphous substitution in minerals is concerned, the classical studies of Mauguin[1] and others[2-4] have demonstrated the deductive principles which have enabled site assignments to be made for those ions which may, in principle, occupy more than one distinct structural location. There remains, however, a need for direct techniques which can identify specific occupied sites, be they regular or interstitial, especially when the degree of occupancy (dopant concentration) is low. X-ray photoelectron diffraction (XPD), as is described below, promises to fulfill that need.

It has for some years been recognized that photoelectrons generated below the surface of a single-crystal specimen may be elastically scattered (diffracted) before their escape into the vacuum, resulting in anisotropy of the ejected electron flux.[5-7] Interest in these phenomena has, however, been relatively slight, probably because on the one hand there existed no immediate prospect of any adequate quantitative interpretation of the diffraction patterns[8]—although this problem now seems closer to solution, at least for simple crystal structures[9]—while on the other their considerable potential value in chemistry has not been emphasized. We report here the first examples of the use of x-ray photoelectron diffraction (XPD) to derive (in an attractively direct noncomputational manner) valuable structural information relating to complex solids—information which would, indeed, be difficult, if not impossible, to obtain from established techniques. In this study, we are concerned with a class of solids, the micaceous sheet silicates, which possess a range of compositions within a fixed structural type. Much has been deduced, indirectly, concerning the structural chemistry of these solids and idealized formulae and structures of two such materials, muscovite and phlogopite, are shown in Figure 1. We seek here direct answers to questions such as these. Is the Al in muscovite indeed partly located at tetrahedral sites? Does phlogopite contain Al in octahedral sites? Do Na^+ and K^+ occupy *exactly* equivalent interlamellar sites?

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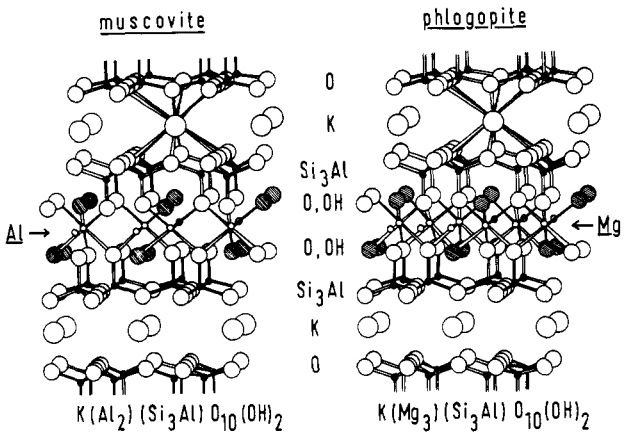

Figure 1. Projection of idealized structures for muscovite, $K(Al_2)(Si_3Al)O_{10}(OH)_2$, and phlogopite, $K(Mg_3)(Si_3Al)O_{10}(OH)_2$, along the *a* axis.

We have recently recorded x-ray photoelectron spectra of a number of vacuum-cleaved micas as a function of electron takeoff angle. As well as the diffraction phenomena mentioned above, the spectra show substantial variations in overall intensity due to purely experimental factors (e.g., probe eccentricity); intensity *ratios* are, however, independent of such factors. For a constant angle between incident photon and ejected electron, no angular variation derives from the angular momentum character of the (core) orbital ionized.[10,11] Essentially all remaining (oscillatory) variations with angle are thus attributable to diffraction. Chemical inhomogeneities, if present in the near-surface region, can give rise to additional, easily-recognized, systematic trends in the angular variation of peak intensity ratios; these effects are themselves of considerable geochemical interest but will be described elsewhere. The spectra described here are free from such complexities.

In Figure 2 we show the angular variation of the principal intensity ratios for muscovite. Qualitatively similar results were obtained from the other materials examined. A priori, a number of factors might be expected to be important in determining XPD patterns from a given crystal in a fixed azimuthal orientation: these include (i) the location (site symmetry) of the ionized atom, (ii) the wavelength, λ, of the photoelectron, and (iii) the radius of the ionized shell. However, all the *intraelemental* ratios examined (e.g., K 2p/3p and Si 2p/2s in Figure 1) have been found to remain essentially invariant with angle, showing clearly that both differences between the photoelectron wavelengths ($\lesssim$30%), and between the radii of the shells ionized, are very much of secondary importance in determining the overall range of values of a peak area ratio.[12] Consequently, we are able in Table I to correlate the overall ranges of variation of each ratio directly with the differences between the sites of the core levels concerned. This fact permits the use of XPD as a structural technique for locating "foreign" atoms substituted into a complex (single-crystal) solid.

Comparison of Figures 1 and 2 immediately demonstrates (cf. Table I) that, when the two core levels compared have different and unique locations in the crystal (Si 2p, K 2p), the range of variation is at its widest, while, when the two levels are situated in the same atom (Si 2s, 2p; K 2p, 3p), the range of variation is minimal. The Si 2p/O 1s ratio varies much less than that for Si 2p/K 2p because oxygen occurs in three distinctly different environments in these minerals so that the O 1s XPD pattern is partly "averaged-out"; the variations in the absolute O 1s intensity with angle are proportionately much lower than those for any other atom in these minerals.[13]

The excess aluminum present in muscovite (including the present specimens[11]) over the proportion required to fill two

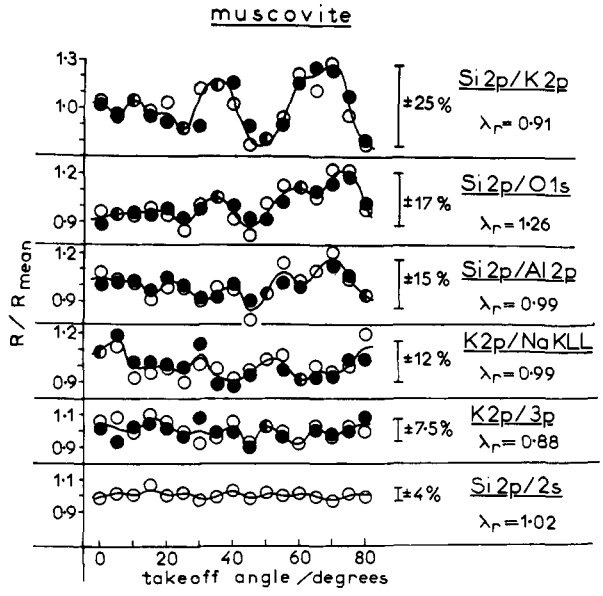

Figure 2. Normalized XPD patterns for muscovite. The takeoff angle is defined as the angle between the electron beam and the normal to the surface of the specimen. Filled and open circles distinguish data from different cleavages in the same specimen; λ_r denotes the ratio of the de Broglie wavelengths of the electrons concerned.

Table I. XPD Range Data for Micas

Ratio classification	Mean range of variation[a] (S.D.[b])	No. of instances	Representative examples (in muscovite[c])
Each core level in atom at different, unique site	25 (3)	7	Si 2p/K 2p
One core level in atoms at several sites	18 (2)	4	Si 2p/O 1s
Both core levels in same atom	6 (2)	8	K 2p/3p, Si 2p/2s

[a] Appreciable changes in the electron acceptance angle may affect the magnitude of the range observed; these data were taken with an AEI ES 200A electron spectrometer. [b] Standard deviation. [c] See Figures 1 and 2.

thirds of the octahedral sites (Figure 2) is believed, from the studies mentioned earlier,[1-4] to replace silicon in tetrahedral sites. The evidence for this hypothesis, however, is largely circumstantial; so XPD data for these elements in micas are of particular interest. The considerable reduction in the range of the Si 2p/Al 2p ratio in muscovite in comparison with the Si 2p/K 2p ratio suggests, directly in line with the arguments (above) concerning the Si 2p/O 1s ratio, that such substitution does indeed occur in muscovite, an interpretation which receives support from studies of related minerals. Thus in phlogopite, which is believed to contain aluminum *only* in substitution for tetrahedral silicon, the Si 2p/Al 2p ratio remains essentially constant (range ±4%), whereas in lepidolite this same ratio varies by ±24%; in this latter mineral the majority of the aluminum is in octahedral rather than tetrahedral coordination.

Sodium is not present in an "ideal" mica, but its presence in trace quantities in the present specimens has been unambiguously established by electron spectroscopy. Naively, one might expect sodium simply to replace potassium in the structure of Figure 2; so K/Na photoelectron intensity ratios should remain essentially constant with angle. The Na 2s and 2p peaks were here too weak for the recording of reliable XPD patterns; however, because photon-excited Auger electrons must display precisely analogous angular phenomena, the K

2p/Na KLL Auger ratio could be used instead. As Figure 1 shows, this ratio varies by ±12%, considerably more than would be expected (cf. Si 2p/Al 2p in phlogopite) if the two atoms occupied *identical* sites. However, it is known that, when Na replaces K in montmorillonite, a closely-related aluminosilicate, the smaller cation (Na^+) is displaced toward the aluminosilicate layer from the central position preferred by the larger ion (K^+) for steric reasons.[14] It would thus seem entirely plausible to postulate a similar effect in muscovite. In any event, it is clear that the Na and K sites are nearly, but not totally, equivalent in this mineral. Information such as this cannot be derived from x-ray or neutron diffraction studies because of the low concentration and random distribution of the substitutional atom. Sodium comprises only about one tenth of the interlayer ions within the sampling depth (the electron inelastic mean free path is here ~35 Å[15]) in these specimens.

The potentialities of XPD for the study of substitutional impurities in minerals are thus clearly considerable, but the technique is not confined to geochemistry. It would, for example, seem possible to distinguish between substitutional and interstitial sites for impurity atoms present in any monocrystalline solid at low concentrations. Much further work will, however, be required to delineate fully the areas in which XPD will prove useful.

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Extended X-Ray Absorption Fine Structure Studies of the Hydrolytic Polymerization of Iron(III). 1. Structural Characterization of the μ-Dihydroxo-octaaquodiiron(III) Dimer[1]

Sir:

The hydrolytic polymerization of iron(III) has been the subject of numerous studies[2] over the last several years. Aqueous solutions of iron(III) hydrolyze over a range of pH forming dimer and polymer complexes. These complexes are of interest because they display unusual magnetic properties[3] and because they are believed to provide useful models[4] for iron storage proteins. Since the complexes tend to exist only in solution, structural characterization by x-ray diffraction is usually lacking. The advent of the extended x-ray absorption fine structure (EXAFS) technique provides a unique opportunity to investigate the structures of the iron complexes in the solution phase.

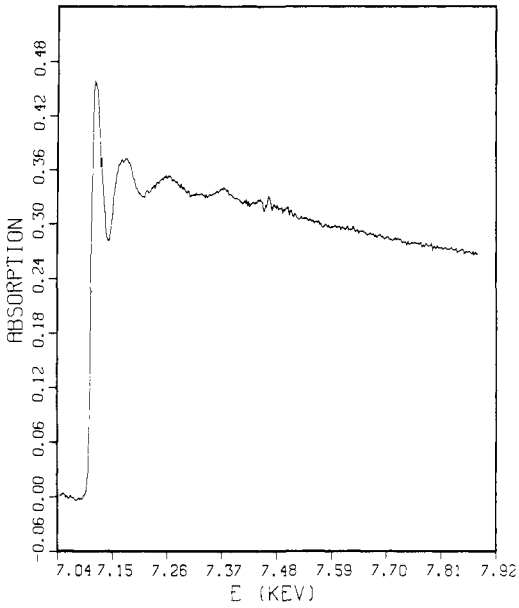

Figure 1. Raw EXAFS pattern. A plot of μx, the absorption coefficient times the effective thickness of the sample as a function of photon energy in electronvolts.

The existence of the dihydroxo-bridged iron(III) dimer μ-dihydroxo-octaaquodiiron, $[(H_2O)_4Fe(OH)_2Fe(OH_2)_4]^{4+}$ (**1**) in low pH solutions has been postulated to be the predominant specie on the basis of electrometric,[5] thermochemical,[6] magnetic,[7] and spectral[3,7] studies. No direct structural evidence has been reported to substantiate this formulation. We now wish to report structural data, based on EXAFS measurements, demonstrating the existence of the postulated dimer, **1**.

The EXAFS data were taken on a modified General Electric XRD-5 diffractometer equipped with a standard line focus Mo x-ray tube, a curved germanium monochromator crystal, an automatic sample positioner, and a translatable scintillation counter. The iron solution samples were prepared by absorbing a 1.819(2) M $Fe(ClO_4)_3$-0.023 M perchloric acid solution (pH 1.2 ± 0.2) on a piece of filter paper (12 μ thick) and sealing the paper with Parafilm to prevent evaporation and concentration changes. Figure 1 shows the resulting raw EXAFS pattern (data taken in 16 h), a plot of μx, the absorption coefficient times the effective thickness of the sample, as a function of energy in electronvolts. Following a procedure described by Lytle, Sayers, and Stern,[8] the raw EXAFS pattern was transformed to a wave vector, $\chi(k)$, spectrum by subtracting the background and setting $k = [2m(E - E_0)/\hbar^2]^{1/2}$ where E_0 and m are, respectively, the threshold energy and mass of the ejected photoelectron (Figure 2). $\chi(k)$ may be related to interatomic distance by

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$

$$= 1/k \sum_i A_i f_i(k) e^{-2\sigma_i^2 k^2} \sin[2kr_i + \Phi_i(k)]$$

where $\mu_0(k)$ is a smoothly decreasing function about which $\mu(k)$ oscillates; r_i is the distance from the absorber to the ith

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