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Microanalysis for Fluorine and Hydrogen in Silicates with the Ion Microprobe Mass Analyzer

JAMES R. HINTHORNE, AND C. A. ANDERSEN

Hasler Research Center, Applied Research Laboratories
95 La Patera Lane, Goleta, California 93017

Abstract

A method for *in situ* quantitative microanalysis of fluorine and hydrogen (water) in silicates has been developed with the ion microprobe mass analyzer. The procedure utilizes working curves constructed from analyzed or stoichiometric minerals. Detection limits of ~20 ppm for fluorine and ~100 ppm by weight for hydrogen are attainable.

Introduction

The ion microprobe mass analyzer (IMMA) has been developed to perform an *in situ* microanalysis of a solid surface by bombarding the surface with a focussed beam of heavy ions at medium energy and then mass analyzing and counting the secondary ions sputtered from the surface (Liebl, 1967; Andersen and Hinthorne, 1972a). Results of general trace element and isotopic microanalysis utilizing the IMMA have been reported previously (*e.g.*, Prinz *et al*, 1973; Fredriksson *et al*, 1971; Andersen and Hinthorne, 1972b, 1973a). This note describes a new method for the microanalysis of fluorine and water in silicate minerals which will hopefully open new avenues of attack on several important geochemical problems.

With present techniques the detection limit for fluorine utilizing the electron microprobe is about 1000 ppm, and there is no technique available for the *in situ* microdetermination of hydrogen or water in silicates. Water determinations have been attempted using charge balance considerations and accurate electron microprobe analyses with some degree of success in simple systems such as topaz (Ribbe and Rosenberg, 1971; Rosenberg, 1972) and humite minerals (Jones, Ribbe and Gibbs, 1969), but with conflicting results in complex minerals such as staurolite (compare Hollister, 1970; Griffen and Ribbe, 1973).

Analytical Procedures

Polished grain mounts and thin sections as standard for microprobe analyses were used in these studies, except for the zeolites, micas, and epidote, which were merely attached with silver paint to a mounting substrate and not polished. All samples were carbon coated to facilitate secondary ion acceleration into the mass spectrometer. The samples were bombarded with a negatively charged primary beam (Andersen, Roden, and Robinson, 1969) of monatomic oxygen ($^{16}O^-$) at 17 keV.

The measurements necessary to determine the H or F concentrations are the secondary ion intensities of the $^1H^+$ or $^{19}F^+$ isotope and a major element isotope for intersample normalization. We have chosen to use silicon for the internal standard because it is obviously present in all silicates and its abundance can normally be easily determined by electron microprobe analysis or inferred from the sample stoichiometry. We use either the $^{28}Si^+$ or $^{30}Si^+$ ion signal for the internal standard measurement.

To form working curves, the measured ion intensity ratios of H^+/Si^+ or F^+/Si^+, corrected for natural isotopic abundance, were measured and plotted against known H or F contents for a series of standard samples that were normalized for the different silicon abundances. Figures 1 and 2 show such curves and indicate the kinds of samples used to construct them. The use of ratios relative to an internal standard is necessary because the absolute ion yield from a surface is a very sensitive function of the electrical properties of the surface of the sample (Andersen, 1970) which can even change with crystallographic orientation. The *ratio* of different sputtered ion species from a given matrix, however, has been observed to be constant. These

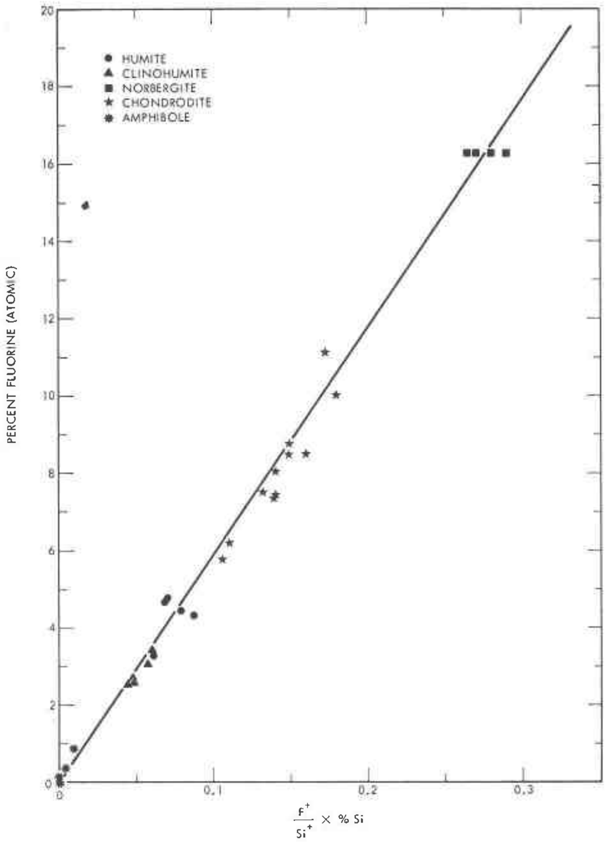

FIG. 1. Working curve for fluorine in silicate minerals. Samples of humite group minerals analyzed are the same ones analyzed by Jones (1968). The amphibole ordinate values were determined by wet chemical methods on bulk mineral separates; data and samples supplied by J. Stout. Slope of working curve = 58.4.

ideas, which we considered to be basic to the interpretation of sputtered ion intensities (Andersen and Hinthorne, 1972a, 1973b), have been documented further by Bence, 1973. Changes in the ion intensity ratios do occur with matrix changes, but for the elements considered here most silicates have apparently similar enough matrices that the ionization efficiency ratios of these species are constant to a first approximation. From our experiences it would be unwise to extend the use of these curves developed for silicates to different matrices, metals for example, without extensive checking.

The working curve approach has been recognized as a valuable technique for secondary ion trace element analysis (Andersen, 1969; Colby, 1973). However, the uncertainty of matrix effects on the relative ionization of different elements and the difficulty of obtaining homogeneous working standards for many trace elements in the wide variety of necessary matrices has led to the development of a theoretical model of ion generation for quantitative analysis (Andersen and Hinthorne, 1973b). Although the theoretical model works well for many elements in a wide variety of matrices, it apparently is not yet complete enough to use reliably on elements with high ionization potentials. Because fluorine and hydrogen have relatively high ionization potentials (17.42 eV and 13.60 eV, respectively), we have found it necessary to use working curves for these elements until the theoretical model can be developed further.

Fluorine and Hydrogen Working Curves

The working curve for fluorine in silicates (Fig. 1) is relatively straightforward. Each point on the plot represents the analysis of a separate sample as keyed in the legend. The four uppermost points represent measurements on four separate grains of the same sample. The ordinate values have been determined for the humite group minerals by electron microprobe analysis (Jones, 1968) and are accurate to approximately 5 percent (P. H. Ribbe, personal communication, 1972). The ordinate values for fluorine in amphibole were determined by wet chemical methods (J. Stout, personal communication, 1971). The fluorine working curve shows good correlation between the fluorine values and the normalized $^{19}F^+$ intensity as measured with the IMMA. The average deviation of the measured points from the linear working curve is approximately 5 percent of the fluorine abundance.

The large number of secondary ions that can be generated by ion bombardment yield typical ion count rates on major elements in silicates in the 10^6–10^7 counts/second range with a background of 1–10 counts/second. This large dynamic range leads to excellent sensitivities, even for elements with high ionization potentials. Using a primary beam current of 1×10^{-8} A, the detection limit (3σ of the measured background counts) for fluorine in silicates is about 20 ppma (parts per million atomic or atoms/10^6 total sample atoms). This current represents a probe diameter of about 25 microns, and proportionately greater sensitivities and better detection limits can be achieved if larger areas are analyzed. In this case the detector background is known to be the limiting factor in determining the detection limit.

The working curve presented here for hydrogen

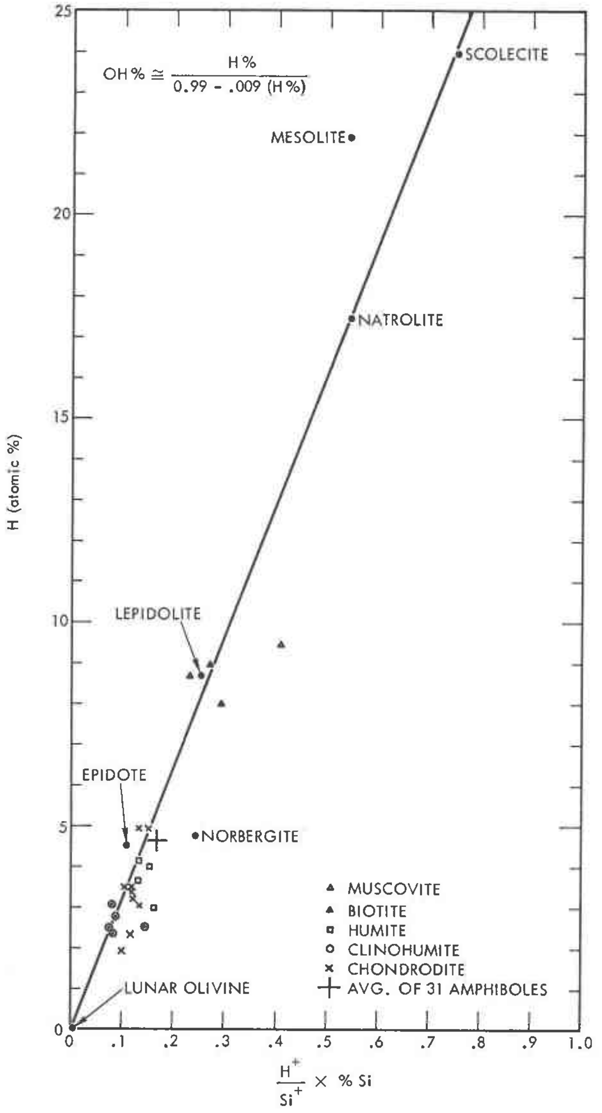

FIG. 2. Working curve for hydrogen in silicates. Stoichiometry was assumed for all water contents (corrected for fluorine as determined from Figure 1), except for the humite group minerals where the values from Jones (1968) are used. The formula for the conversion to "atomic percent OH" is given. Slope of working curve = 32.1.

(Fig. 2) is not as tightly defined as the one for fluorine. The fault is possibly due to the assumptions of stoichiometry used in calculating the atomic percent hydrogen plotted on the ordinate. The average error in these standard samples is approximately 20 percent of the hydrogen abundance. The atomic percent hydrogen for a stoichiometric compound is easily calculated from the chemical formula (*e.g.*, H = 40% in $Ca(OH)_2$ and H = 21.5% in lawsonite, $CaAl_2(OH)_2[Si_2O_7]H_2O$). The conversion to "atomic percent OH" is given by the equation in Figure 2 (OH = 66.6% in $Ca(OH)_2$, and OH = 26.7% in lawsonite. It should be noted that to a first approximation, the IMMA measures hydrogen with the same efficiency whether it occurs as OH or H_2O in the specimen. For example, zeolites such as scolecite, mesolite, and natrolite, although they contain hydrogen as H_2O, plot on the same curve as silicates which contain hydrogen as OH. This is because the secondary atomic and molecular ions observed in the mass spectrum are not directly related to the molecular structure of the solid but are the equilibrium reaction products of a collection of implanted and sample atoms interacting at an elevated temperature (Andersen and Hinthorne, 1973b, p. 1424). Therefore, differentiation of OH from H_2O in an unknown specimen would appear to be difficult from these initial experiments.

The detection limit for hydrogen in the IMMA is not limited by the detector background (as in the case of fluorine) but by the recontamination rate of residual hydrogen-bearing gases present in the working vacuum system onto the surface being sputtered. Several modifications of instrumental design have resulted in a lowered level of hydrogen-bearing species in the working vacuum system. These include the use of an ion pump to maintain the system operating pressure at 10^{-7}–10^{-6} torr was gas flowing from the ion source, a mass separated primary ion beam to ensure that it is free of hydrogen, and a cold plate kept at liquid nitrogen temperatures in close proximity to the region being analyzed. The cold plate effectively removes water and heavier hydrocarbon molecules from the residual gas but is less effective with gases such as H_2 and CH_4.

With hydrogen present in the vacuum system it is necessary to choose samples with very low hydrogen contents in order to define the detection limit. In this case, we have attempted to determine the detection limit by using lunar silicates. Even with "dry" systems such as these lunar minerals, it is not certain how much of the hydrogen that is detected originates within the lunar minerals and how much is due to vacuum system surface contamination. The measured values of [$H^+/Si^+ \times$ % Si] in some lunar phases range from 0.009 to 0.004 (olivine, pyroxene, and glass). A value of 0.006 would correspond to 1900 ppma on the working curve in Figure 2 (approximately 100 ppm by weight). Recent work on the hydrogen contents of lunar minerals and glasses show residual hydrogen levels of approximately 1000–2000 ppma at depths greater than 2000 Å below the grain surfaces (Leich, Tombrello, and Burnett, 1973). Thus the low hydrogen contents we have measured with the IMMA may include hydrogen from the samples as well as hydrogen introduced from the vacuum system, and the real detection limit is yet to be defined.

The data on Figure 2 were obtained over a period of two years on two different ion microprobes. No bias between the two instruments is discernible. The main variation that might be expected between different ion microprobes would be in the vacuum system's contribution of H to the background due to minor vacuum leaks or sample handling procedures. The "vacuum sample holder" recently described by McLaughlin and Cristy (1974) will make it possible to load hygroscopic samples into the ion probe's vacuum system without exposure to air.

Applications

There are undoubtedly many geochemical problems which would benefit from a detailed knowledge of the distribution of fluorine and/or hydrogen at major to trace concentrations. The following list indicates some possibilities. These applications appear to us to be relatively straightforward with respect to sample requirements and data acquisition. Most of these problems would be better solved with a combined electron microprobe and IMMA study, utilizing the strengths of each technique.

1. Role of water in the gradation from garnet to hydrogarnet.
2. Partitioning of F and OH among silicate phases in igneous and metamorphic rocks.
3. OH contents as an indicator of water pressure during crystallization of minerals such as feldspars—does oscillatory zoning reflect changing water pressure?
4. Distribution of hydrogen in depth in lunar surface material.
5. Hydration of minerals as a first step in the weathering process.
6. Determination of fluorine contents of micas so that results from experimental phase equilibria may be realistically applied to natural materials.

Our experience with terrestrial minerals typically considered anhydrous (garnet, kyanite, pyroxene, olivine, and feldspar) suggests that these phases contain variable amounts of hydrogen (water). These observations support the conclusions of Wilkins and Sabine (1973, p. 508) who "have established the presence of small and variable amounts of OH ions in the structures of various nominally anhydrous silicate minerals."

We are presently studying a suite of staurolite samples to determine their water contents and hopefully to resolve the dilemma summarized in Griffen and Ribbe, 1973. The initial results on five samples indicate a spread in (OH) contents from two to three (OH) per formula unit containing 44 oxygen atoms.

The IMMA has recently been used to determine the (OH) contents of $BaTh_4Si_4O_{16}(OH)_2$, a new barium-thorium-silicate mineral, of which only a few impure grains less than 0.5 mm in size have so far been found (Wise and Hinthorne, in preparation).

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