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Determination of hydrogen in silicates using the ion beam spectrochemical analyzer: application to hydrolytic weakening

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Abstract

The ion beam spectrochemical analyzer (IBSCA), which utilizes the emitted radiation from sputtered atoms, has been used for the quantitative analysis of hydrogen content in a number of silicate samples. An attempt is made to interpret the role of hydrogen in the process of hydrolytic weakening in these materials.

Introduction

Accurate analyses of hydrogen in the form of water have been obtained by Wilkins and Sabine (1973) on nominally anhydrous silicates using an electrolytic method. Information on water content in minerals can also be obtained by well-established techniques such as differential thermal analysis/thermogravimetric analysis (DTA/TGA) and infrared absorption spectroscopy, but such information is generally only approximate. The possibility of determining hydrogen in minerals using the ion microprobe mass analyzer (IMMA) has recently been demonstrated by Hinthorn and Andersen (1975). Novel methods using nuclear reactions and proton scattering with MeV ion beams to analyze hydrogen have been reported by Cohen *et al.* (1972), Leich and Tombrello (1973), and Ligeon and Guivarch (1974), but these cannot be considered as instrumental techniques which can be used in the laboratory on a routine basis. Conventional *in situ* analytical methods such as X-ray fluorescence and electron probe micro-analysis fail completely for the detection of hydrogen and other light elements.

A relatively inexpensive and yet versatile instrument, the ion beam spectrochemical analyzer (IBSCA), has been developed to perform rapid and accurate elemental analysis of solid surfaces. This is done by bombarding the surface with a focussed beam of medium-energy heavy ions and detecting the emitted radiation from excited atoms ejected from the target surface. As successive surface layers are sputtered away in the process of bombardment, the bulk composition of a homogeneous solid or the concentration profile of an inhomogeneous solid can be analyzed. Qualitative and quantitative analyses of solids using this method have been described by Tsong and McLaren (1974, 1975). A similar method has also been used by White *et al.* (1972, 1974) for the same purpose.

In this paper we show that IBSCA provides a new method for the detection of hydrogen in a variety of silicate samples. Accurate measurement of hydrogen content will enable us to understand more fully the problems concerning the hydrolytic weakening of natural and synthetic materials (Griggs 1967).

Method

The IBSCA apparatus used for the detection of hydrogen in solids is shown in Figure 1. Specpure argon gas was used to provide the bombarding ions. An intense, stable, and near-monoenergetic ion beam was produced by the duoplasmatron ion source. When the ion source was operated at +12 kV, the ion current density at the target was about 20 μA mm^{-2}. The einzel lens focused the beam to a spot of ~2 mm in diameter at the target surface. The charge accumulation on the nonconducting surface was alleviated by inserting a metallic mask with a 2 mm diameter hole over the target surface. The mask under bombardment acted as a source of secondary electrons which

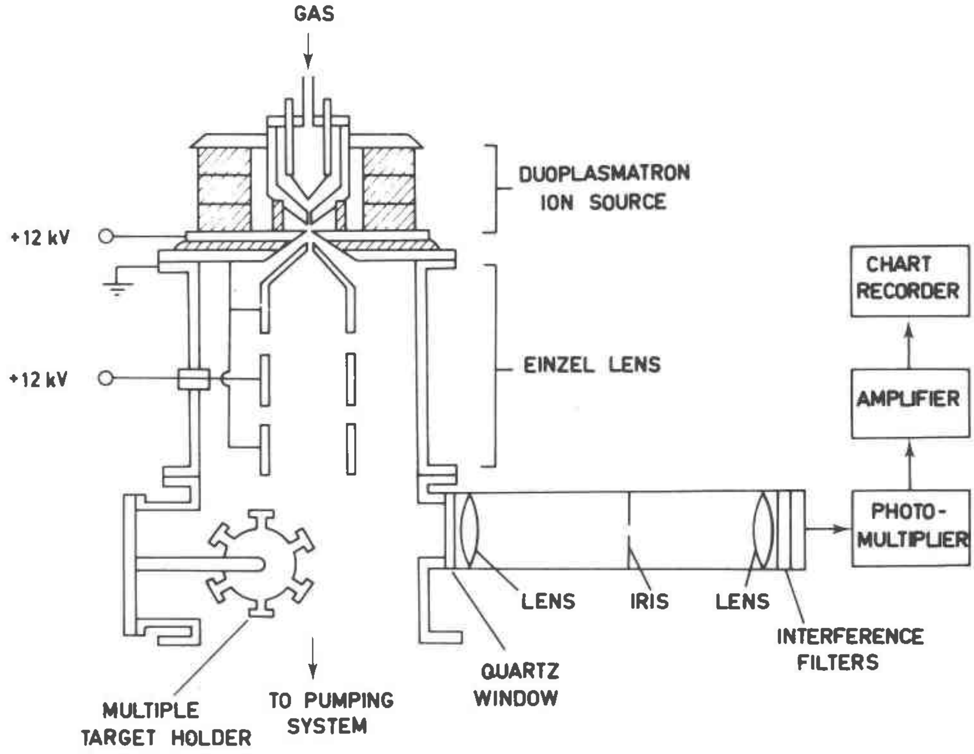

FIG. 1. Schematic diagram of the IBSCA apparatus for the determination of hydrogen in solids.

neutralized the charge on the surface of the target. The background pressure in the vacuum system was ~10^{-7} torr. The partial pressure of argon was 1×10^{-5} torr when the ion source was in operation.

The multiple target holder can accommodate up to six samples. For the analysis of hydrogen, one target was usually an inert (*i.e.* hydrogen-free) sample such as pure copper or aluminum. The light collection optical system utilized interference filters for maximum sensitivity. Two narrow band interference filters (HBW 10 Å) were used to isolate the hydrogen 6563 line. If only one filter was used, the intense Li 6707 line from lithium-rich minerals would interfere with the hydrogen line. A one-to-one image of the target was formed on the iris by the first lens. The iris was installed to cut out any stray light which did not come from the bombarded target. For maximum signal-to-noise ratio, the iris had to be adjusted to about the same size as the area under bombardment, *i.e.*, 2 mm in diameter.

In a previous report (Tsong and McLaren 1975), it has been shown that quantitative analysis of a particular element, x, can be carried out if a plot of the intensity, I, *vs.* $\Delta M.W_x$ is constructed from standard samples. It has also been shown that the results are independent of the matrix composition of the silicate minerals. In the present study, I is the intensity of the H6563 line, ΔM is the rate of total mass loss of the sample during sputtering determined by weighing the sample with a microbalance (Mettler M5/SA) before and after 10 minutes' bombardment, and W_H is the weight percent of hydrogen in the solid sample. Figure 2 shows a working curve of $I(6563)$ *vs.* $\Delta M.W_H$. The hydrogen concentration in these standard samples lies in the range of 0.17–0.54 weight percent or 2–11 atomic percent. The hydrogen content in the form of water of the mica samples was estimated from DTA/TGA measurements or from ignition loss. In the other samples, the hydrogen was estimated from the chemical formulae assuming stoichiometry; the errors involved in these could therefore be substantial. Nevertheless, the plot shows a reasonable straight line similar to the plots for the major elements in feldspars reported previously (Tsong and McLaren 1975).

When the inert (hydrogen-free) sample was bombarded, a signal corresponding to about 0.6 on the intensity scale in Figure 2 was observed. This was taken as the background optical noise level and was about six times higher than the level given by the dark current limit of the photomultiplier. The intensities shown in Figure 2 have all been corrected for this

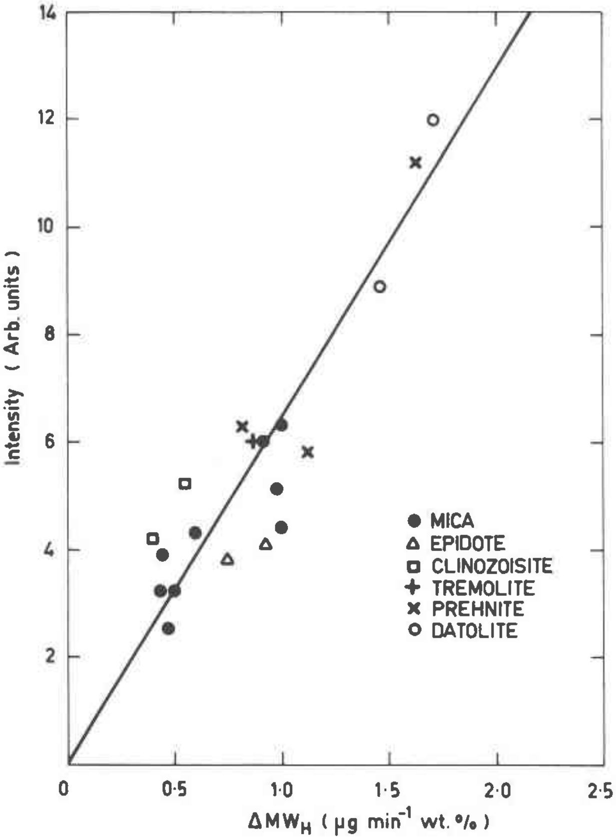

FIG. 2. Working curve for determining hydrogen in silicates. The intensity of the H6563 line is plotted against the product of the rate of mass loss, ΔM, and the weight percent of hydrogen in the material, W_H.

background. If we consider that the background hydrogen signal was due to the residual hydrogen in the vacuum system present as excited atoms in the ion beam, then this signal would correspond to a hydrogen partial pressure of 10^{-12} torr, *i.e.*, about 10 ppm of the residual gas in the chamber was hydrogen. This is probably rather high, considering hydrogen in the atmosphere is only about 0.5 ppm.

Results

Using the working curve in Figure 2 the weight concentration of hydrogen in a number of natural and synthetic quartz and silicate samples was determined by measuring the intensity of the H6563 line and the rate of mass loss during sputtering. The results are shown in Table 1. Typical rate of mass loss in quartz was about 5 μg min^{-1}. In some quartz samples the intensity signal was found to rise to an initial peak before decaying very rapidly with time until an equilibrium value was reached. This effect was most striking in quartz crystals from the polycrystalline quartzite. Water was used in the surface preparation of the quartzite sample. When the sample was bombarded in the target chamber, the light intensity signal reached a very high peak before slowly decaying, as seen in Figure 3a. However, when the sample was heated for 48 hours in an oven at 130°C, bombardment of the sample produced a signal which quickly rose to an equilibrium value (Fig. 3b). From this, it was concluded that the initial rise was due to water adsorbed on the sample surface. To avoid this effect, all samples were heat-treated at 130°C prior to bombardment. We were therefore analyzing the content of hydrogen in the bulk of the silicate sample.

Discussion

The considerable scatter in the working curve (Fig. 2) is due to the unknown uncertainties in hydrogen concentration in the standard samples. This partly reflects the difficulty in making an accurate analysis of the hydrogen or water content of minerals. The scatter in the IBSCA working curve is similar to that obtained by Hinthorn and Andersen (1975) using IMMA.

The hydrogen background imposes a lower detection limit to the present work. If a signal-to-noise ratio of 2 : 1 is defined as an acceptable limit, then this will correspond to about 160 ppm by weight or 3000 ppm of atoms of hydrogen in quartz. This compares well with the detection limit of approximately

TABLE 1. Comparison of the hydrogen content in a number of quartz and silicate samples as determined by IBSCA and IR absorption spectroscopy.

Sample	IBSCA (wt.% hydrogen)	IR-absorption* (wt.% hydrogen)
Xo synth. quartz	0.23	0.0150
S1 synth. quartz	0.17	0.0100
W2 synth. quartz	0.13	0.0026
W3 synth. quartz	0.12	0.0026
W4 synth. quartz	0.06-0.18	0.0014
Suprasil synth. quartz	0.17	Not analysed
Vitrosil natural quartz	0.10	-
Smoky quartz (natural)	0.06	-
Toyo quartz (synth.)	0.03	-
Feldspar 190 (An66)	0.12	-
Feldspar 112 (An52)	0.12	-
Microscope coverslip glass	0.22	-
Grains in quartzite from Central Australia	0.04-0.14	-

*These values are taken from Griggs (1967) and Hobbs et al. (1972). Recently, however, Kirby (private communication) pointed out that these values should be corrected by a factor of 0.5.

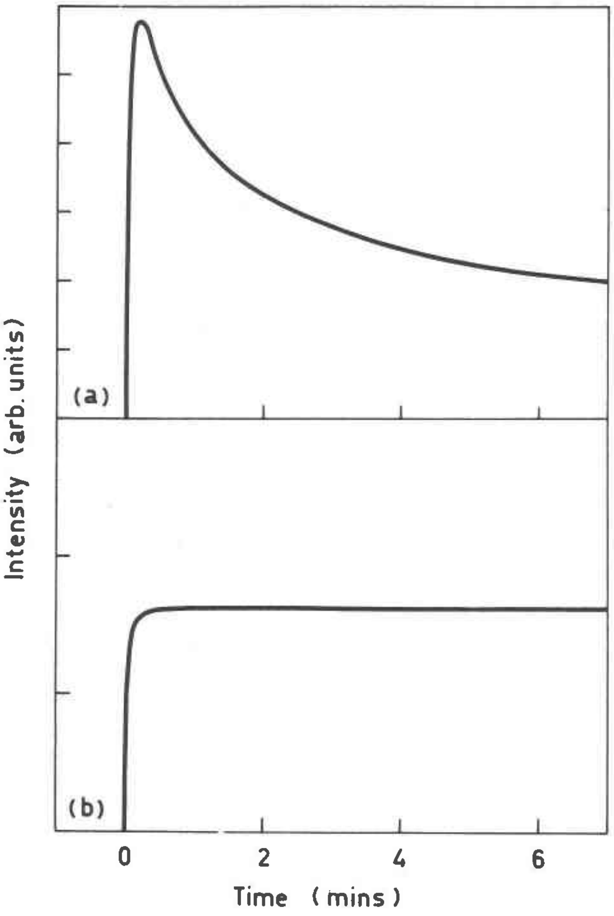

FIG. 3. Intensity of the H6563 line plotted as a function of time for quartzite, (a) showing adsorbed water on the surface and (b) showing no adsorbed water after the sample has been heat-treated at 130°C for 48 hours.

2000 ppma in IMMA (Hinthorn and Andersen, 1975). Much of the background hydrogen can probably be attributed to the contamination of hydrocarbon from the silicone fluid used in the oil diffusion pump, despite liquid nitrogen trapping. A lower background may be expected if a fluorocarbon fluid is used as the pump fluid (Holland *et al.*, 1972). Perhaps the best solution to this problem would be to ion-pump the vacuum system.

The hydrogen concentration in two of the samples, W4 and quartzite (Table 1), was found to vary in different parts of the sample. In the case of quartzite this is not surprising, as the quartz crystals contain mica inclusions. Bombardment of an area with mica yields a higher hydrogen concentration than bombardment of an area free of these inclusions. In the case of W4, however, the heterogeneous hydrogen content is thought to be due to inhomogeneity in the crystals, because of the existence of large OH banding parallel to the growth surface (Morrison-Smith *et al.*, in press).

The hydrogen content of the two feldspars (Table 1) seems reasonable, considering that the hydrogen in nominally anhydrous silicates has been shown to be as high as 0.08 weight percent when measured by the electrolytic technique (Wilkins and Sabine 1973).

Application to hydrolytic weakening

Many workers (Carter *et al.*, 1964; Griggs and Blacic, 1965; Griggs 1967; Hobbs, 1968; Hobbs *et al.*, 1972; Blacic 1972; and Morrison-Smith *et al.*, in press) have demonstrated a correlation between the mechanical and recrystallisation behavior of silicates and the hydrogen content incorporated in the structure. In general, the higher the hydrogen content, the weaker the silicate and the easier the material recrystallizes at a particular temperature. All of the work mentioned has relied upon infrared absorption spectroscopy for the determination of the hydrogen content. The absorption spectrum in the vicinity of 3300 wavenumbers was measured, and the results of Brunner *et al.* (1961) and Kats *et al.* (1962) were used to interpret the hydrogen content in terms of hydrolyzed silicon-oxygen bridges; the total hydrogen content was assumed to be incorporated into the silicate structure in the form of Si-OH.HO-Si groups.

Two observations now seem to detract from such an interpretation: (1) Wilkins and Sabine (1973) have made an intensive study of hydrogen in nominally anhydrous silicates. They point out that the infrared technique is not suitable for quantitative determination of hydrogen because the amount of absorption is dependent not only on the crystal plate thickness but also on bond orientation and other structural factors. Moreover, the presence of OH bonds must be confirmed by deuterium substitution, otherwise other interpretations may be placed on the structural site occupied by the hydrogen. It should perhaps be emphasized that the infrared method only measures the concentration of OH bonds, from which the hydrogen content is calculated. There are other ways, such as interstitial sites and complicated point defects, which may be important means of incorporating the hydrogen in quartz.

(2) The IBSCA results reported in Table 1 show large discrepancies from the infrared results. Between 10 and 100 times more hydrogen was detected in the synthetic quartz crystals using IBSCA than was calculated from the infrared data. This discrepancy could be due to the problems in the infrared determi-

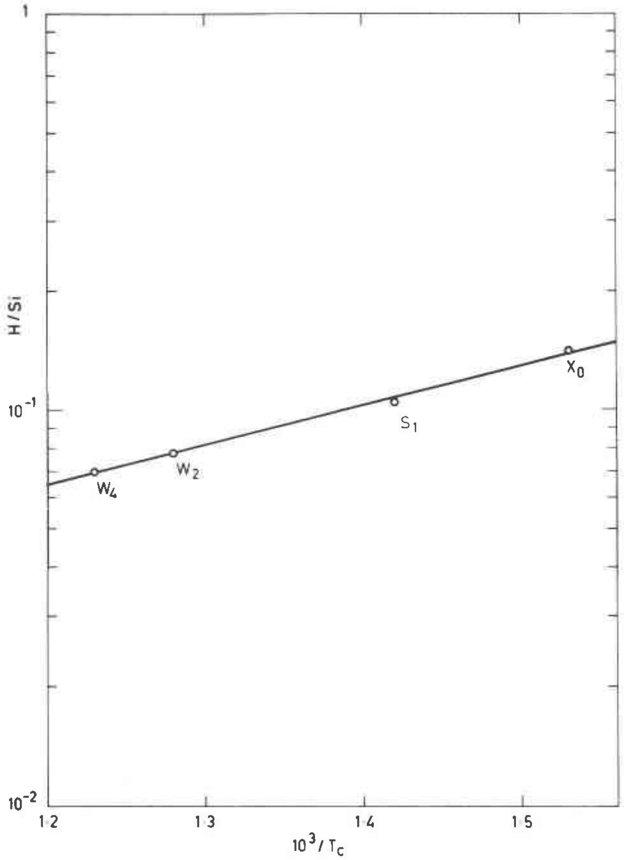

FIG. 4. Plot of log(H/Si) versus $1/T_c$ (the critical temperature of weakening) for 4 synthetic quartz crystals. The values of T_c are taken from Griggs (1967) and Hobbs *et al.* (1972). An average value of 0.12 weight percent or 7.0×10^{-2} H/Si is taken for W4.

nation mentioned above or to unknown errors in the IBSCA technique. Since fluid inclusions are known to exist in these materials, the possibility remains that much of the excess hydrogen recorded by the IBSCA technique could be free water in the form of small bubbles in the solid. If the diameter of such a small bubble is ~500 Å, then for 1.0 atomic percent or 0.05 weight percent of hydrogen in quartz, the density of bubbles required will be $\sim 10^{14}$ cm^{-3}. This estimated size and number density of bubbles has been observed in the electron microscope for heat-treated amethyst and citrine quartz which are known to contain hydrogen (McLaren and Phakey 1966). In unheated synthetic quartz, however, such bubbles have not been observed (McLaren and Retchford 1969). Recently, Morrison-Smith *et al.* (in press) have reported bubble-like inclusions with density up to 10^{14} cm^{-3} in localized regions of unheated synthetic quartz, but available evidence seems to suggest that these inclusions are due to acmite (sodium iron silicate) rather than water. Therefore it appears unlikely that the hydrogen determined by IBSCA originates from submicron size bubbles. Moreover, if bubbles did exist in the estimated density, the synthetic quartz would have a milky appearance.

If the IBSCA results are taken at face value and a plot is made to examine the relation between hydrogen content and the critical temperature of hydrolytic weakening (similar to Fig. 9 in Griggs, 1967, and Fig. 16 in Hobbs *et al.*, 1972), a linear relationship between the logarithmic hydrogen content and the reciprocal of the critical temperature for weakening is preserved (Fig. 4). Thus the general lines of argument used in hydrolytic weakening discussions seem not to be altered by the IBSCA results, but the precise structural role played by hydrogen in silicates now needs careful study.

Conclusion

The IBSCA technique has provided a new way of measuring the hydrogen content in quartz and silicates. Whether the hydrogen occurs as OH, H_2O, or any other form, IBSCA measures it with similar efficiency. The absolute concentration of hydrogen in synthetic quartz crystals determined by IBSCA appears to be much higher than previous measurements by infrared absorption spectroscopy, and this has opened up the question concerning the precise structural role of hydrogen in these materials.

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References

BLACIC, J. D. (1972) Effect of water in the experimental deformation of olivine. In, H. C. Heard, I. Y. Borg, N. L. Carter and C. B.Raleigh, Eds., *Flow and Fracture of Rocks, Geophysical Monograph,* Vol. 16, 109–115.

BRUNNER, G. O., H. WONDRATSCHEK AND F. LAVES (1961) Ultrarotuntersuchungen uber den Einbau von H in naturalichen Quarz. *Z. Elektrochem.* **65,** 735–750.

CARTER, N. L., J. M. CHRISTIE AND D. T. GRIGGS (1964) Experimental deformation and recrystallisation of quartz. *J. Geol.* **72,** 687–733.

COHEN, B. L., C. L. FINK AND J. H. DEGNAN (1972) Nondestructive analysis for trace amounts of hydrogen. *J. Appl. Phys.* **43,** 19–25.

GRIGGS, D. T. (1967) Hydrolytic weakening of quartz and other silicates. *Geophys. J. R. Astron. Soc.* **14,** 19–31.

——— AND J. D. BLACIC (1965) Quartz: anomalous weakness of synthetic crystals. *Science,* **147,** 292–295.

HINTHORNE, J. R. AND C. A. ANDERSEN (1975) Microanalysis for fluorine and hydrogen in silicates with the ion microprobe mass analyzer. *Am. Mineral.* **60,** 143–147.

HOBBS, B. E. (1968) Recrystallisation of single crystals of quartz. *Tectonophysics,* **6,** 353–401.

——, A. C. MCLAREN AND M. S. PATTERSON (1972) Plasticity of single crystals of synthetic quartz. In, H. C. Heard, I. Y. Borg, N. L. Carter and C. B. Raleigh, Eds., *Flow and Fracture of Rocks, Geophysical Monograph,* Vol. 16, 29–53.

HOLLAND, L., L. LAURENSON AND P. N. BAKER (1972) The use of perfluoropolyether fluids in vapour stream pumps. *Vacuum,* **22,** 315–319.

KATS, A., Y. HAVEN AND J. M. STEVELS (1962) Hydroxyl groups in α-quartz. *Phys. Chem. Glasses,* **3,** 69–75.

LEICH, D. A. AND T. A. TOMBRELLO (1973) A technique for measuring hydrogen concentration versus depth in solid samples. *Nucl. Instrum. Meth.* **108,** 67–71.

LIGEON, E. AND A. GUIVARCH (1974), A new utilisation of ^{11}B ion beams: hydrogen analysis by ^{1}H(^{11}B, α)$\alpha\alpha$ nuclear reaction. *Rad. Effects* **22,** 101–105.

MCLAREN, A. C. AND P. P. PHAKEY (1966) Transmission electron microscope study of bubbles and dislocations in amethyst and citrine quartz. *Aust. J. Phys.* **19,** 19–24.

—— AND J. A. RETCHFORD (1969) Transmission electron microscope study of the dislocations in plastically deformed synthetic quartz. *Phys. Stat. Solidii,* **33,** 657–667.

MORRISON-SMITH, D. J., M. S. PATERSON AND B. E. HOBBS. An electron microscope study of plastic deformation in single crystals of synthetic quartz. *Tectonophysics* (in press).

TSONG, I. S. T. AND A. C. MCLAREN (1974) Quantitative spectrochemical analyses of feldspars by ion bombardment. *Nature* **248,** 43–45.

—— AND —— (1975) An ion beam spectrochemical analyser with application to the analysis of silicate minerals. *Spectrochim. Acta,* **30B,** 343–351.

WHITE, C. W., D. L. SIMMS AND N. H. TOLK (1972) Surface composition determined by analysis of impact radiation. *Science,* **177,** 481–486.

——, —— AND —— (1974) Surface composition by analysis of neutral and ion impact radiation. In, P. F. Kane and G. B. Larrabee, Eds., *Characterisation of solid surfaces.* 641–662.

WILKINS, R. W. T. AND W. SABINE (1973) Water content of some nominally anhydrous silicates. *Am. Mineral.* **58,** 508–516.

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