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Ion Scattering Spectroscopy and Secondary Ion Mass Spectrometry (ISS/SIMS) Studies of Zeolites

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In an attempt to determine the applicability of ion scattering spectroscopy (ISS) and secondary ion mass spectrometry (SIMS) techniques to the analysis of zeolite systems, surface analyses of various natural and ion-exchanged synthetic zeolite samples have been carried out. A number of different mineral single crystals were studied both in an exchanged and in a natural form; also, ion-exchanged synthetic powder samples, both hydrated and dehydrated, were subjected to analysis. The analyses were performed to obtain an elemental composition of the surface to determine such information as Si/Al ratios and changes in the relative concentrations of exchanged metal species. The use of a high current density Ne^{20} ion beam made possible depth profiling studies to monitor changes in Si/Al ratios and metal ion concentrations as a function of depth from the surface. Depth profiling of both powder and single crystal metal-exchanged samples revealed that bulk and surface Si/Al ratios are essentially the same. Changes in surface metal concentration of metal-exchanged samples as the result of dehydration were also observed in accord with previously reported results. Quantification of data was attempted through the use of relative elemental sensitivity factors and published sputter yields corrected for instrumental conditions. The results, even considering their semi-quantitative nature, display a good agreement with data obtained from previous scanning Auger microscopy, X-ray photoelectron studies, and fast atom bombardment mass spectrometry studies of zeolites as well as with other independent means of analysis to indicate the value of ISS/SIMS analyses to the study of zeolites.

INTRODUCTION

In the field of heterogeneous catalysis, an understanding of surface phenomena is a vital key to the unraveling of complex catalytic processes. Consequently, much attention in recent years has been focused on the application of analytical techniques to the study of solid surfaces. Techniques that yield physical information on surfaces, such as BET measurements, have been utilized for years, yet the determination of chemical information on the state of a surface was not really possible until the advent of various surface spectroscopies. Techniques such as scanning Auger microscopy (SAM), X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), and secondary ion mass spectrometry (SIMS) find frequent application in this regard. These techniques are all characterized by a sampling depth which is sensitive to primarily the outermost atomic layers of a solid. This is the principal characteristic which sets them apart from other spectroscopic techniques as applied to solids. These techniques have been the object of considerable attention and have been extensively reviewed in the literature (*1–5*).

An examination of the literature will reveal that, while there is some overlap between the capabilities of such techniques,

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each of these techniques has its own strong and weak points. The value of the chemical information obtained through surface analysis can frequently be enhanced through the simultaneous use of two or more techniques since the information they give is complementary (*6, 7*). The present study is an example of the combining of two such techniques.

The application of surface analytical techniques to zeolite systems is not entirely new. Studies already in the literature have utilized X-ray photoelectron spectroscopy (*8–10*), scanning Auger microscopy (*11, 12*), secondary ion mass spectrometry (*13, 14*), and fast atom bombardment mass spectrometry (*15*). These studies have, for the most part, dealt with determining the effect of various treatments on zeolites. In this paper we discuss the application of two surface analysis techniques, ion scattering spectroscopy and secondary ion mass spectrometry, for the analysis of different zeolites. By a comparison of the results obtained for both powder and crystal samples we shall attempt to address the impact of factors such as preferential sputtering and particle size/grain boundary effects which have generally proven to be barriers to the quantification of data obtained from ion beam techniques.

The advantages to be gained from the use of these two techniques in tandem are that in an ISS/SIMS analysis there can be a sensitivity as high as one part of a monolayer per million (*2*); identifying information on compounds can be obtained; hydrogen and different isotopes can be distinguished; and the analysis is sensitive to just the outer monolayer of the surface. In addition, the ISS/SIMS analysis may give better depth profiling information because it monitors what is on the surface with ISS as well as what is leaving the surface with SIMS. For additional details on the theory and application of these techniques the reader is directed to those reviews and papers previously cited.

This report details the use of ISS/SIMS analyses for several small, intermediate, and large pore zeolites that have been ion-exchanged with several transition metals and combinations of transition metals. Some of these materials have been heat treated and others have been analyzed in the hydrated state. Crystalline samples of a number of naturally occurring zeolites have been analyzed and depth profiles have been made. These analyses have been performed on crystalline samples both in an untreated form and after undergoing long-term ion exchange with a solution of uranyl cations. Other supporting spectroscopic analyses for the metal-exchanged zeolites that we have studied include scanning electron microscopy with energy dispersive X-ray (EDX) analysis and neutron activation analyses. Wet chemical methods were also performed. Special precautions and analytical conditions have been detailed and a comparison of the results obtained through ISS/SIMS analyses has been made to studies of zeolites with various other surface analysis techniques.

EXPERIMENTAL METHODS

A. Materials

Zeolites A, X, and Y were obtained from Alfa-Ventron Corporation. Zeolite ZSM-5 was prepared according to procedures found in U.S. Patent 3,702,886. Single crystalline samples of chabazite, faujasite, offretite, mordenite, and ferrierite were obtained from various museums including the U.S. National Museum, Division of Minerology, in Washington, D.C., the American Museum of Natural History in New York City, and the Harvard Minerological Museum of Cambridge, Massachusetts.

Metal-exchanged zeolites were prepared in the following manner. Approximately 1.0 g of zeolite was added to 100 ml of a 0.1 *N* metal chloride aqueous solution and exchanged with continual stirring in a round bottom flask for 24 hr at room temperature. The exchanged zeolite was removed by suction filtration and air dried. In the case

of silver and copper, nitrate salt solutions were used. These solid salts were also used as calibration materials for surface analysis measurements. All materials were analyzed with X-ray powder diffraction techniques prior to the surface analysis experiments.

The following procedure was used for the preparation of ion-exchanged crystals of the natural zeolite samples. Crystalline segments were carefully removed under an optical microscope from the mineralogical matrix in which they were obtained. They were then placed in flat-bottomed Florence flasks containing 25.0 ml of a 0.01 *N* uranyl nitrate hexahydrate solution. Solutions were drained and refilled on a weekly basis for a period of 8 months time.

B. Procedure

The powdered samples were prepared for ISS/SIMS analysis in two different ways. Hydrated zeolites were either pressed into indium wire or they were pelletized in a hydraulic pellet press at a pressure of approximately 15,000 psi. Dehydrated zeolites were prepared by first pelletizing and then heat treating to 550°C in a 0.01-μm vacuum. The dehydrated samples were transferred into a nitrogen atmosphere and mounted onto a sample holder. They were then loaded into the transfer chamber of the instrument under a nitrogen purge. We are assuming that this procedure provides adequate safeguards to insure that the samples remain essentially dehydrated in the bulk, although this may not be true for the surface. The chamber was then evacuated to approximately 1 μm and the mounted samples were transferred into the ultra-high vacuum (UHV) chamber.

Crystalline samples of natural zeolites were mounted by means of what we will refer to as a metal "sandwich." The crystals were examined visually with the aid of an optical microscope to determine which face was most suited to be exposed to the probe beam. The crystal was then oriented to ensure exposure of this face to the beam and subsequently pressed into a piece of flattened indium wire. The sandwich was completed by covering the sample with a piece of palladium foil which was crimped onto the indium. Access of the beam to the sample was through a circular hole previously punched into the palladium foil. This arrangement allowed the physical transfer of the crystalline sample from the ISS/SIMS instrument to an SEM instrument without changing orientation of the sample in the holder.

The ion scattering spectroscopy and secondary ion mass spectrometry experiments were performed with a 3M Model 520B ISS/SIMS instrument. The electron ionization current was 12 mA. The angle of the target to the ion beam was 22.5°. The target current during data gathering scans was usually 40 nA. Acquisition of data was accomplished through a channel electron multiplier operating in a pulse taking mode and signal averaging was performed through digital interfacing. A second gun, a Physical Electronics Industries model 04191 sputter-ion gun, was used for high rate sputtering in the depth profile studies. The target current for these high rate sputters was 4 μA. Primary ion beams were either helium (He^3) or neon (Ne^{20}) and 2.5-keV ion guns were used. The sample chamber was initially evacuated to 1×10^{-8} Torr prior to introduction of the probe gas. During analysis the probe gas pressure was 1×10^{-5} Torr. Charge neutralization was accomplished by use of a thoriated tungsten filament. Neutralization currents generally an order of magnitude greater than the target currents were needed to prevent charging of the sample surface. When lower neutralization currents are used, distortion of the baseline in the ISS spectrum, presumably arising from the deflection of the ion beam as the sample charges, is apparent. Thus, neutralization currents were adjusted until all features of the displayed spectra were normal. There is also a cryopump which can be used at 27°K to trap volatiles that could be produced by outgassing of the sample. In addition to the basic ISS/SIMS

instrument there is a residual gas analyzer (RGA) which makes possible the monitoring of background gases.

The model 520B ISS/SIMS spectrometer was interfaced to a PDP8 minicomputer so that data could be taken, treated (Fourier transformed), and stored in the computer; the computer was also used to control the time length of the scan and the range of masses and energy ratios to be scanned in both ISS and SIMS.

Scanning electron microscopy (SEM) was performed on an AMR model 1000A instrument. EDX analysis was done with an EDAX 9100/60 system. The accelerating voltage was 20 keV.

Available tables (*16*) of scattered ion energy ratios for common probe ions were used for the identification of elements present in the samples for the ISS experiments. The He^3 and Ne^{20} classical atomic scattering cross sections for angles of 138° were obtained by using the Moliere approximation of the Thomas–Fermi potential (*17*). For the SIMS experiments relative abundances of naturally occurring isotopes and relative ion yields were used for identification of elemental species.

A standard surface analysis of powdered zeolite samples consisted of a 3-min He^3 scan, followed by a 3-min Ne^{20} scan; sample surfaces were then cleaned by a 10-min low rate sputter with Ne^{20} and again subjected to a 3-min Ne^{20} scan followed by a 3-min He^3 scan. For depth profiles of crystalline zeolite samples, analytical scans were alternated with 10 min of low rate sputtering and 10–30 min of high rate sputtering. High rate sputtering was done with a 4-μA target current and low rate sputtering was done with a 40-nA target current.

The ion gun used for low rate sputtering and analytical scans produces an ion beam with a diameter of approximately 0.5 mm which rasters an area on the order of 1 × 2 mm. The signal is also subjected to a 10% gate for obtaining better depth profile information. This raster–gate system has been used to raster the beam in two directions and to accept (gate) output signal only while the beam is in a selected area in the center of the rastered area. This permits one to sputter in a controlled fashion and to obtain high depth resolution by eliminating "edge" effects from the sputtered "pit."

TABLE 1

Sputtering Rate Ne^{20} (angstroms/minute)

Element	Target current I = 10 μA (10% raster) Av.	Target current I = 10 μA (10% raster) Center	Target current I = 40 nA 10% raster	Target current I = 40 nA 20% raster
Si	17	34	3.7	0.92
Al	17	34	3.7	0.92
Au	23	46	5.0	1.25
Cu	52	105	11.2	2.8
Fe	19	38	4.0	1.0
Cr	47	94	10.0	2.5
Ag	23	46	5.0	1.25
Ni	47	94	10.0	2.5
Ti	8	16	1.7	0.42
W	8	16	1.7	0.42

RESULTS

Table 1 gives the calculated sputtering rates for Ne^{20} in angstroms per minute for various elements, among them several transition metals. These sputtering rates are reported for the range of low target current (40 nA) associated with the ion gun used for actual data-gathering analysis as well as for the higher target currents (10 μA) that result from the conditions for the operation of the ion gun used for depth profile studies.

The sputter rates listed in Table 1 have been calculated from literature data on experimentally determined sputter yields such as reported by Wehner (*18, 19*) and others. These values are generally reported, in the form of sputtered atoms per incident ion, for a beam incidence angle of 90° to the sample surface with a fixed beam energy of 500 or 1000 eV. These sputter yields are then converted to sputter rates in angstroms per minute (*20*). These sputter rates are then adjusted for specific instru-

mental parameters such as differences in mass of beam ion, angle of beam incident to sample surface, and target current. Although the sputter rates that finally result are for the pure elements we feel that their application to the systems under study here is not unreasonable. All of the zeolite materials under investigation in this study can be characterized by their aluminosilicate framework structure. We can infer from this that it is the sputter rates of Al and Si that should serve as the basis for determining etch depth as a function of sputter time. Although the Si^{4+} and Al^{3+} are believed to be bound in similar ways, there is a chance that dealumination with concomitant alumina residue is present. However, no evidence for dealumination was found through the use of bulk microanalytical methods or X-ray powder diffraction. Thus, for a sample subjected to a 10-min PHI gun scan at a target current of 4 μA, the sputter depth should be approximately 70 Å on the average and 140 Å in the center. Since the data signal is gated to the central 10% of the sputtered area, the 140 Å/10 min sputter ratio generally served as the basis for our estimation of crater depth in the depth profile studies.

In an attempt to experimentally verify the sputter rates on which the etch depth estimates were based, scanning electron microscopy has been performed on some of the uranyl-exchanged crystals that have been subjected to extensive depth profiling. Micrographs of the sample surfaces were taken both before and after the sample was subjected to prolonged sputtering. These micrographs reveal the polycrystalline nature of the samples as exemplified by the extensive microtopography that characterizes the surface of the sample. While the micrographs reveal definite changes in the sample surface as a result of the sputtering, the nature of the surface makes it difficult to pinpoint the exact location struck by the sputtering beam. While the ion gun used for actual data gathering analysis rasters an area only about 1 by 2 mm, the Physical Electronics gun used for high rate sputtering rasters a much larger area which is about 4 by 7 mm. Although a certain amount of overlap of the beam onto the upper Pd layer of the metal mounting sandwich takes place, as evidenced by the appearance of a strong Pd peak in the ISS spectrum, the area of sample exposed to the beam is small enough in relation to the area rastered by the beam that the beam in essence is sputtering the entire surface of the sample. This makes rather difficult the task of using crater imaging techniques to check the thickness of material sputtered away. However, since a portion of the surface of the crystal was covered by the upper half of the metallic mounting sandwich, a demarcation between sputtered and unsputtered surface was visible even to the naked eye upon removal of the top of the Pd foil. The differences between the areas exposed to the beam and those protected from the beam become even more pronounced when examined with a microscope. Since the depth of field is so great in an electron microscope an optical microscope was used in an attempt to measure the depth of material sputtered away by the beam. To do this the fine focus adjustment knob was calibrated against a step of measured height mounted on a glass slide. A point was chosen on an upper portion of the crystal surface which appeared to have escaped beam damage and was brought into focus. The crystal was moved slightly to an area which showed evidence of sputtering damage and it in turn was brought into focus using only the fine focus adjustment. The amount of adjustment necessary was converted to an actual height difference using the calibration of the focus adjustment control. The resulting depth was determined to be on the order of 2000 Å which is in good agreement with that predicted by use of the sputter rates from Table 1. Thus we feel reasonably confident in the use of these sputter rates in light of these results and other ISS/SIMS studies (*21*) that have been made on Si and Al containing com-

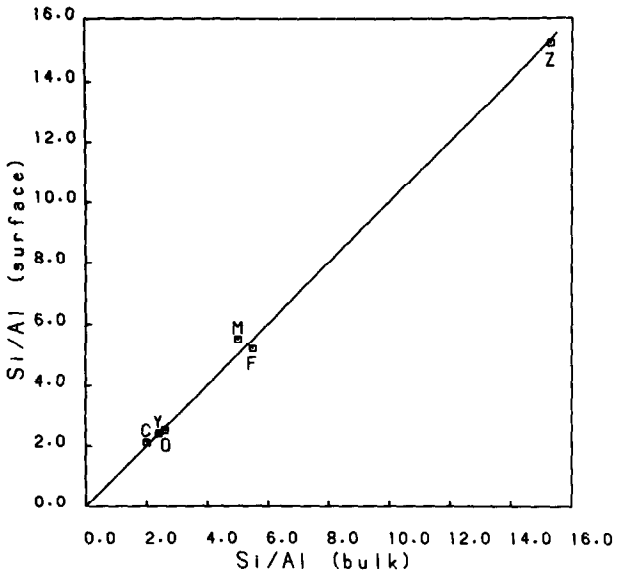

FIG. 1. Surface Si/Al ratios versus Bulk Si/Al ratios for the following zeolites: C, (chabazite); Y, (zeolite NaY); O, (offretite); M, (mordenite); F (ferrierite); Z, (ZSM-5).

pounds. While not exact, they allow for some handle on the amount of sputtering accomplished.

The Si/Al ratios for both synthetic and unexchanged natural zeolites are given in Fig. 1. The Si/Al ratio of the surface is determined by the SIMS analysis and the Si/Al ratio of the bulk has been determined by neutron activation analysis and bulk wet chemical techniques. Deviation of data points from the line bisecting the two axes represents the relative difference between the surface and the bulk. Small pore zeolite A, intermediate pore zeolites-like mordenite, and large pore zeolites like zeolite Y are all included in this figure. The overall range of Si/Al ratios varies from approximately 2 for chabazite up to 15 for ZSM-5.

What is of interest to note from Fig. 1 is that the straight line relationship indicated there implies that the surface composition of the zeolite is essentially the same as the bulk composition. This is in agreement with results from other surface spectroscopies (*11*) and from other investigators (*10, 13, 15*). What should be noted here also is that the slope of the line as shown in Fig. 1 is approximately 1, which agrees with SAM data (*11*) but is in conflict with the data of Dwyer and Vickerman (*13, 15*) derived from both SIMS and fast atom bombardment mass spectrometry. More will be said concerning this matter in the next section.

The SIMS analyses for the natural zeolites offretite and ferrierite are given in Table 2. The elements detected in the offretite sample were Na, Mg, Al, Si, K, and Ca. The ferrierite sample which was from Kamloops, British Columbia, was found to give

TABLE 2

Surface Analysis of Offretite and Ferrierite

	Offretite		Ferrierite	
	Surface	Bulk	Surface	Bulk
Si/Al	2.5	2.6	5.2	5.5
Na/Mg	—	—	1.8	2.1
Al/Ca	3.8	4.8	—	—
Al/Mg	6.1	7.1	—	—
Al/K	3.9	3.7	—	—

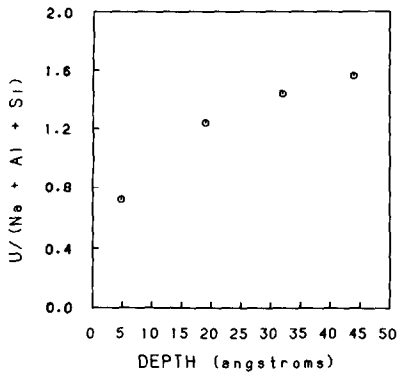

FIG. 2. Surface uranium to (sodium + silicon + aluminum) ratio versus depth in angstroms for zeolite UO_2Y.

peaks for Na, Mg, Al, Si, K, Ca, Cr, Mn, and Fe.

A depth profile for a pressed pellet of uranyl-exchanged Y zeolite is given in Fig. 2. The uranium count was detected from the ISS spectrum. What is apparent here is that there is a general increase in the uranium signal with sputtering time to a point which corresponds to about 30 Å from the surface. A similar type of behavior, at least in the early stages of the experiment, is demonstrated in Fig. 3 for a uranyl-exchanged single crystal of mordenite. There

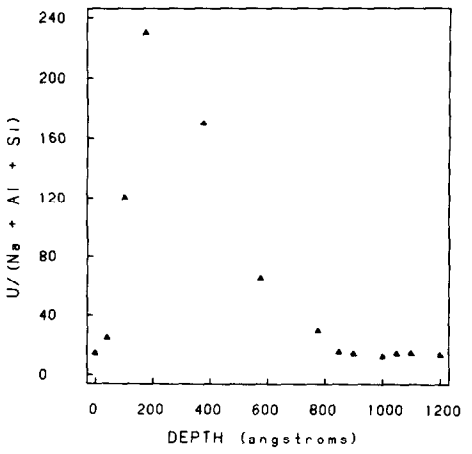

FIG. 3. Surface uranium to (sodium + silicon +aluminum) ratio versus depth in angstroms for uranyl-exchanged mordenite.

are, however, at long sputtering times major differences with respect to the powdered sample. We can only speculate that the decline is due to lower levels of exchange in interior sites and channels. In this figure, the uranium count is normalized against the total Na + Si + Al SIMS counts. Ideally, elements as heavy as uranium and even molecular fragments with *m/e* ratios well over 500 have been successfully detected with SIMS. However, the quadrupole mass analyzer on the instrument used in the present study, even though it is rated up to $m/e = 300$, produces an unsatisfactory signal-to-noise ratio for mass scans which extend into the range of *m/e* ratios above approximately 175. As a result, we have limited our use of SIMS to the detection of the lighter elements. Fortunately, the ISS spectrum usually shows very reasonable sensitivity to heavy elements so that where one technique is unsatisfactory the complementary technique fills the gap. However, it is generally not possible to apply the ISS counts for all of the elements of interest here, since, with a Ne^{20} ion beam, elements as light as sodium and aluminum and silicon are not resolvable. Better resolution is possible with a lighter ion beam, but secondary ion yield would be sacrificed. Also, it has proven impossible to utilize SIMS for the detection of molecular ion species such as UO_2^+ whose existence might be expected.

A long sputtering profile, this time of a single crystal of chabazite, is shown in Fig. 4. The results for the Si/Al ratio as a function of depth as calculated from sputter times and etch rates are reported in this figure. It can be seen that the Si/Al ratio remains essentially constant with depth from the surface. This behavior is remarkably similar to results obtained from SAM measurements (*11*). Both surface analysis methods indicate a slight decrease in the Si/Al ratio as a function of depth into the crystal. If results for the two techniques are compared, it can be noted that the SIMS data shows considerably less scatter. Also,

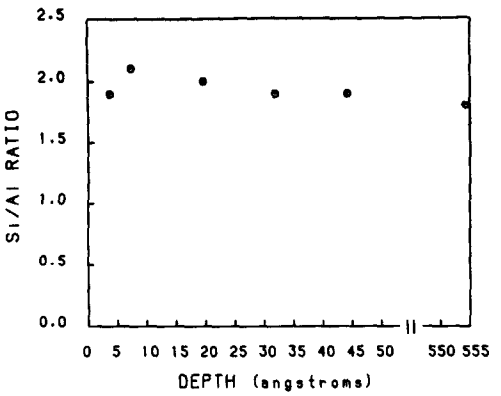

FIG. 4. Depth profile of chabazite: Si/Al ratio versus depth in angstroms.

the measured Si/Al ratio is more in agreement with accepted mineralogical assay (*22*) when determined by SIMS than by SAM.

The data in Table 3 reveal values of normalized metal concentrations for hydrated and dehydrated AgY, CoY, CsY, CuY, and NiY zeolites. The surface metal enhancement ratio is shown as calculated from both ISS and SIMS data. As can be seen here, the ratios of normalized metal concentration as determined by ISS are indeed in the same relative order as that determined by the SIMS experiments. However, variations are apparent as the value for cesium as determined by ISS is higher than in the SIMS experiment. Also the copper and nickel values are virtually identical and the cobalt ISS counts are lower than the SIMS counts. As mentioned throughout this paper and as referenced elsewhere, bimetallic catalysts of metals with similar molecular weights are very difficult to resolve with ion scattering methods. Consequently we were not able to resolve ISS peaks for the bimetallic systems and as a result relied entirely on SIMS data for these samples.

The data in Table 3 reveal values of normalized metal concentrations for hydrated and dehydrated AgY, CoY, CsY, CuY, and NiY zeolites. The Si/Al ratios for the hydrated and dehydrated samples are also included. All data are derived from peak intensity counts in the SIMS spectrum after being empirically adjusted for relative elemental sensitivity factors (*23*).

What can be seen here is that the normalized metal concentration for all of the metal-exchanged samples increases as a result of dehydration treatment. Examination of the values reveals that the metals can be arranged in order of decreasing degree of surface enhancement as follows: Ag > Cs > Cu > Ni > Co. These results are in very good agreement with those determined by both SAM (*12*) and XPS (*24*) analyses.

TABLE 3

Surface Analysis of Metal-Exchanged Zeolites

Sample	Normalized metal concentration[a] SIMS		Surface metal Enhancement[b]		Si/Al SIMS	
	Hydrated	Dehydrated	SIMS	ISS	Hydrated	Dehydrated
AgY	1.0	4.2	4.2	4.1	2.3	2.5
CoY	0.89	1.1	1.2	0.9	2.4	2.6
CsY	0.72	1.9	2.6	3.6	2.2	2.6
CuY	1.0	2.3	2.3	2.0	2.6	2.4
NiY	1.2	1.9	1.6	1.9	2.4	2.2

[a] The normalized metal concentrations are determined by the following ratio: M/(M + Si + Al).

[b] The surface metal enhancement is determined by the M/(M + Si + Al) ratio of the dehydrated sample to the hydrated sample.

TABLE 4

Surface Analysis of Mixed Metal Exchanged Zeolites

M–M′	Normalized metal concentration[a]		Surface metal enhancement	Si/Al	
	Hydrated	Dehydrated		Hydrated	Dehydrated
AgCoY	1.0	4.2	4.2	2.3	2.5
AgNiY	0.89	1.1	1.2	2.4	2.6

[a] The normalized metal concentrations are determined by the following ratio: M/(M + Si + Al).

[b] The surface metal enhancement data are determined by the M/(M + M′ + Si + Al) ratio of the dehydrated sample to the hydrated sample.

Table 4 shows the data for mixed metal zeolite samples. The surface metal enhancement is taken to be the ratio of the metal that has the higher concentration on the surface as determined by ISS/SIMS analysis to the metal that has the lower surface concentration. The results here are what would be expected for the order of surface migration predicted by the data shown in Table 3. In both cases, silver was found to preferentially migrate to the surface over the accompanying metal. A comparison of the surface metal enhancement ratios for both of the mixed metal samples shows that relative enhancements are in qualitative agreement with the metal migration order given above.

DISCUSSION

Of concern in any attempt to derive even semi-quantitative data from analyses based on the use of energetic ion probes is the nature of the surface "seen" by the instrument. This concern is even more important in cases such as the present study where extensive sputter etching has been employed. It has been recognized that, due to the dynamics of the interaction of the ion beam with the sample surface, changes can be induced in the composition of multicomponent systems. These changes can arise from either of two mechanisms. As was revealed by scanning electron microscopy, the surfaces of the crystal samples that were subjected to extensive sputtering exhibited considerable roughness which increased as a result of the ion bombardment. Due to the geometry of the interaction of the beam with the surface topography this roughness is capable of causing variable sputter rates from point to point within the analysis area. A second effect which must be considered is the phenomenon of preferential sputtering. This can result in a distortion of the relative concentrations of surface species as the surface is depleted of those components preferentially sputtered.

While it is recognized that ion beam techniques such as SIMS are capable of functioning with a shallowness of information depth which is unmatched by any other type of surface analysis technique, the extent of interaction of the beam with the sample surface is a function of instrumental parameters. Winograd and co-workers (*25*) have recently reported some elegant angle resolved SIMS studies of CO on Ni(001). These data were obtained by modification of the spectrometer to allow rotation of the polar collection angle of secondary ions. Their results suggest that the probability of ionization of the ejecting particles is isotropic and only slightly dependent on particle velocity. Our results are for the most part in agreement with the results of Winograd (*25*); however, the angle resolved SIMS experiments clearly show that the inclusion of an image force for the neutral

atom trajectories provides much better quantitative SIMS results for the well-defined single crystal nickel surface. When the beam current density is kept sufficiently low ($< 10^{-8}$ A/cm^2), the instrument can be considered to be operating in a "static" mode where the ion beam is interacting with only the outermost atomic layers (*26*). Under the operating conditions described previously, the actual data gathering scans performed in the present study were done with a target current which would approach such a static mode. Thus changes in sample composition are more significant for the use of the PHI ion gun utilized in the depth profiling experiments than for the 3M gun. This, in the end, is not trivial since the amount of time the samples were exposed to the sputtering beam in the depth profile studies was considerably greater than the total time that they were subjected to analysis.

Perhaps the most relevant way to evaluate the effects of preferential sputtering on the analyses performed is to examine the results closely, in light of the conditions under which they were performed, and in comparison to results obtained by other methods and by other investigators. If one examines the data in Fig. 1, it is apparent that no variation in the Si/Al ratio occurs between the surface and the bulk for the various samples analyzed. This is in agreement with the findings of Suib and Stucky (SAM) (*11*), Derouane *et al.* (XPS) (*10*), and Dwyer and Vickerman (SIMS, FABMS) (*13, 15*). They are in contrast, however, with the XPS results of Tempere and co-workers (*8*) who found a surface depletion of aluminum. Figure 4 shows a slight decrease in Si/Al ratio with sputter depth, but nowhere near the factor of 2 decrease reported by Tempere and co-workers. This deficiency of surface aluminum shown in the study of Tempere and Delafosse was explained in part by possible screening effects which could affect XPS measurements and which would be greater for aluminum than for silicon. However, the XPS results of Derouane (*10*) show that it is possible to measure surface composition without too much distortion from screening effects. We also agree with the comments of Derouane and co-workers (*10*) concerning the possible overgeneralization of this type of data for all zeolites, especially those materials in the ZSM-5 class. Many different preparations of ZSM-5 are known, the Si/Al ratio can vary over a wide range, and the nature of the starting materials, the autoclave, and its lining are all important variables in the production of this class of zeolite materials. It is very likely, as pointed out by Derouane and co-workers (*10*), that the particle size and exact method of preparation of ZSM-5 materials is quite important as regards the nonhomogeneous distribution of aluminum. The ZSM-5 material studied in this work and in work published by several others (*10, 11, 13, 15*) indicates that at least some ZSM-5 preparations are essentially homogeneous with respect to Si/Al distribution.

The results of Dwyer and co-workers (*15*), while agreeing in terms of surface vs bulk composition, differ in another important aspect. Their plots of surface Si/Al vs bulk Si/Al show a linear relationship indicative of a uniform composition into the bulk. However, the slope of the line is approximately 0.2, indicating a surface Si/Al which differs by a factor of 5 from the bulk. This discrepancy is attributed to preferential sputtering of Al during the FABMS analysis (*15*) using an argon atom beam. This type of result was not apparent either in the current work or in SAM work previously reported (*11*). One possible factor in the deviation may be the more massive argon beam used in the work of Dwyer and co-workers (*13*). It may be possible then to infer that under the conditions of the analyses reported in this work, preferential sputtering of framework species is not of an order to appreciably affect the reported results.

One artifact of preferential sputtering such as that suggested by the results of

Dwyer and co-workers (*13*) is that as sputtering time increases, the Si/Al ratio should be observed to gradually decrease. This was not observed for any of our samples or for the samples studied by FABMS (*15*). For our samples studied in the powdered form this perhaps is understandable since it is difficult to fully evaluate the effects of such factors as grain boundaries, particle size, etc. on the analyses. However, the data shown in Fig. 4 are for a single crystal sample where such effects should be minimal. Again, there is no significant change observable in the Si/Al ratio with depth which would suggest that preferential sputtering of aluminum is not occurring to an appreciable extent.

Figures 2 and 3 report the results for depth profiles of uranyl-exchanged samples. Both figures show that, at least in the early stages, there is an increase in the concentration of uranium with depth, as determined with ion scattering spectrometry. Bulk analyses of both powder and single crystal samples were performed by energy dispersive X-ray analysis to determine a bulk concentration of the uranium species exchanged into the samples. In the case of the uranyl-exchanged Y zeolite, the analysis determined that the uranium was present at a level of 4% by weight. This amount corresponds to a low to intermediate level of exchange with a zeolite composition of $(UO_2)_3Na_{50}Si_{136}O_{384}$ $256H_2O$. Single crystals of mordenite exchanged with uranyl ions did not show any signal for uranium by EDX analysis indicating that the uranium concentration was less than 1% by weight. The depth profile shown in Fig. 2 was done on a powder sample which means that while the data may be distorted by grain boundary and/or shadowing effects, there is an observable increase in the uranium concentration on sputtering. Preferential sputtering of the lighter atoms is probably occurring to some extent yet this increase in uranium concentration is consistent with ion-exchange isotherm data (*27*) and luminescence quenching experiments (*28*). Scanning transmission electron microscopy performed by Thomas (*29*) and co-workers also suggests that significant amounts of uranyl ions exist in the supercages of zeolites like zeolite Y. Perhaps more importantly, the results as shown in both Figs. 2 and 3 show similar trends. What we infer from this comparison is that when ISS/SIMS techniques are applied to powdered samples prepared as previously described, the resulting data is not extensively distorted by such factors as grain boundaries and particle sizes. This belief is further implied by the results of several other surface analysis experiments on zeolites from various laboratories (*10–15, 22*).

One apparent feature of the data shown in Fig. 3 that should be commented on is the gradual decrease in uranium concentration with continued sputtering that is apparent. This has some significance when assessing the effects of preferential sputtering involving the uranium species. It would be expected that an atom as heavy as uranium would be less likely to undergo sputtering than the other, lighter atoms found in a zeolite matrix. This should result then in a gradual buildup of the heavier uranium species on the surface, not the decrease which has been observed. An energy dispersive X-ray analysis (EDX) performed on the mordenite sample after completion of the depth profiling shown in Fig. 3 showed that whatever uranium remained in the sample was present in a concentration below the detection limits of the instrument. This can then be viewed as further support of the results suggested by these depth profile studies, that the uranium concentration is higher in the interior of the zeolite.

In Table 2 it is observed that the Si/Al ratios, the Al/Mg ratios, and the Al/K ratios for the crystals of offretite are approximately the same on the surface, detected with secondary ion mass spectrometry, as the bulk composition. The data for ferrierite show similar correlations and also show the presence of trace impurities as reported by Wise (*30*). The detection of these

trace elements may be of interest to those interested in studying transport processes in these geological materials from Canada. The presence of these trace elements may also be of importance in catalytic and molecular sieving studies.

The data in Tables 3 and 4 show the values of normalized metal concentrations for metallic and bimetallic zeolite systems. Similar studies have been carried out with scanning Auger microscopy (*12*) and with X-ray photoelectron microscopy (*22*). The agreement between these three different experimental methods is quite good. The general trends of surface metal enhancement of the zeolites as determined from the ISS/SIMS experiments are almost the same as those of the SAM and XPS studies for the single metal zeolite systems and are virtually the same for the mixed metal systems. For instance, luminescence (*31*), Raman (*32*), electron microscopy (*32*), and absorption experiments (*33*), also indicate that metallic silver is readily formed on dehydration of silver-exchanged zeolites and that silver migrates to the external surface. The ordering of degree of migration for the different ions to the external surface on thermal treatment of the zeolites is very close to that of the ordering predicted from electrochemical potentials proposed by Uytterhoeven (*34*) and Barthomeuf (*35*).

One final comment on the quantitative nature of the results of these analyses is in order here. Due to a variety of factors which have been outlined in the course of this paper, the experimental results we have obtained must be considered semi-quantitative at best. However, the conditions of analysis have been selected and applied with the single purpose of improving the quantitative validity of the data. The concentrations referred to and the composition ratios cited in our results are not at all intended to represent absolute numbers. The application of our data to other aluminum or silicon containing compounds would be a dangerous practice. However, as long as comparisons are made only between systems as similar as those that have been the subject of analysis here, it is not unreasonable to view the results in a semi-quantitative manner.

CONCLUSION

In this paper we have shown the usefulness of the ISS/SIMS technique and that the two techniques give complimentary data that aid in the interpretation of depth profiles and surface analyses of materials like zeolites. Our results on the comparison of surface and bulk Si/Al ratios have agreed quite well with the results obtained by other analytical methods. The behavior of metal and mixed metal exchanged zeolites upon heat treatment has been shown to correlate well with the results and predictions of other investigators. Finally, the semi-quantitative nature of the results of these experiments has been pointed out and the data compare reasonably well with studies in other surface analysis research laboratories.

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