[Scanning Electron Microscopy](https://digitalcommons.usu.edu/electron)

Volume 1985
Number 2 *Part II*

Article 10

3-11-1985

Mineralogical Application of the Ion Microscope Elementary Analysis

A. Havette
Université Paris-Sud

Follow this and additional works at: https://digitalcommons.usu.edu/electron

Part of the Biology Commons

Recommended Citation
Havette, A. (1985) "Mineralogical Application of the Ion Microscope Elementary Analysis," *Scanning Electron Microscopy*: Vol. 1985 : No. 2 , Article 10.
Available at: https://digitalcommons.usu.edu/electron/vol1985/iss2/10

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Electron Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.

SCANNING ELECTRON MICROSCOPY/1985/II (Pages 585-594)
SEM Inc., AMF O'Hare (Chicago), IL 60666 USA

0586-5581/85$1.00+.05

MINERALOGICAL APPLICATION OF THE ION MICROSCOPE ELEMENTARY ANALYSIS

A. Havette

Laboratoire de Pétrographie-Volcanologie
Université Paris-Sud - 91405 Orsay Cédex (France)

(Paper received January 25 1984, Completed manuscript received March 11 1985)

Abstract

The ion microscope is an instrument which allows the study "in-situ" of polished solid surfaces by means of analysis of secondary ions emitted by the sample, this one being bombarded with neutral or ionized particles.

This instrument is a mass spectrometer and an ion microscope. It is then possible to study elements and their isotopes (mass spectra, counting, isotope abundances...) and to know the distribution of these elements in an area of around one hundred micrometers. Molecular and multicharged ions can be superimposed to elementary ions. Two methods can be used to suppress them but, in any case, it results in a lowering of secondary current. In spite of this disadvantage, the detection limit is at a level of a few ppm for cation elements. Matrix effect is studied in silicates where the influence of each element on the ionization probabilities has been determined.

We propose a method for quantitative elementary analysis in silicates taking the matrix effect into account.

Keywords secondary ion mass spectrometry
ion microscope
charging-up effect
matrix effect
elementary quantitative analysis.

Address for correspondence :

A. Havette
Laboratoire de Physique des Solides Bât. 510,
Université Paris-Sud - 91405 Orsay Cédex (France)
Phone : (6) 941.53.62

Introduction

A young brother of the electron microprobe, the ion microscope belongs to the family of instruments with which "in-situ analysis" is feasible. But if it is true that the two instruments are closely related as regards their goal, the physical processes on which they are based are very different and, eventually, results obtained with the second one bring forth information which shed a different light upon analysis with the electron microprobe. Numerous works have been made on a quantitative interpretation of secondary ion mass spectra in mineralogical applications but no simple model can be applied in general so that quantitative results are still punctual. Ion images are currently used only in few laboratories (Orsay, Creteil, Antwerpen..) and, furthermore, very important phenomena as the "charging-up effect" (Slodzian et al., 1975) on insulating samples or the "isotope effect" related to the velocity of ions are rarely indicated or studied (Slodzian et al, 1980 ; Shimizu and Hart, 1982). Moreover, matrix effect limits the study of trace elements because of the necessity to dispose of homogeneous standard samples similar to the studied samples.

In this work, we present an empirical method for elementary analysis and comment on the artefactual phenomena.

Principle of the instrument

The ion microanalyzer (Fig. 1) conceived by Castaing and Slodzian (Castaing and Slodzian, 1960 Slodzian, 1964) is both an ion spectrometer and an ion microscope. The sample is bombarded with a primary beam of either positive, negative or neutral particles (A^+, O_2^+, O^-). The bombardment can be either defocussed (a few 100 µm) or focussed and swept, over a square area, the side of which is a few 10 µm. Due to the effect of this bombardment the sample is sputtered away giving rise to mono or polyatomic particles, either neutral or (positively or negatively) charged. These particles are accelerated and collected by a set of three electrostatic lenses so called "Transfer optics" (Slodzian and Figueras, 1980) set at different voltages. For extracting positive ions, the sample is set at a voltage of + 4500 V and at a voltage

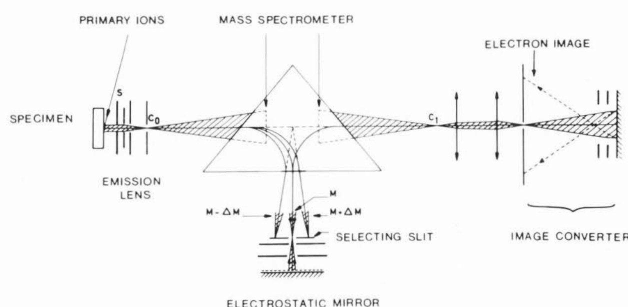

Figure 1

Principle of the instrument.

of - 4500 V for extracting negative ions.

The different masses are filtered in momentum with a magnetic sector, then in energy with an electrostatic mirror. After conversion of these particles into electrons or photons, it is possible either to measure the intensity of the current emitted by each of these ions or to observe their distribution on a fluorescent screen or a multichannel analyser, or to record this distribution on a photographic film. Indeed, from the design of the electrostatic optics of the instrument, the images of each of the ions coming from the sample are superposed before entering the magnetic sector and separated afterwards, and the topography of each of them is preserved whatever the chosen treatment.

A choice of a value of the magnetic field makes it possible, by means of a binocular head to view the distribution of the corresponding ion on an area of a few tens or hundreds micrometers. When the images are recorded on a photographic film, the spatial resolution at surface level may be as good as 0.5 µm (Fig. 2). It is also possible to measure the intensity on a small area of the sample by placing a diaphragm on the ion beam trajectory.

By evenly scanning the magnetic field it is possible to obtain a mass spectrum from hydrogen to uranium. In this spectrum also appear multicharged ions (Ca^{++}, Ba^{++}) and polyatomic ions (Fig. 3 a,b,c) (for Si, for instance : SiO, SiO_2, Si_2O, Si_2...). Polyatomic ions can be superimposed on elementary ions. In this case the ion beam is energy filtered by means of an electrostatic sector which makes it possible to focus for a mass M all ions M^+ with different energies. Ions of masses $M \pm \Delta M$ are focussed in a neighbouring point and it is possible to separate them by a slit in a number of cases : for $M/\Delta M \leq 5000$, the Orsay ion microanalyser provides high mass resolution measurements. Another method is used by some analysts (Shimizu et al., 1978) to suppress polyatomic ions, using the fact that the energy distribution of elementary ions is broader than that of polyatomic ions (Fig. 4). This method cannot be used to suppress hydrides (Fig. 5) and multicharged ions or monoxide ions of REEs (Reed, 1984) ; in fact, each case is a special case and it must be studied with respect to the matrix composition. For the measurement of Sc in a pyroxene for instance the method is limited by the presence of ^{29}SiO the contribution of which is corresponding to about 20 ppm (weight) of Sc.

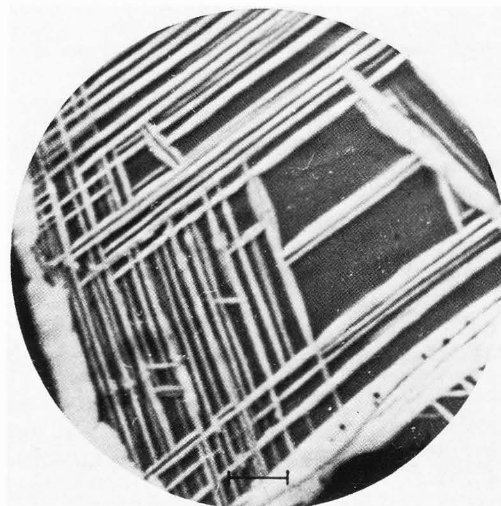

Figure 2

Micrograph of magnetite (background) and ilmenite (needles) ; $^{48}Ti^+$ distribution ; scale 10 µm.

Sample preparation

Samples are carefully polished and prepared as polished thin sections (rock fragment) which can be studied with the polarizing microscope in transmitted or reflected light, or polished sections (minerals...). When possible, it is preferable to embed minerals in metal rather than in a synthetic resin. Indeed the outgassing of these products give H^+ and OH^+ ions which combine with elements to form hydrides or hydroxides (Fig. 5) which contaminate the spectra and are sometimes difficult to separate from elementary ions such as hydrides for instance for masses $M > 35$. Besides conduction is ineffective with a grid with narrow bars.

Analysis of insulating minerals requires coating with a conducting material which can be done in different ways according to the type of study to be effected :

- a uniform coating (several 1000 Å) can be achieved by evaporation ; it is necessary, then, to sputter away this coating on the selected spot with a focussed beam till the sample is uncovered : for instance, vitreous inclusions trapped in a mineral.
- a metal grid with narrow bars deposited by means of two successive evaporations for studying a rock fragment for instance.
- grid with wide bars in order to have only small areas uncovered with the metal. This preparation is necessary for measuring the depth of the crater produced by sputtering in the study of diffusion profiles or for the calibration of standards.

In these procedures, we use a defocussed beam for analysis and aluminum is employed for coating because of the low sputtering rate of this metal. A nickel coating is used when aluminum traces have to be detected. People who are working with focussed beams generally use gold coating.

Once the sample is ready, it is placed into the instrument under vacuum (10^{-7} torr).

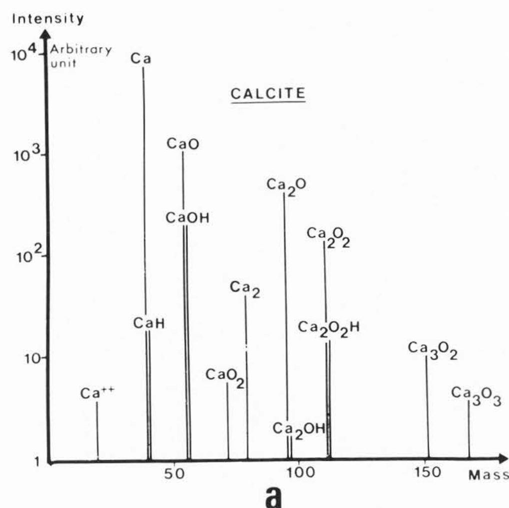

Figure 3 (a)

Mass spectrum from calcite : Ca^{++}, $^{40}Ca^+$ and molecular ions formed with ^{40}Ca.

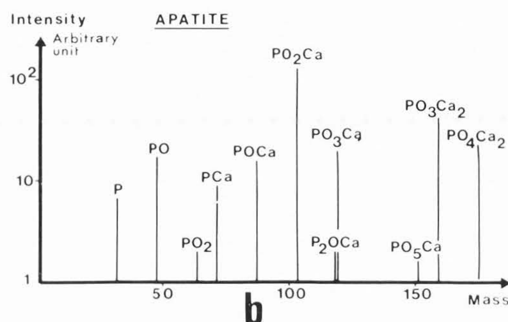

Figure 3 (b)

Mass spectrum from apatite : P^+ and molecular ions formed with P.

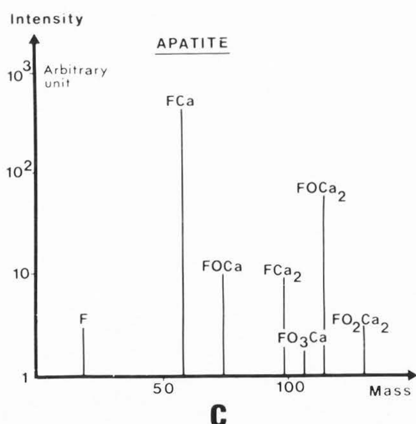

Figure 3 (c)

Mass spectrum from apatite : F^+ and molecular ions formed with F.

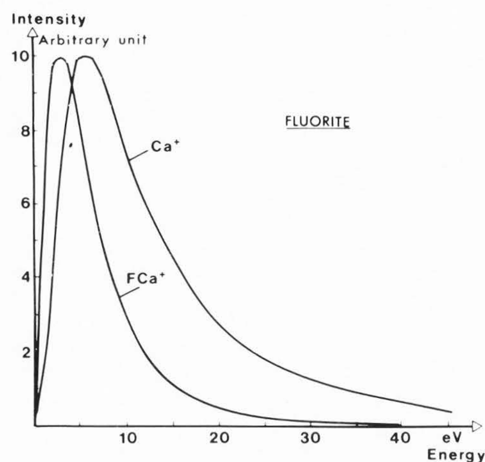

Figure 4

Energy distribution of Ca^+ (elementary ion) and CaF^+ (molecular ion). The Ca^+ energy distribution is larger than that of CaF^+.

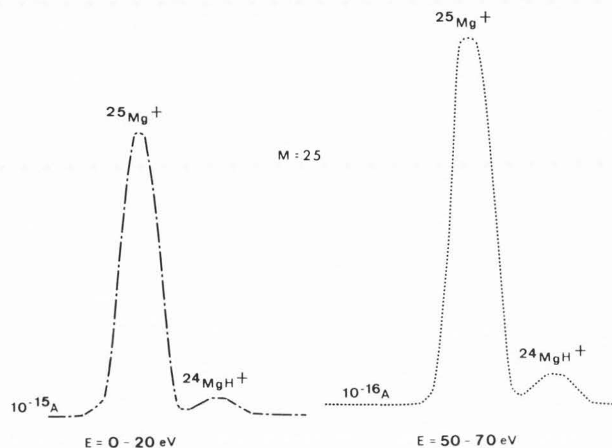

Figure 5

High resolution mass spectrum (M = 25). The ratio $^{25}Mg^+/^{24}Mg^+$ is the same for energy bands in the range of 0 to 20 eV and 50 to 70 eV. This ratio does not vary with the energy band (from Havette et al., 1981).

Potentialities of the instrument

Mass spectrum. It takes a few minutes to obtain a mass spectrum from H to V. With a good knowledge of polyatomic ions, it is possible to determine the nature of elements present in a mineral (Fig. 3 a,b,c). In most cases, it is necessary to get a high mass resolution spectrum for each atomic mass corresponding to an element (Fig. 6).

The detection limits depend upon numerous factors :

- the ionization potential : alkaline and calc-alkaline elements of low ionization potential exhibit high ionization probabilities.
- the sputtering rate of minerals : it varies from one mineral to another and even from one zone to the other in minerals considered as solid–

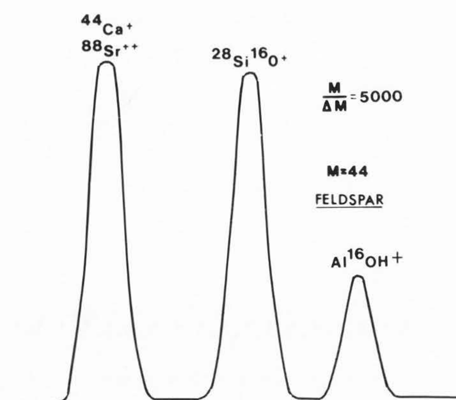

Figure 6

High resolution mass spectrum (M = 44) in a feldspar.

solutions the composition of which is often inhomogeneous.

- the mineral composition : the composition of the sample acts upon the ionization probabilities of elements (matrix effect).
- the presence of molecular ions : when the use of high mass resolution or energy filtering is necessary for discriminating elements from polyatomic species, the intensity of emitted ions is lowered.
- the energy-band chosen : the intensity of the secondary current is related to the surface of the energy-band chosen.
- the size of the analysed zone : the intensity of the emitted current is proportional to the surface of the area analysed.
- the fact that the mineral is a conductor or an insulator : conductors can be exposed to intense bombardment whereas it is necessary to fit the bombardment to the charging-up of the sample surface in insulating minerals.

For the sake of illustration, let us say that, at low mass resolution, it is easy to detect 0.5 ppm of an alkaline element in silicates when extracting positive ions and ∿ 20 ppm for Si or Cu.

Visualization of elements on a selected zone. (generally from 125 to 250 µm diameter). Two types of study may be particularly interesting :

- Determination of minerals the size of which is close to 1 µm (lava mesostasis for instance). Indeed the image when the exposure time is not too long represents the sample surface without interference from what is located below, depth resolution being a few 10 Å and sputtering rate about 1 Å/s in silicates.
- Study of zoned structures. Microscopy information and electron microprobe studies have shown for a long time that a large number of minerals have a zoned structure while others have a uniform composition with respect to major elements. On the other hand elements present at low levels of concentrations show zoned structures most frequently (Fig. 7). In fact, if these zoned structures exist for trace elements, that means that major elements also present the same peculiarity ; but this feature may not be visible in those elements because relative compositional changes are usually small for major elements and large for trace elements. In a way, trace elements reveal compositional variations in the major elements.

Quantitative analysis. Knowledge of topography of elements in a mineral or a rock is absolutely necessary to understand the phenomena. Naturalists know well how precious is observation when carefully made and are also aware that knowledge has been promoted with the use of the electron microprobe enabling quantitation of effects observed in minerals as regards major elements. If the ion microanalyser is to have the same aptitude in the study of trace elements it is necessary to develop a reliable method for quantitative analysis to be coupled to micrography observation.

A first method of quantitative analysis has been developed by Andersen and Hinthorne (1973) in the United States of America. Other teams have used this method with modification in order to improve it, but results obtained are not precise enough to be a useful tool for quantitative analysis (this model has been used for laser probe mass spectrometry (LPMS) by Eloy, SCEN Grenoble, but this work is too recent to be discussed here). It is based on some properties of plasmas (local thermal equilibrium)but, actually, its application to secondary emission is not justified. In Orsay we have developed a semi-empirical method in several steps.

Principle. Because of the primary current instability and the relative variation of sputter rates with mineral composition, it is not possible to directly compare the current emitted by the same element in a standard sample. It is therefore necessary to resort to an internal standard and as the minerals under study are silicates, we have used $^{28}Si^+$ as a reference (Havette, 1974).

To obtain the chemical analysis of a mineral one has to :

a) measure the intensity of the current emitted by the main isotope of each of the elements present in a standard mineral ($I_{o1} \ldots I_{oi} \ldots I_{on}$), the cationic concentration of which is known : $C_{o1} \ldots C_{on}$ for elements M_1 to M_n.

b) calculate a correction coefficient for each element : R_{o1} to R_{on} with :

$$R_{oi} = \frac{I_{oi}}{I_{o^{28}Si}} \times \frac{C_{oSi}}{C_{oi}} \quad (R_{oSi} = 1) \qquad (1)$$

c) measure the intensity of the current emitted by the main isotope of each of the elements present in the studied mineral ($I_1 \ldots I_n$).

d) divide each of these intensities by the corresponding coefficient R_{oi} and normalize to 100. One obtains in this way the cation percentage (or oxide molecules) of each element.

$$\%\ \text{cat. element i} : \frac{(I_i/R_{oi}) \times 100}{I_i/R_{oi} + I_{Si} + \ldots + I_n/R_{on}} \qquad (2)$$

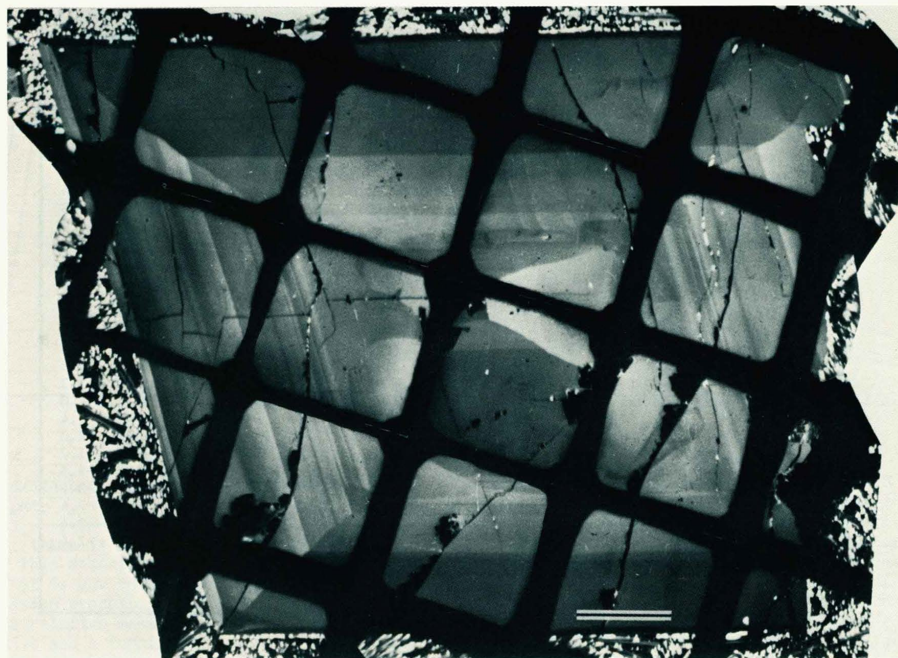

Figure 7 *Bar = 100 µm.*
Anorthoclase crystal ; Ca^+ distribution. Zoned structures, sector-zoning and numerous other phenomena are distinctly visible on this micrograph (from Havette and Nativel, 1977).

Reproducibility of measurements. To be reproducible, measurements must always be made under the same conditions. For instance, elements not having all the same energy distribution, the ratio of the intensity of two elements varies with the energy bandwidth. But on insulating materials, there is a factor of reproducibility generally neglected, the importance of which is, however, great : "The charge effect". Indeed, whatever the type of conducting coating used, the potential on the uncovered sample surface is not equal to that of the conducting coating and a potential gradient is established between the center and the borders of the measured area. This charge effect causes differences in the measured values (Fig. 9) (Havette et al., 1981) but, above all, causes migration of the most mobile ions, alkaline and calc-alkaline. To obtain reliable results charge effect should be minimized, which can be achieved by adjusting the primary beam current.

For the extraction of positive ions, the charges emitted by the sample have a negative effect : loss of positive ions, gain of electrons from the immersion lens surface located in front of the sample. Compensation requires bombarding with positive ions and proper adjusting of the focussing and bombardment density (Havette and Slodzian, 1982). An electron gun can be used (Blanchard et al., 1975) to increase the intensity of the primary current but the surface of the sample is not equipotential.

For the extraction of negative ions, it is obviously necessary to bombard with negative ions but the current is too weak to compensate for charges lost by the sample and positive charge accumulation prevents experiments being done with insulating materials. An electron gun can also be used to compensate for charges (Chaintreau, Slodzian, Dennebouy, Brevet n° 8300538).

Matrix effects. We have observed along with many other experimentalists (Shimizu et al., 1978 ; Reed, 1980 ; Steele et al., 1981) that the coefficient R_{0i} previously calculated (eq.1) is variable for a given element from one mineral to the other. There is then a matrix effect. The ordering or site of atoms do not appear to be the relevant factor, at the precision obtained. Indeed, R_{Al} is the same in the different minerals that are andalousite, kyanite and sillimanite (5.2) of composition $[SiO_4]Al_2O$. Adding a molecule $Fe(OH)_2$ (Staurolite) the value of R_{Al} increases to 6.7. It is observed that R_{Al} varies from 4 (iron poor obsidian) to 12 (sphene) - Table 1.

As metallurgists have shown to be true for conducting material made up of 2 elements (Pivin et al., 1978) we have observed that, as a first approximation, R_i varies linearly with element

Table 1

Matrix effect. R_i : measured from equation (1) - R'_i : measured from equation (3).

Standard \ C%	Si	Al	Na	K	Ca	Mg	Fe^{2+}	Fe^{3+}	Ti	R_i mes.	R'_i calc.	$\frac{R_i - R'_i}{R_i}$ %
glass	69.2	I5.I	6.2	4.8	I.3	.8	.5	0	.2	4.07	4.05	- .5
glass	68.4	I4.5	9.3	5.3	.4	0	2.I	0	0	4.29	4.39	2.3
albite	60.I	20.2	I9.7	0	0	0	0	0	0	4.42	4.49	I.6
leucite	5I.0	24.8	0	24.2	0	0	0	0	0	4.45	4.6I	3.6
oligoclase	55.0	25.I	I3.5	I.I	5.0	0	.3	0	0	4.46	4.70	5.4
sanidine	59.8	20.4	5.3	I4.5	0	0	0	0	0	4.5I	4.36	-3.3
oligoclase	56.3	24.0	I5.3	I.2	3.0	0	0	0	0	4.6I	4.60	-0,2
labradorite	45.7	33.5	6.6	0	I3.5	0	0	0	0	4.78	4.94	3.3
glass	70.I	I0.6	9.0	5.6	0	0	4.6	0	0	4.82	4.67	-3.2
glass	68.4	I0.5	I0.6	5.3	.3	0	3.0	I.6	0	5.07	5.03	-0.8
bytownite	42.7	37.0	2.9	0	I6.7	.2	.5	0	0	5.09	5.I6	I.8
anorthite	4I.3	38.7	I.3	0	I8.7	0	0	0	0	5.I5	5.I4	-0.3
cyanite	33.3	66.7	0	0	0	0	0	0	0	5.24	5.I7	-I.4
glaucophane	48.0	I0.8	II.5	0	.3	II.I	6.3	2.0	0	5.59	5.89	5.4
cordierite	43.7	35.2	.I	.2	0	9.2	9.0	0	0	5.87	6.02	2.6
glass	45.5	I5.9	5.3	.3	II.8	II.6	8.2	0	I.2	6.36	6.57	3.3
glass	46.6	I5.4	5.7	.7	II.3	9.7	8.2	0	I.8	6.5I	6.64	2.0
staurolite	25.5	57.4				I.9	I0.9		.4	6.57	6.66	I.4
chlorite	2I.4	I0.9	0	0	0	30.0	I.6	I.4	0	6.69	6.56	-2.0
salite	45.3	4.3	0	0	22.0	I9.9	6.9	0	I.7	6.87	6.75	-I.7
melilite	36.9	I2.9	7.3	0	32.5	7.5	0	2.9	.I	7.08	6.62	-6.5
garnet	38.0	24.3	0	0	I0.4	I.6	2I.2	0	0	8.56	8.28	-3.2
glass	43.3	I9.I	0	0	25.0	0	0	I2.5	0	8.89	9.I0	2.4
fassaïte	34.5	I4.8	.4	0	23.8	II.3	0	I0.8	2.2	9.82	9.49	-3.4
sphene	3I.7	I.3	.7	0	3I.3	0	I.5	0	27.3	I2.89	I2.55	-2.6
$X_{ij}(M_i=Al)$	3.26	5.96	6.I3	5.9I	7.67	8.54	I8.2	39.7	35.7			

in a mineral.

$$R_{Al} = X_{Al,Si}C_{Si} + X_{Al,Al}C_{Al} + \dots X_{Al\,n}C_n \quad (3)$$

X_{ij} = ratio of ionisation probability of element i in a matrix j to ionisation probability of Si in the same matrix.

C_j = concentration of element j in standard minerals.

In silicates we have established a set of coefficients X_{ij} for the most frequent major elements " Si, Al, Na, K, Ca, Fe, Mg and Ti (see table 1 for Al). They are computed by means of a program using the least square method applied to relative deviations $[(R_{calculated} - R_{measured})/R_{measured}]$ as determined in each of the standard minerals (for Al, 25 minerals have been used).

Under identical experimental conditions the values of X_{ij} are the same and may therefore be calculated once and for all from a set of standard minerals. To determine the unknown mineral composition one uses a rapidly converging iterative procedure : R_i are calculated from the known coefficient X_{ij} and assumed concentrations (equation (3)), the concentrations C_j are calculated from values R_i previously computed (equation (2)) and so on up to convergence .

Coefficients R_i can be obtained with a relative precision of 10 % for alkaline elements (because of migration) and equal to or better than 5 % for other elements. Extension to elements in trace concentration does not cause degradation of the measurement precision.

This analytical procedure can be applied to ion images. Optical density of the films should in this case be measured. If a calibration curve is obtained which relates intensity with optical density, it is possible to get the intensity emitted by each element of the image after having divided the values obtained by the corresponding exposure time (Massare et al., 1982).

Isotope abundance. The study of the isotope abundances is a very important subject but it would require a special paper. I will only point out that secondary ion analysis makes the calculation of isotope ratios feasible. For instance datation* U/Pb have been made on uraninite from Oklo (Gabon) natural reactor. In the first and only sample discovered in 1973 (clays + uraninite) in which radiogenic lead was strongly depleted we obtained $\geqslant 1,6\ 10^9$ years by measuring $(^{235/238}U)/(^{207}Pb/^{206}Pb)$ ratio (Slodzian and Havette, 1973). In another sample discovered later where lead was little depleted we obtained $\geqslant 1,75\ 10^9$ (Havette and Naudet, 1977). This datation was consistent with that determined by the Rb-Sr method ($1,8\ 10^9$ years, Bonhomme et al., 1977). Datations have also been performed in zircon with a recent mass spectrometer (Shrimp) by Froude et al., 1983) at a mass resolution of 6500. I indicate that polyatomic ions are generally well separated for masses > 200 except for ^{206}PbH - ^{207}Pb for which separation requires a resolution of 32,000.

Most recently we have observed that the results on isotope abundance differed from that given by the

*datation = age determination.

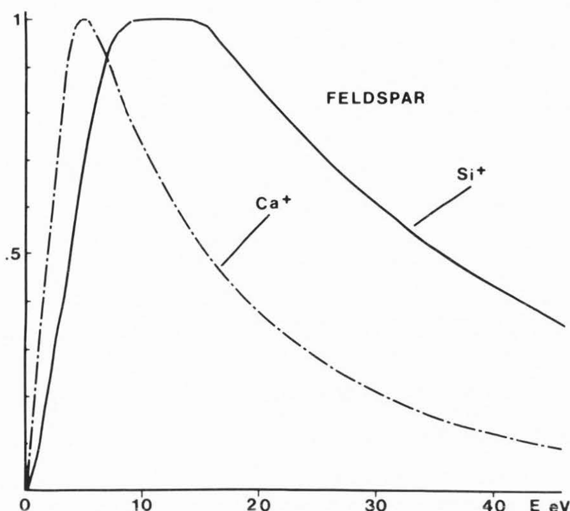

Figure 8

Energy distribution curves for Si^+ and Ca^+ in a feldspar.

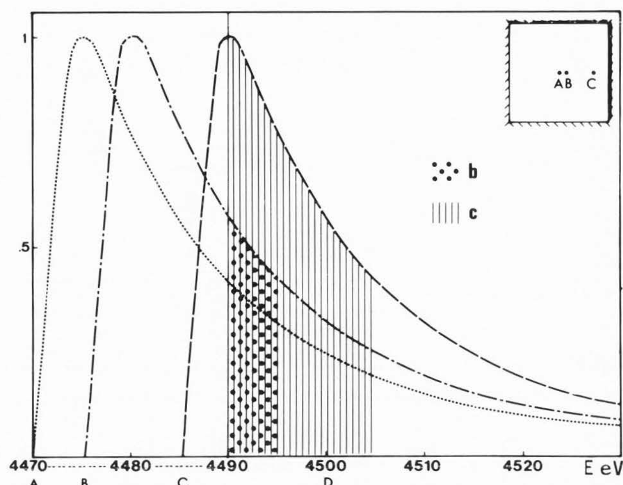

Figure 9

Energy distribution curves from points A, B and C in an insulating sample. We suppose that the surface sample is negatively charged (with a O^- beam for instance). The surface of the sample is not equipotential and ions which are extracted from different points have different accelerating energies. If we select the 4470-4490 eV energy band (by means of the selection slit and magnetic field value), the energy bandwidth is different for A, B and C : 20 eV for A, 15 eV for B and 5 eV for C. The shadings b and c represent the energy band which is not taken into account for the points B and C respectively at the time of the measurement on the area in which are situated A, B and C. D is the origin of the distribution curve when there is no charging-up effect on the surface sample (conducting sample for instance).

tables : there is an isotopic discrimination. If part of this discrimination may be instrumental, most of it is due to the physics of the secondary ion emission process.

The relative mass discrimination is :

- negative and a function of the chemical properties of the element (smaller for alkaline elements),
- proportional to the mass difference for a given element,
- increasing with decreasing ion energy,
- variable for an element when the chemical composition of the mineral varies (matrix effect) (Slodzian et al., 1980 ; Lorin et al., 1982).

The whole phenomenon can be explained by a simple model based upon electronic exchange as in the generalized Landau-Zener model (Slodzian et al., 1980).

A comparison of respective performances of the ion microanalyser and the electron microprobe.

Advantages of the ion microanalyser.

- Analysis of light elements : this analysis is eased by the fact that there are few interferences at low masses.
- Analysis of elements in small concentrations : the detection limit being low, a greater number of elements may be studied.
- Surface analysis : ions penetrate in the sample over a few 10 Å and the sputtering rate is 1 Å/s. In the case of major elements, the duration of analysis is a few 10 s (sets of images for instance). The depth of analysis is then of the order of 100 Å. On the other hand with the electron microprobe the penetration depth of electrons is much higher. The ion microanalyser makes it then feasible to study very thin layers or minerals with very small dimensions.
- The very fine visualization of the element topography allows a detailed study of heterogeneities and zoned structures ; these are often conspicuous with trace elements. Additional data on crystallisation processes are obtained in this way. It is possible to measure isotope abundance ratios with a precision of 1°/₀₀ if the concentrations are not too low.

Drawbacks.

- Precision of measurements with ion microanalysis is smaller than what can be obtained with the electron microprobe (the relative error is about twice as great).
- The study of aqueous minerals.
- The study of minerals which contain Fe^{2+} and Fe^{3+}.
- Several years of experience are necessary to take full advantage of the multiple potentialities of this instrument and above all to correctly interpret the results (measurements or images).

Conclusion

The coupling of the electron microprobe and the microanalyser makes it possible to go further in the study of a subject by accumulating information and especially the direct visualization of

the distribution of an element and its image gives evidence of phenomena which would otherwise pass unnoticed.

References

Andersen CA, Hinthorne JR.(1973). Thermodynamic approach to the quantitative interpretation of sputtered ion mass spectra. Analytical Chemistry, 45, 1421-1488.

Blanchard B, Carrier P, Hilleret N, Marguerite JL, Rocco JC. (1975). Utilisation du canon a electron pour l'analyse des isolants a l'analyseur ionique. 28th Colloquium Spectroscopicum Internationale, Vol. III, 918-924. G.A.M.S. (Paris) ed.

Bonhomme M, Leclerc J , Weber F. (1977). Etude radiochronologique complémentaire de la série du Francevillien et de son environnement. Les réacteurs de fission naturels. IAEA (119/6) Vienne.

Borchardt G, Weber S , Scherrer H , Scherrer S. (1984). Analyse des surfaces solides par SIMS utilisant un faisceau primaire de particules neutralisées. J. Phys., Colloques C2, 45, 801-804.

Castaing R, Slodzian G. (1960). Microanalyse par émission ionique secondaire. Proc. Eur. Reg. Conf. on EM, Academic Press, Delft-Holland, I, 169-172.

Froude DO, Ireland TR, Kinny PD, Williams IS, Compston W, Williams IR, Myers JS.(1983). Ion microprobe identification of 4,100-4,200 Myr-old Terrestrial zircons. Nature, 304, 616-618.

Havette A. (1974). Examen de certains problèmes méthodologiques posés par l'utilisation de l'analyseur ionique en géologie. Application à l'étude de quelques sujets pétrologiques. Thèse de spécialité, Paris XI.

Havette A, Naudet R. (1977). Etude locale par analyse ionique de nouveaux échantillons d'Oklo. Les réacteurs de fission naturels. 397-405, IAEA Vienne.

Havette A, Nativel P. (1977). Apport de l'analyse ionique à l'étude minéralogique d'une ignimbrite à chimisme de benmoréite du cirque de Salazie (Ile de la Réunion). Bull. Soc. Fr. Minéral. Cristallog. 100, 20-27.

Havette A, Lorin JC, Slodzian G. (1981). Rapports d'abondance isotopique à l'analyseur ionique : méthode de mesure et mise en évidence d'un effet isotopique d'émission. J. Microsc. Spectrosc. Electron. 6, 169-178.

Havette A, Slodzian G. (1982). Experimental procedures for quantitative analysis of silicate minerals. In Secondary Ion Mass Spectrometry SIMS III (Eds. A. Benninghoven, J. Giber, J. Laszlo, M. Riedel et H.W. Werner, 288-291, Springer-Verlag, Berlin.

Lorin JC, Havette A , Slodzian G. (1982). Isotope effect in secondary ion emission. In Secondary Ion Mass Spectrometry SIMS III (Eds. A. Benninghoven, J. Giber, J. Laszlo, M. Riedel et H.W. Werner), 140-150, Springer-Verlag, Berlin.

Massare D, Havette A , Slodzian G.(1982). Analyse quantitative de feldspaths synthétiques par images ioniques. J. Microsc. Spectrosc. Electron. 7, 477-486.

Pivin JC, Roques-Carmes C , Slodzian G. (1978). Variation des rendements d'émission ionique secondaire des alliages Ni-Cr, Fe-Cr, Fe-Ni en fonction de la teneur en soluté. Int. J. Mass Spectrom. Ion Phys., 26, 219-235.

Ray G , Hart SR (1982). Quantitative analysis of silicates by ion microprobe. Int. J. Mass Spectrom. Ion Phys., 44, 231-255.

Reed SJB.(1980). Trace element analysis with the Ion Probe. Scanning, 3, 119-127.

Shimizu N , Semet MP, Allègre CJ.(1978). Geochemical applications of quantitative ion microprobe analysis. Geochim. Cosmochim. Acta, 42, 1321-1334.

Shimizu N , Hart SR.(1982). Isotope fractionation in secondary ion mass spectrometry. J. Appl. Phys. 53 (3), 1303-1311.

Slodzian G. (1964). Etude d'une méthode d'analyse locale chimique et isotopique utilisant l'émission ionique secondaire (thèse de doctorat, Paris 1963). Ann. Phys. 9, 591-648.

Slodzian G , Dennebouy R , Havette A. (1975). Influence des effets de charge sur l'analyse des échantillons minéralogiques isolants par émission ionique. XVIII Colloquium Spectroscopicum Internationale, II, 590-595. GAMS Paris.

Slodzian G , Figueras A. (1980). A transfer optics for microanalysis by secondary ion emission. Proc. 8th Intl. Conf. X-Rays Opt. Microanal., Pendell, Midland, MI. 659-665.

Slodzian G , Havette A. (1973). Ion microanalyser observation of samples from the natural reactor of Oklo : preliminary results. 6th International Mass Spectrometry Conference, 6, 629-636. ASP Ltd., U.K.

Slodzian G , Lorin JC, Havette A. (1980). Isotopic effect on the ionization probabilities in secondary ion emission. J. de Physique Lettres, 41, 551-558.

Steele IM, Hervig RL, Hutcheon ID, Smith JV.(1981). Ion microprobe techniques and analyses of olivine and low-Ca pyroxene. Amer. Mineral., 66, 526-546.

Discussion with Reviewers

D.S. Simons : Have you encountered situations in mineralogical applications where energy discrimination for selective suppression of polyatomic ions is preferable to high mass resolution discrimination ?
Authors : No ! Generally, polyatomic ions which are the most difficult to suppress are the hydrides and in this case the energy discrimination is not effective.

D.S. Simons : When doing elemental or isotopic abundance measurements is a wide or a narrow energy acceptance preferred ?
Authors : The calibration and the measurement are made under the same conditions (20 to 25 eV) which allows to work at high resolution. If the energy band width is too narrow, the elementary ratios are not well reproducible at low energy because of the different forms of the elementary ions energy distributions. If the energy-band is too wide, there is a degradation of the resolution.

D.S. Simons : For the extraction of negative ions from an insulating sample, could an auxiliary electron gun be used in conjunction with negative ion bombardment to compensate for the lost negative charge ? What other methods of charge compensation are possible in this case ?
Authors : Yes. An electron gun has been set up on the Orsay instrument and the first results are very satisfactory. Bombardment with neutral ions is also used (Borschardt et al,1984) but results in the field of geological applications are not developed. In this case, the charge effect is neighbouring - 20 V.

D.S. Simons : In an unknown mineral, how does one determine the relative abundances of Fe2+ and Fe3+ with the ion microanalyser, since they do not produce separately distinct signals ?
Authors: The chemical composition of an unknown mineral which contains Fe^{2+} and Fe^{3+} is impossible to directly determine.

S.J.B. Reed : It is suggested that insulating samples should be bombarded with positive primary ions, the current density being adjusted to obtain a balance between these and incoming secondary electrons from the surface of the immersion lens. Others use negative primary ions with apparent success : to what extent is this a function of instrumental geometry and the size of the bombarded area (which is much smaller when a focussed probe is used) ? Further, would the author comment on the use of an electron flood gun for charge neutralisation ?
Authors : When a sample is bombarded with a O^- primary beam, the charge on the surface can be a few tens of volts on a 50 µm area. We have measured the charging-up effect produced by a O^+_2 defocussed beam on a 8 µm area : + 2.5, 3.1 and 6.9 V on areas which are situated in the core of holes whose diameters are respectively 10, 20 and 100 µm. We have also measured the ratio $INa^+/I^{28}Si^+$ on an area the charge on the surface of which is null and on another area the charge on the surface of which is + 4 V. The second ratio is 10% lower than the first ratio because of the migrations of Na induced in the sample (Figs. 10-11-12-13-14). If the bombardment conditions are always identical, the results can be reproducible but the standard mineral used must be the same as the studied mineral. Indeed, the charging-up effect is different for different minerals and then no general law can be established. For instance in the work of Ray and Hart (1982) the migration of the ions is obvious. Indeed the structural effect defined by the authors is, in fact, a migration effect, the charging-up effect being different in glass and in crystal. Furthermore the glass/cpx calibration factors are different from one element to another because of the differential migration of the elements. The investigators have problems but they do not know how to interpret them. The use of an electron flood gun for charge neutralisation when the extracted ions are positive cannot suppress the migrations while the surface of the sample is not equipotential before the electron bombardment. The charges produced by this bombardment being uniform, the surface of the sample has a different charge but remains not equipotential.

G. Remond : While discussing the merits of the ion microanalyser you mention that the depth of analysis is in the order of magnitude of 10 nm for major elements. Are such quantitative data consistent with EPMA results being characteristic of deeper analysed depths ? Have you verified the invariability of quantitative data at different depths below the surface ? What are the respective contributions on the reliability of quantitative data of in-depth composition changes which may result in mechanical polishing procedure and/or preferential sputtering during ion bombardment ?
Authors : The depth resolution is well demonstrated by the anorthosite image (Fig. 6) ; you can observe that the crystal is above the groundmass on the left of the image and under the groundmass on the right. There is then a wedge effect ; now the whole image has required 240 s (10 s for each image) and we do not observe any rim effect.
The reproducibility of the data has been verified a number of times. The influence of the polishing procedure and/or preferential sputtering is very limited. The intensity of the ion current is stable after a few minutes. Nevertheless, when the sample has been bombarded without care (with O^- ions for instance) the intensity of the secondary current emitted by the sample which has no charge on the surface varies because of the induced migrations.

R. Tixier : Spatial resolution is given as 0.5 µm. Is there any hope to improve this limit either with the present instruments or with future instruments? Are we close, or not, to physical limitations ?
Authors : The spatial resolution can be improved and future instruments will certainly attain spatial resolutions equal to or better than 1000 Å.

R. Tixier : Standardisation - One has to rely on standard minerals the elemental composition of which is assumed to be known. Considering the sensitivity of the method to local heterogeneities either in composition or in chemical bondings, is it better to use natural or synthetic standards ?
Authors : The use of synthetic standards is preferable but the crystals are often very small. Glass standards can also be used but the migrations are more important than in crystals. We prefer the use of natural standards the uniformity of composition of which is verified by means of ion images. Then the measurements are made with the electron probe.

R. Tixier : A very simple iterative procedure is described. Does it always converge to the best point ? Is there any possibility for it to diverge or to stop on an improper solution ?
Authors : Calculation has been carried out on a solid solution of SiO_4 (Mg, Fe)$_2$. The coefficients R_{0i} have been determined in a forsterite ($Si_{0,33}O_4 Fe_{0,07}Mg_{0,50}$) and we have calculated the composition of a fayalite ($Si_{0,33}O_4Fe_{0,60}Mg_{0,07}$). The second mineral being very rich in Fe, the coefficients R'_{0i} determined by the iterative procedure are very different from the R_{0i} values. Nevertheless the convergence is very fast. We have also calculated the composition of plagioclases which contains Si, Al, Na, Ca, K, Mg and the results are in agreement with the structural formula.

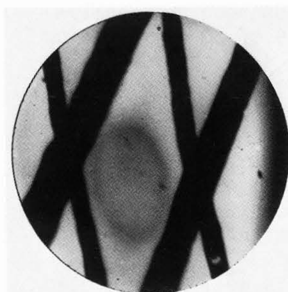

Figure 10

Migrations ; Na^+ distribution in an oligoclase. The sample has been bombarded with a 80 µm focussed beam. This bombardment has induced migrations of Na which can be observed on a micrograph achieved with a defocussed beam.

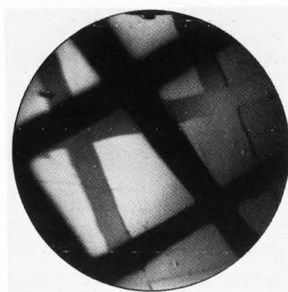

Figure 11

Migrations ; Na^+ distribution in an oligoclase. The sample has been first coated with a Al grid and bombarded by means of a O_2^+ beam (charge effect of some volts). The first grid has been taken away without any polishing of the surface of the sample. After the deposition of a new grid (black on the micrograph), the ghost of the first one appears on Na^+, Si^+.. images. In fact, Na^+ and some other elements have migrated. Simultaneously, the sputtering rate has changed (because of the composition variation) and Si^+ distribution also appears to be altered. The concentration of Na^+ under the grid (which is conducting) is then different from that of Na^+ in the sample.

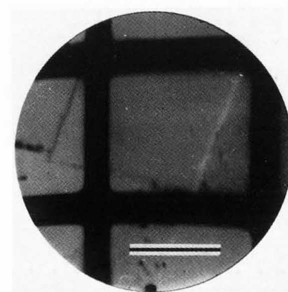

Figure 12

Migrations (Na^+ distribution in an oligoclase). The square the relief of which can be observed on the image has been used to calculate the practical ionisation yield of Si. The charging-up effect has been set to zero and the grid has been taken away without polishing. We can observe that Na concentration is identical in the square (sample) and out of the square (under the previous Al deposit).

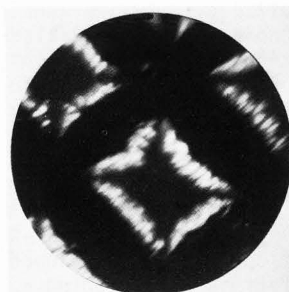

Figure 13

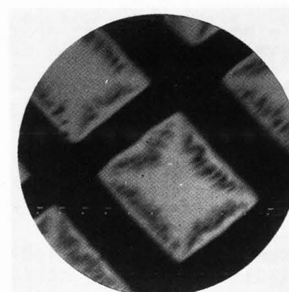

Figure 14

Figures 13 and 14

Na^+ and Si^+ (respectively) distribution in a float glass.
The sample has been bombarded with O^- beam and negative ions have been extracted during a short time. Then the sample has been bombarded with O_2^+ beam and positive ions have been extracted. At that time, we have observed Na^+ and Si^+ distributions and have been surprised to see their distributions correlated with equipotential curves.

Figures 10 - 14: Bar = 100 µm.