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Mass spectrometric study of rock like lunar surface material

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Chimica. — *Mass spectrometric study of rock like lunar surface material* [*]. Nota di GIOVANNI DE MARIA e VINCENZO PIACENTE, presentata [**] dal Socio V. CAGLIOTI.

RIASSUNTO. — Il processo di vaporizzazione di un campione di basalto andesinico di Nuraghe Silvanis, avente una composizione chimica simile a quella del materiale lunare analizzato dal Surveyor V, è stato studiato in un campo di temperatura 300°–2330° K mediante l'accoppiamento della tecnica di effusione di Knudsen e di uno spettrometro di massa.

Gli spettri di massa rilevati alle diverse temperature vengono discussi, caratterizzando al tempo stesso le fasi principali del processo di vaporizzazione del campione di roccia.

INTRODUCTION.

As part of a systematic study of the vaporization process of rocks at high temperature undertaken in our laboratory, the investigation of a basalt similar in composition to lunar surface material was carried out. The interest of these studies lies not only in the possibility that they may offer to elucidate important aspects of cosmochemical problems but also in the contribution they may make to the solution of serious problems connected with the future colonization of the moon and the planets.

It is generally agreed that condensation from the primeval nebula led to processes that formed the solid bodies we now observe in the solar system [1, 2]. Therefore the knowledge of molecular dissociative equilibria in the gas phase over the condensed materials, which may be considered representative of the primary crust of the planets, should prove helpful in treating the physico-chemical aspects of the mechanism of condensation of the primeval nebula [3, 4].

Furthermore the knowledge of the gas-phase composition over rock like lunar surface material in a wide range of temperatures may suggest the optimum conditions for the production of oxygen and perhaps of other utilizable compounds and materials, by vaporizing the lunar powder. This possibility does not appear to be far distant, especially if one considers the moon as the largest ultra-vacuum laboratory. The absence of atmosphere and the reduced gravitational field should make feasible the construction of large solar furnaces to vaporize the lunar powder.

The present paper deals with some preliminary results obtained for the vaporization of an andesinic basalt in a molybdenum container.

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EXPERIMENTAL PROCEDURE.

The general characteristics of the method and the experimental technique utilized have been described earlier [5, 6, 7].

In the present experiments a high temperature Bendix Co. time-of-flight mass spectrometer, mod. 3015, with a resolving power of 750 and an ion flight path of 200 cm was used. Both radiation heating and electron bombardment were used to vaporize the sample from the Knudsen cell. With the latter mode of heating, temperatures as high as 2400° K were reached. Temperatures were measured using both a Leeds and Northrup optical pyrometer, sighting the effusion hole through the top viewing window, and a W, W—Re thermocouple enclosed in the central crucible support leg. The agreement between the two readings was always satisfactory; the discrepancies observed never exceeded 12° C. The optical pyrometer was calibrated at the melting point of gold [8] and temperature correction for bottom-window transmission was based on the diagram given by Benford [9].

A differential pumping system provided an efficient vacuum pumpout of the Knudsen-cell compartment and of the flight tube.

In the course of the experiments the background pressure was maintained at values below 10^{-6} Torr in the Knudsen-cell region, and 10^{-7} Torr in the analyzer.

A molecular beam shutter assembly was mounted on the top of the Knudsen cell housing, allowing one to distinguish ions formed by neutral particles in the molecular beam from the ones created by surface ionization or background gases.

Two standard readout channels insured reasonable accuracy for ion intensity ratio measurements and isotopic distribution determinations. A molybdenum effusion cell, 1.2 cm high and 1 cm external diameter, with 1 mm knife-edge orifice diameter, previously outgassed at 1800° K, was filled with a crushed sample of andesinic basalt of Nuraghe Silvanis, having a composition corresponding to the one recorded in Table IV (sample no. 2) of reference 10.

A comparison of the atomic composition of the sample with the observed chemical composition of the lunar material at the Surveyor V landing site [11, 12] is given in fig. 1. The agreement appears to be quite satisfactory.

The rock sample analyzed was characterized by a marked vesicular aspect and a porphyritic structure of vitrophyric type.

Two silver calibrations were made, before and after the vaporization of the sample. The reproducibility of the instrument sensitivity factor was within 15%. On the basis of an extensive observation made during several years in this laboratory, we are led to believe that this procedure would affect the pressure calibration within an uncertainty of 10–15% at the most.

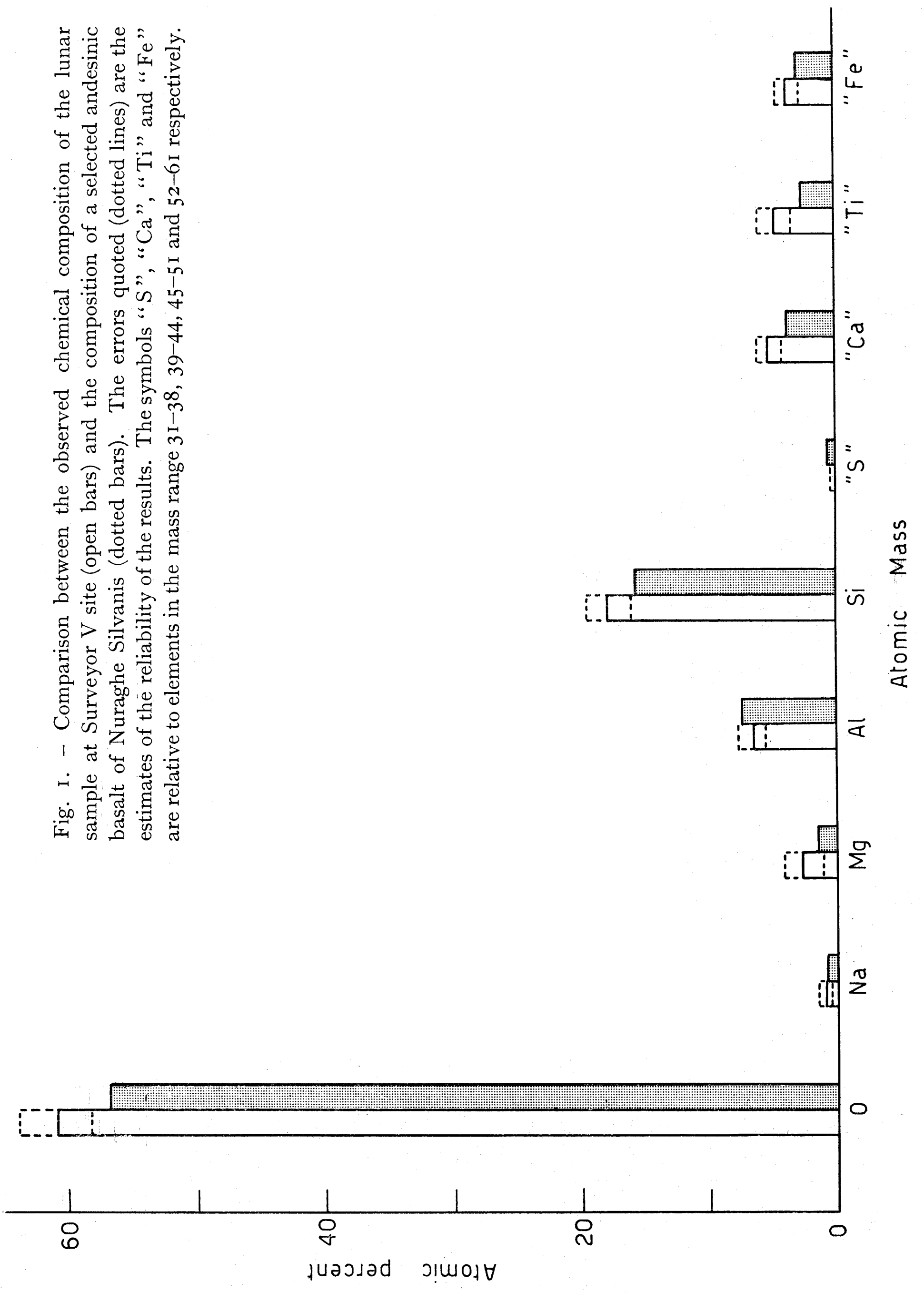

Fig. 1. – Comparison between the observed chemical composition of the lunar sample at Surveyor V site (open bars) and the composition of a selected andesinic basalt of Nuraghe Silvanis (dotted bars). The errors quoted (dotted lines) are the estimates of the reliability of the results. The symbols "S", "Ca", "Ti" and "Fe" are relative to elements in the mass range 31–38, 39–44, 45–51 and 52–61 respectively.

RESULTS.

Preliminary experiments carried out at different temperatures with appreciable quantities of the sample have shown the complexity of the mass spectra, at the same time giving indication of the selective mode of evaporation of the various components and of the extent and significance of the interaction with the container.

The quantitative evaporation of 178 mgr of the sample was carried out by stages, at temperature intervals of about 100° C, starting from room temperature and for a duration of about four hours at each stage. The entire series of experiments lasted five days. At the end of each stage the crucible was weighed in order to determine the weight loss. In the first phase, with a temperature interval of 300–500° K, a weight loss of 7.3 mgr, corresponding to 4.1 % of the sample, was observed. This value can be compared with the calculated amount of water in the original sample, which was equal to 4.71 %. At the same time the evaporation of water was followed throughout the reading of the mass spectra.

In the temperature range 500°–1800° K the weight loss was negligible, while the almost complete volatilization of the alkaline metals, and presumably of an appreciable part of the alkaline-earth elements, occurred. This anomaly can be accounted for by assuming that the molybdenum container reacted appreciably with the background oxygen because of the long exposure to background vapors, and hence compensated for the weight loss due to the vaporization of the rock sample. This working hypothesis seems to be supported by the observation that at a temperature of 1200° K the inner free surfaces of the crucible started to become covered with sporadic granules of brown material, which at the end of the experiments was analyzed by X–ray and found to be composed of a mixture of nonstoichiometric molybdenum oxides.

Melting of the sample occurred between 1200° and 1300° K, and the material lost its original gray color and assumed a characteristic lava-brown vitrophyric aspect.

Table I shows the mass spectra recorded at different temperatures, using 70 eV electron energy and measuring the intensity distribution in the molecular beam. The ion intensity values were corrected for surface ionization and "photo-effect", following the usual procedure [5].

The presence of ions created by surface ionization was observed mainly for the atomic and molecular species containing alkaline and alkaline-earth elements. The extent of this effect was variable. For example, at the temperature of 1600° K the surface ionization contribution to the Na^+ ion intensity measured at 70 eV was about 15 % of the total peak.

Due to the small values of the ion intensities it was not possible in all cases to draw the ionization efficiency curves or to measure the isotopic abundance. Moreover, in some cases the overlap of the isotopic distribution spectra made it difficult to identify the molecular species and to clarify the mechanism that led to the formation of the ions observed.

TABLE I.

Typical Mass Spectra at different temperatures recorded in the vaporization of a sample of andesinic basalt of Nuraghe Silvanis. Ion intensities (in amp.) were measured at 70 eV *electron energy and corrected for " surface ionization " contribution.*

T °K \ m/q	23	24	25	26	27	39	40	44
1210	2.10^{-13}	—	12.10^{-13}	$4.5\cdot10^{-12}$	—	$10\cdot10^{-13}$	—	—
1280	$5\cdot10^{-13}$	$4\cdot10^{-13}$	$10\cdot10^{-13}$	$3.0\cdot10^{-12}$	—	$15\cdot10^{-13}$	—	—
1350	$15\cdot10^{-13}$	$\sim 2\cdot10^{-13}$	$10\cdot10^{-13}$	$2.5\cdot10^{-12}$	—	$30\cdot10^{-13}$	—	—
1420	$15\cdot10^{-13}$	$<0.5\cdot10^{-13}$	$2\cdot10^{-13}$	$3.0\cdot10^{-12}$	—	$21\cdot10^{-13}$	—	—
1500	$18\cdot10^{-13}$	—	$5\cdot10^{-13}$	$2.5\cdot10^{-12}$	—	$35\cdot10^{-13}$	—	—
1560	$20\cdot10^{-13}$	—	$5\cdot10^{-13}$	$4.8\cdot10^{-12}$	—	$6\cdot10^{-12}$	$10\cdot10^{-13}$	—
1600	$5.0\cdot10^{-12}$	$2\cdot10^{-13}$	$5\cdot10^{-13}$	$9.0\cdot10^{-12}$	—	$8\cdot10^{-12}$	—	—
1660	$8.0\cdot10^{-12}$	$5\cdot10^{-13}$	10.10^{-13}	$10\ \cdot10^{-12}$	$15\cdot10^{-13}$	8.10^{-12}	$10\cdot10^{-13}$	—
1710	$7.2\cdot10^{-12}$	$10\cdot10^{-13}$	$10\cdot10^{-13}$	$8.2\cdot10^{-12}$	$3\cdot10^{-13}$	$12\cdot10^{-12}$	$\sim 5\cdot10^{-13}$	—
1780	$<0.5\cdot10^{-13}$	$<0.5\cdot10^{-13}$	$\sim 1\cdot10^{-13}$	$2.0\cdot10^{-12}$	$5\cdot10^{-13}$	$10\cdot10^{-13}$	—	—
1830	—	—	$<0.5\cdot10^{-13}$	$9.0\cdot10^{-13}$	—	$0\cdot10^{-13}$	—	$5\cdot10^{-13}$
1880	—	—	—	$\sim 2.0\cdot10^{-13}$	—	$<0.5\cdot10^{-13}$	—	$10\cdot10^{-12}$
1900	—	—	—	$5.0\cdot10^{-13}$	—	—	—	$20\cdot10^{-12}$
1980	—	—	—	$<0.5\cdot10^{-13}$	—	—	—	$40\cdot10^{-12}$
2150	—	—	—	—	—	—	—	$35\cdot10^{-12}$
2250	—	—	—	—	—	—	—	$52\cdot10^{-13}$
2330	—	—	—	—	—	—	—	$48\cdot10^{-13}$

Segue: TABLE I.

T °K \ m/q	45	46	50	51	52	56	78
1210	—	—	$25\cdot 10^{-13}$	$20\cdot 10^{-13}$	$18\cdot 10^{-13}$	—	$11\cdot 10^{-12}$
1280	—	—	$20\cdot 10^{-13}$	$18\cdot 10^{-13}$	$15\cdot 10^{-13}$	—	$6.5\cdot 10^{-12}$
1350	—	—	$10\cdot 10^{-13}$	$10\cdot 10^{-13}$	$5\cdot 10^{-13}$	—	$6.0\cdot 10^{-12}$
1420	—	—	$12\cdot 10^{-13}$	$10\cdot 10^{-13}$	$6\cdot 10^{-13}$	—	$6.0\cdot 10^{-12}$
1500	—	—	$10\cdot 10^{-13}$	$8\cdot 10^{-13}$	$6\cdot 10^{-13}$	—	$4.5\cdot 10^{-12}$
1560	—	—	$15\cdot 10^{-13}$	$12\cdot 10^{-13}$	$7\cdot 10^{-13}$	—	$28\cdot 10^{-13}$
1600	—	—	$15\cdot 10^{-13}$	$13\cdot 10^{-13}$	$10\cdot 10^{-13}$	—	$30\cdot 10^{-13}$
1660	—	—	$17\cdot 10^{-13}$	$15\cdot 10^{-13}$	$13\cdot 10^{-13}$	—	$18\cdot 10^{-13}$
1710	—	—	$20\cdot 10^{-13}$	$15\cdot 10^{-13}$	$15\cdot 10^{-13}$	—	$15\cdot 10^{-13}$
1780	—	—	$15\cdot 10^{-13}$	$11\cdot 10^{-13}$	$11\cdot 10^{-13}$	—	$10\cdot 10^{-13}$
1830	—	—	$5\cdot 10^{-13}$	$5\cdot 10^{-13}$	$3\cdot 10^{-13}$	—	$2\cdot 10^{-13}$
1880	$4\cdot 10^{-13}$	$4\cdot 10^{-13}$	$\sim 1\cdot 10^{-13}$	$1\cdot 10^{-13}$	$1\cdot 10^{-13}$	$25\cdot 10^{-13}$	—
1900	$7\cdot 10^{-13}$	$6\cdot 10^{-13}$	$< 0.5\cdot 10^{-13}$	$0.5\cdot 10^{-13}$	$0.5\cdot 10^{-13}$	$20\cdot 10^{-13}$	—
1980	$15\cdot 10^{-13}$	$12\cdot 10^{-13}$	—	—	—	$12.6\cdot 10^{-12}$	—
2150	$12\cdot 10^{-13}$	$10\cdot 10^{-13}$	—	—	—	$< 0.5\cdot 10^{-13}$	—
2250	$2\cdot 10^{-13}$	$\sim 0.5\cdot 10^{-13}$	—	—	—	—	—
2330	$2\cdot 10^{-13}$	$\sim 0.5\cdot 10^{-13}$	—	—	—	—	—

The ion intensities measured at masses 23, 27, 39, 44 (45 and 46 isotopic peaks) and 56 are to be attributed to the parent ions Na$^+$, Al$^+$, K$^+$, SiO$^+$ and Fe$^+$, respectively. The ionization efficiency curves, where measurement was possible, are given in figs. 2, 3 and 4. The ionization potentials which were determined by using the method of linear extrapolation and by assuming Hg$^+$ as a standard to calibrate the energy scale, are given in Table II. The second column lists the molecules that can be considered as possible primary species of the observed ions. The molecules given in parenthesis are considered less likely.

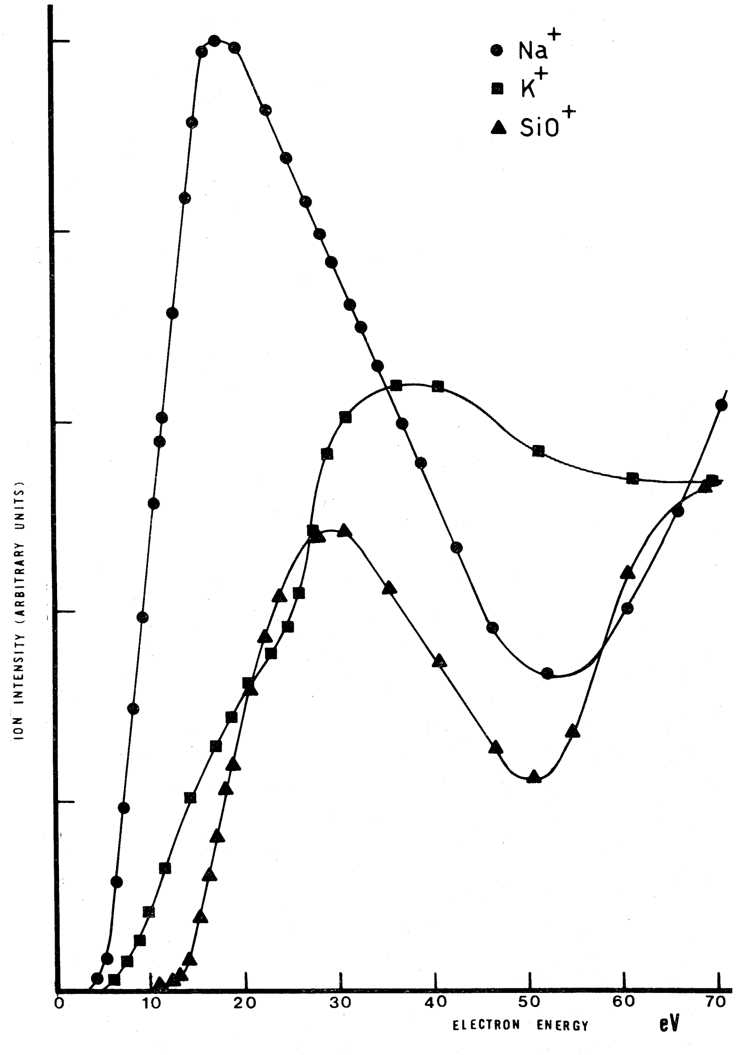

Fig. 2. – Ionization-efficiency curves for observed species (Na$^+$, K$^+$ and SiO$^+$) over a sample of andesinic basalt of Nuraghe Silvanis.

A general examination of the data gives some indication of the mode of vaporization of the rock sample. One can distinguish three main phases:

a) In the initial phase, corresponding to the temperature range between 1300° and 1900° K, the vaporization of the alkaline and alkaline-earth metals is observed to occur largely in the form or atomic or heteronuclear polyatomic species containing oxygen and to a lesser degree Al and presumably Si.

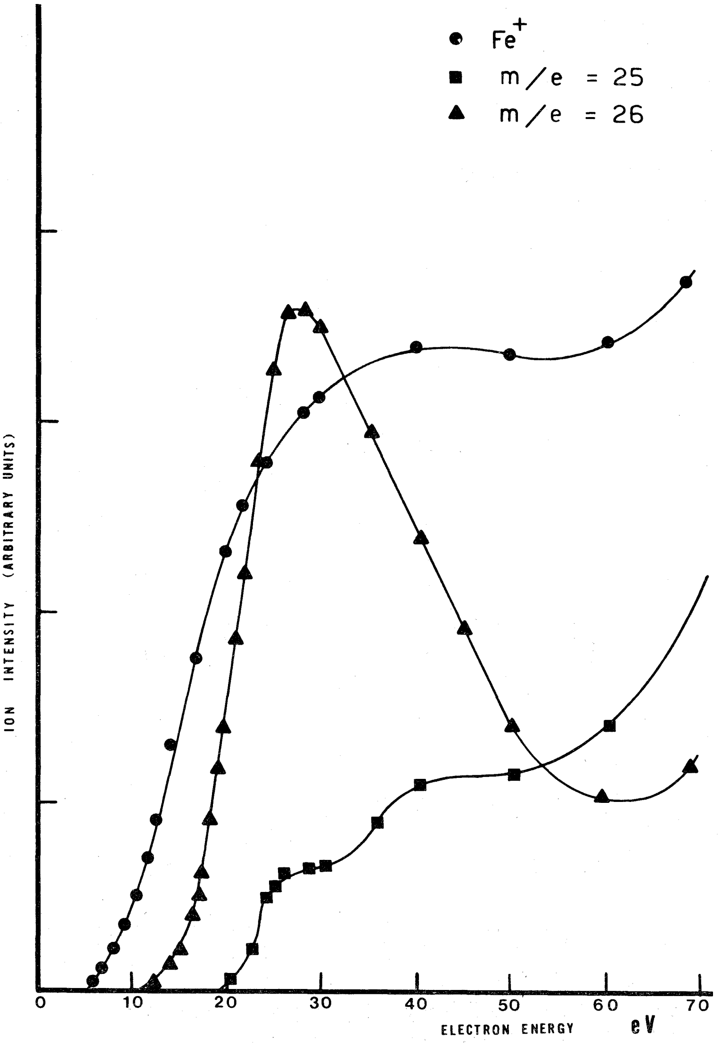

Fig. 3. – Ionization-efficiency curves for observed ions (Fe^+, $m/q = 25$ and 26) over a sample of andesinic basalt of Nuraghe Silvanis.

b) A second phase corresponds approximately to a temperature range of 2000°–2300° K, where volatilization of Si and Fe and part of Al occurred. Si volatilized mainly in the form of SiO, while iron and aluminum volatilized as monoatomic species.

c) A third phase, corresponding to temperatures above 2300° K, was characterized by the volatilization of the residue, largely composed of Al_2O_3 and that molybdenum oxide which was formed at lower temperatures by reaction with the oxygen produced during the volatilization of the alkaline and alkaline-earth metals. In the present experiments the evaporation of the residue was not carried out to completion because the residue appeared to have reacted strongly with the container material and because the weight loss exceeded the initial weight of the sample.

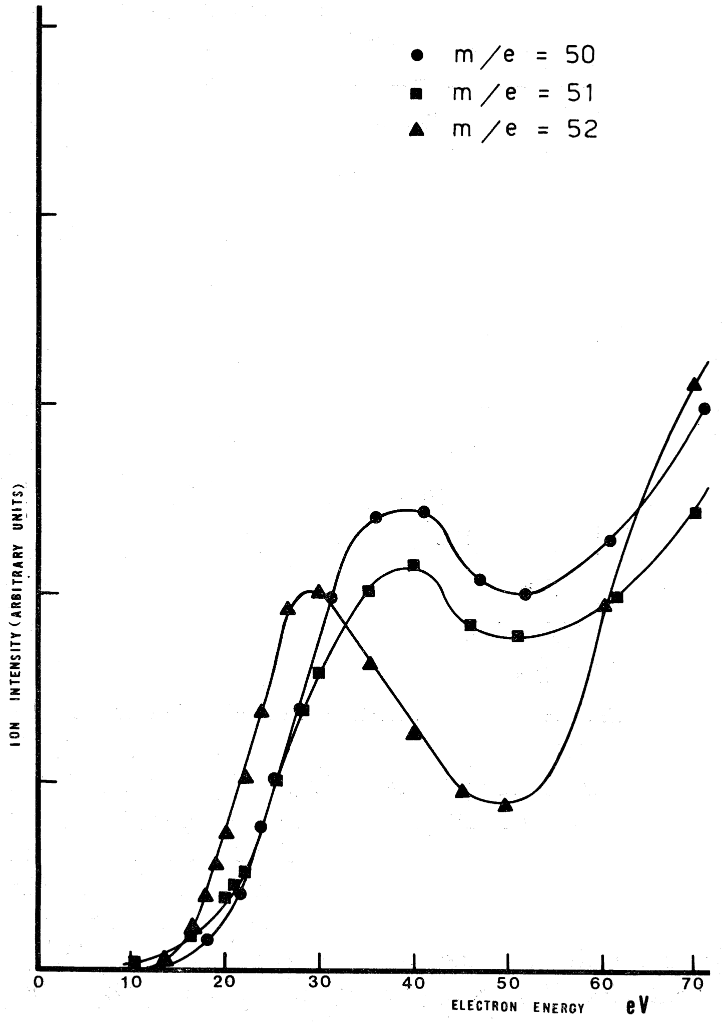

Fig. 4. – Ionization-efficiency curves for observed ions (m/q = 50, 51 and 52) over a sample of andesinic basalt of Nuraghe Silvanis.

Volatilization of the molybdenum oxide was observed. In the mass spectrum detected at 70 eV, it produced ion peaks corresponding to MoO_3^+, MoO_2^+ and MoO^+ [13, 14]. It was noticed that these were produced mainly by the outer surfaces of the crucible.

There is considerable uncertainty concerning the interpretation of the ion peaks at mass 25 and 26. From the appearance potentials and the shape of ionization efficiency curves, one can infer that the peak at mass 26 might correspond to a parent species, while the peak at mass 25 should be considered a fragment of an undetermined higher-mass species, presumably formed by pyrolyzable organic matter.

TABLE II.

Appearance potentials of detected ions. The species in parenthesis are to be considered less likely parents.

m/e	PARENT SPECIES	A.P. (eV)
23	Na	5.1 ± 0.3
24	(fragment)	~ 40
25	(fragment)	21 ± 1
26	—	15.0 ± 0.8
39	K, (NaO)	6.0 ± 0.3
44	SiO	12.5 ± 0.3
50	(NaAl), fragment	18.5 ± 1.0
51	(NaSi), (MgAl)	15.5 ± 1.0
52	(MgSi)	15.5 ± 1.0
56	Fe, (CaO), (MgO_2)	8.0 ± 0.3
78	KNaO, (Na_2O_2)	~ 15

In the temperature range 1400°–1800° K, a peak of high intensity was noticed at mass 40. It was attributed to the reevaporation of calcium from the shields. The peak showed a small " shutter effect ", characterized by a typical build up of pressure in the ionization chamber. The ion intensities observed at mass 44, 45 and 46 are in reasonable agreement with the isotopic distribution of the SiO molecule, whose appearance was noticed at a temperature of about 1800° K. Its appearance potential of 12.0 ± 0.8 eV as determined in the present experiment, is slightly higher than the value reported by Porter *et al.* [15].

The contribution of surface ionization to the total ion intensities measured at mass 50, 51 and 52 was relatively slight (of the order of magnitude of 5–10% of the whole peak). Thus, in view of the moderate value of the appearance potentials, they ought presumably to be ascribed to biatomic heteronuclear species. The overlap of isotopic distributions corresponding to the various species that are presumed to be the sources of the ions observed made it impossible to establish their nature with certainty. The high value of the appearance potential observed at mass 50 could suggest a likely origin from organic molecular species.

The appreciable ion contribution due to surface ionization and the value of 15 eV of the appearance potential observed for the peak at mass 78 suggest a KNaO parent species, while Na_2O_2 seems less probable because of thermodynamic considerations [16]. Furthermore the peak at mass 80 also shows an appreciable contribution due to surface ionization, while the ion intensity ratio $\frac{I^{+}80}{I^{+}78}$ measured at three different temperatures 1550°, 1720° and 1840° K gave an average value of 10.2 for the isotopic abundance of mass 80. This value, compared with the expected 6.3 theoretical abundance due to K reveals the probable overlap of another ionic species of difficult determination. Magnesium seems to vaporize predominantly in the form of polyatomic species. The high value of the appearance potential measured at mass 24 (40 eV) rules out the possibility of elementary magnesium.

There are some indications concerning the presence in the mass spectra of the products of the pyrolysis of organic matter. In this connection, in addition to the peaks at m/e 24, 25 and 50, a partial contribution of ions derived from aromatic hydrocarbon should be considered likely at the m/e 78 peak.

Partial pressures of the observed species were estimated following the procedure described in reference 6. The relative values for Na and K at 1200° K are of the order 10^{-5} atm. and 10^{-4} atm. and for Fe one obtains $5 \cdot 10^{-5}$ atm. at 2000° K. From these values one calculates an order of 10^{-5}, 10^{-6} and $4 \cdot 10^{-2}$ for the activity of Na, K and Fe respectively, utilizing the vapor pressure data revised by Nesmeyanov [17].

CONCLUSIONS.

These first experiments have brought to light certain special aspects of the manner in which vaporization occurs in a certain kind of basaltic rock. The failure to detect oxygen—made more difficult because of the relatively high background peak at mass 16—shows that most of the oxygen in the sample reacted with the molybdenum to form non-stoichiometric oxides that began to volatilize at approximately 2000° K.

An assessment of the extent of the gas-condensed phase reaction as compared to the condensed phase-solid phase reaction cannot be made on the basis of the present data. Nevertheless it seems likely that the latter type of reaction was predominant, even though the compensation of the weight loss of the alkaline and the alkaline-earth components that occurred in the first phase must be attributed to the long exposure of the molybdenum to the background oxygen and, hence, to the former type of reaction. Nevertheless it is legitimate to argue that a respectable amount of the oxygen in the sample could, in neutral conditions, vaporize in free form at a temperature as low as 1700° K. Furthermore, if the possible recombination of oxygen with other molecular species in its collision with the surface of the container is not excessive, oxygen could be obtained in elemental form.

The present study illustrates the necessity of finding a suitable container to study the material in the most perfect neutral conditions possible. Experiments are now being carried out, and provisional results have already pointed the way to a satisfactory solution of the problem.

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