

MASS SPECTROMETRIC INVESTIGATION OF THE OLIVINE VAPORIZATION PROCESS

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Vaporization of the olivine sample containing 10% fayalite was followed by means of mass spectrometric technique and using different Knudsen cells. The temperature dependence of partial pressures of the species identified in gaseous phase was established. The tensimetric values of the species were used to write the corresponding Clausius-Clapeyron equations. The comparison of the data obtained with the literature ones allows to draw some conclusions about vaporization mechanism of the sample treated.

INTRODUCTION

Characterization of the vapour species in the vaporization of lunar samples has been proved [1] very valuable in connection not only with cosmochemical and astrochemical problems, but also with geochemical ones. The exploitation of resources of lunar soil and the mechanism of the condensation processes of the primeval nebula are only two interesting aspects among many others. The easiest approach to the problem is to start with very simple minerals whose chemical composition is found in some lunar rock samples. Olivine containing 10 % fayalite, being a well characterized mineral, was chosen as the starting point of a systematic study of the vaporization process of such systems.

PROCEDURE AND EXPERIMENTAL RESULTS

The olivine samples used for the vaporization experiments were cut from samples of andesinic basalts rocks and their composition was tested by standard analytical methods.

A Bendix time of flight mass-spectrometer (mod. 3015) with a Knudsen cell as molecular source was used.

The apparatus and the essentials of the method have been described previously [2], [3]. The ionic species were produced by electron impact into the Knudsen beam. A movable beam defining slit (shutter) located between the Knudsen cell orifice and the ion source allowed to distinguish species originating

from the crucible and the background gases [4]. The ionic species were identified by mass/charge ratio, isotopic distribution, appearance potential and intensity profile.

The absolute values of the partial pressures of such ionic species were calculated using the relation [4]:

$$P_i = I_i^+ T / S \sigma_i a_i \quad (1)$$

in which I_i^+ represents the ionic intensity of the measured isotopic peak, a_i its abundance, T temperature of the effusion cell, S the sensitivity factor of the mass-spectrometer, and σ_i the relative cross section at the maximum of the ionizing electron beam. The temperature of the cell was measured with a calibrated optical pyrometer (Leeds and Northrup), focused directly at the effusion hole. In order to detect possible interactions of the olivine sample with the cell, crucibles of various materials were used, namely alumina, thorium dioxide, zirconium dioxide, platinum and rhenium.

Alumina crucible

A strong interaction of the olivine sample (200 mg) with the alumina crucible was detected. The decrease of the SiO^+ , Fe^+ and Mg^+ ion intensities and also fusion of the bottom part of the container was noticed at nearly 1900 K. The measurements were, therefore, unreliable and the results obtained were not taken into account.

Thorium dioxide crucible

Two experiments were performed using this crucible. 160 mg of the sample was vaporized at temperatures ranging from 1680 to 2050 K in the first experiment. Fe^+ , SiO^+ and Mg^+ ions were observed with appearance potentials, relative to Hg (10,44 eV [2]) (see Fig. 1), 8.4 ± 0.3 ; 2.0 ± 0.3 and 7.4 ± 0.4 eV,

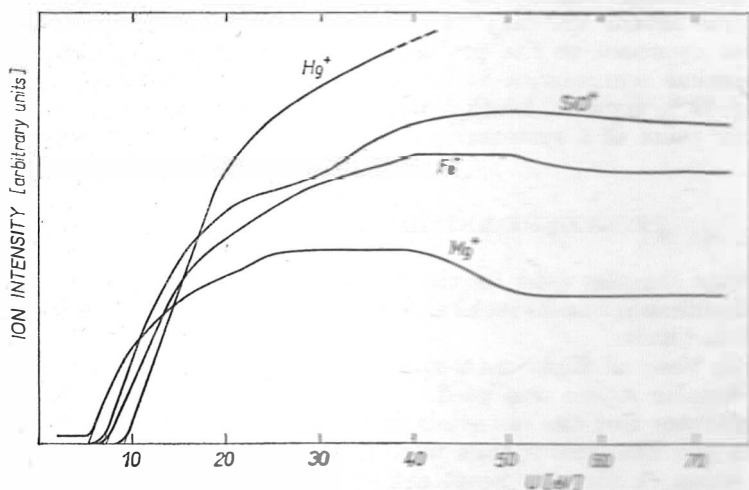


Fig. 1. Ionic intensity v. ionizing voltage.

of respectively indicating the first ionization processes. The ionic intensities have been measured with ionizing electronic energy at its maximum efficiency (45 eV). A fast decrease in all ionic intensities measured occurred at the temperature 1920 ± 15 K. However, the decrease can not be explained by the interaction of the olivine sample and thorium dioxide, as no evident effects of such interaction were observed on the crucible. A possible explanation of the decrease is that some phenomena arising by fusion of the sample can diminish

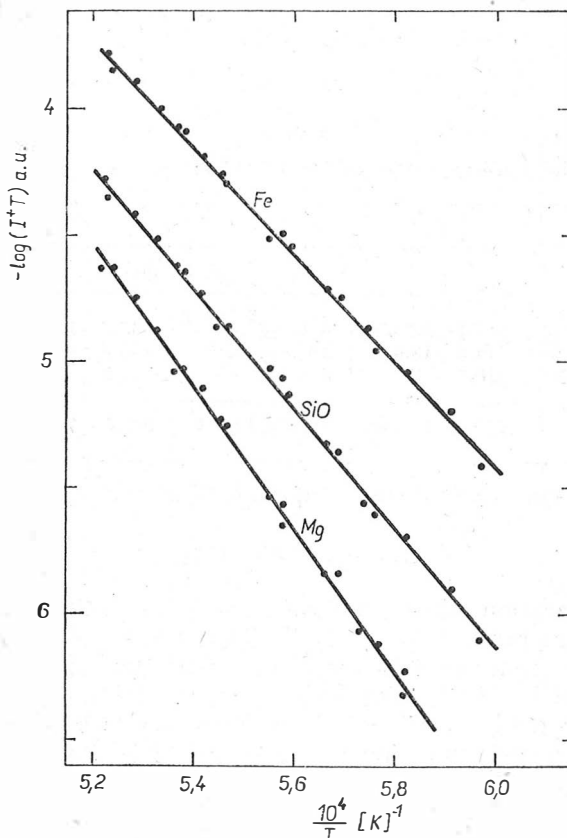


Fig. 2. Vaporization with the use of a thoria cell; $\log(I+T)$ vs. $1/T$.

the activities observed. Only the results obtained below the temperature 1920 K were therefore taken into account. The second experiment was carried out utilizing larger amount of the olivine sample (363 mg). The ionic intensities of the species composing the vapour were measured in the temperature range of 1870—2080 K after melting of the sample at 2000 K. In contrast to the first experiment only the ionic intensities of SiO^+ and Mg^+ were measured with a satisfactory reproducibility.

However, their values were about two-three times smaller than those obtained in the first experiment. The Fe tensimetric values were even far

lower (8 times) and not reproducible during the experiment. The latter phenomenon could be explained as an interaction of iron with the container material, which may arise during melting of the sample. The consequence of this interaction is probably a quite different composition of the condensed phase as compared to the original sample. Therefore, only the data obtained from the first experiment below 1920 K were taken into account.

The values of $\log(I^+T)$ vs. $1/T$ of the three ionic species observed are plotted in Fig. 2. The partial molar enthalpy of sublimation of Fe, SiO and Mg from the olivine sample at the average temperature of 1800 °K have been calculated from the relative slopes using the second law method. The enthalpy values are listed in Table I.

Table I

Sublimation enthalpies of iron, magnesium and SiO from an olivine sample (10 % fayalite)

Crucible	T [K]	Fe	SiO	Mg	O ₂
		[kJ/mole]			
ThO ₂	1680—1920	407.4 ± 9.2	456.8 ± 13.0	545.5 ± 13.4	
ZrO ₂	1673—1925	414.9 ± 13.4	463.9 ± 11.30	549.5 ± 12.6	
Re	1699—1920	410.3 ± 7.9	461.4 ± 8.8	553.9 ± 10.0	473.1 ± 13.0
		410.3 ± 12.6 ^(a)	460.5 ± 12.6 ^(a)	548.5 ± 12.6 ^(a)	473.1 ± 13.0 ^(b)

(a) The associated errors are standard deviations, (b) Estimated errors.

Zirconia crucible

The next evaporation experiment was carried out with a zirconia crucible in the temperature range 1673—2013 K. The amount of olivine sample was 388 mg. The ionic species identified were Fe⁺, SiO⁺ and Mg⁺ and their intensity values are plotted in Fig. 3. The fusion process of the sample, detected by a steep decrease of the intensities of all the ionic species, occurs at 1925 ± 10 K. Above this temperature only ion intensity values of Mg⁺ and SiO⁺ species were reproducible. The fast decrease in iron activity can be attributed to an interaction of the sample with the ZrO₂ cell. The relative partial enthalpies of sublimation at the average temperature of 1800 K of the species are listed in Table I.

Platinum and rhenium crucibles

From the point of view of the stoichiometry of the olivine evaporation it is evident that the gaseous phase should contain also oxygen. However, the oxygen has been not detected with certainty in any of the experiments carried out with alumina, thoria and zirconia crucibles. On the contrary a fair amount of oxygen was detected in addition to iron, magnesium and SiO⁺ species, when a platinum container was used to evaporate the sample. Owing to the low melting point of platinum very limited number of measurements were carried out in a restricted temperature range (1400—1445 K). Therefore, the

data obtained were insufficient to evaluate the partial enthalpies of evaporation.

Similar results were obtained by evaporation of the olivine sample from a rhenium crucible. This experiment was carried out in the 1699—1920 K temperature range i. e. below the melting point of the sample, as indicated by steep decrease of the ionic intensities. Fe^+ , SiO^+ , O_2^+ and Mg^+ ions were observed and the corresponding values are plotted in Fig. 4. The composition of gaseous phase has been changed, when the sample was evaporated at higher temperatures (up to 2100 K). SiO_2^+ , FeO^+ species, atomic oxygen and two rhenium oxides (ReO_2^+ , ReO_3^+) were identified in this temperature range. The concentration of the rhenium compounds was very small in comparison with the other components of the gaseous phase.

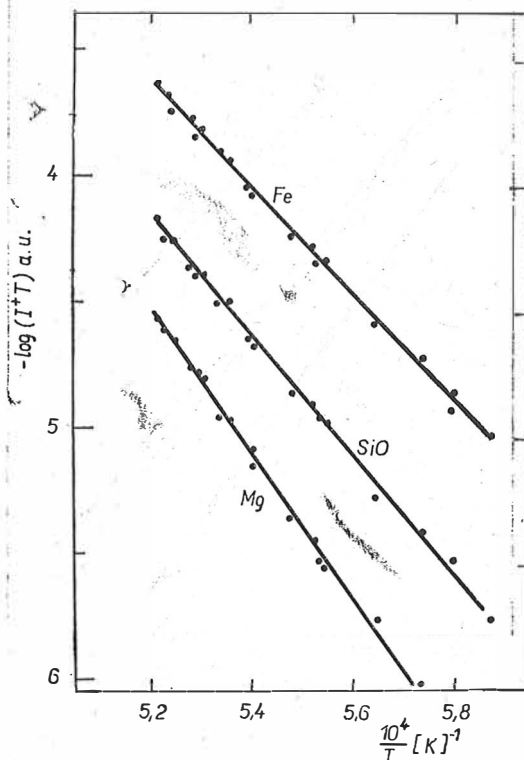


Fig. 3. Vaporization with the use of a zirconia cell; $\log(I+T)$ vs. $1/T$

DISCUSSION

The partial pressures of the gaseous species in equilibrium with the solid phase have been determined from the ionic intensities using equation (1). The instrument was calibrated before each experiment by complete evaporation of a known quantity of silver. For the atomic species Mann's (5) cross sections were employed; for the molecular species the values 1.83 and 4.37

for O_2 and SiO respectively were obtained by multiplying the sum of the ionization cross sections of each atom by a factor of 0.7 (6).

The tensimetric values thus determined in the three experiments with ThO_2 , ZrO_2 and Re crucibles are in agreement within 20–30 %. Such an agreement can be considered satisfactory within the uncertainties associated with the experimental procedures: temperature measurements, ionization cross sections, geometric and electronic parameters (the effective area of the

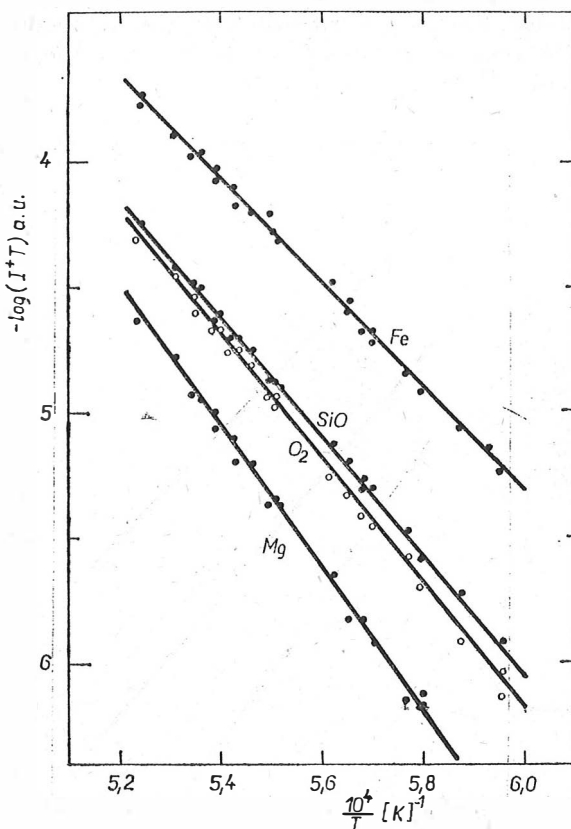


Fig. 4. Vaporization with the use of a rhenium cell; $\log(I+T)$ vs. $1/T$.

effusion holes and the gain of the electron multiplier, etc.) which are included in the instrument constant S . The tensimetric values of each species were used to write the corresponding Clausius-Clapeyron equations. The final equations, reported as follows, were determined by averaging the coefficients of every equation obtained in each series of experiments:

$$\begin{aligned}
 \log P_{Fe} \text{ (kPa)} &= (9.34 \pm 0.72) - (21.4 \pm 0.8) 10^3/T, \\
 \log P_{SiO} \text{ (kPa)} &= (10.21 \pm 0.36) - (24.0 \pm 0.8) 10^3/T, \\
 \log P_{Mg} \text{ (kPa)} &= (12.18 \pm 0.68) - (28.6 \pm 0.7) 10^3/T.
 \end{aligned}
 \tag{2}$$

The errors correspond to the maximum semi dispersion. The tensimetric values of the oxygen are given by the following equation:

$$\log P_{O_2} \text{ (kPa)} = (10.4 \pm 0.9) - (24.7 \pm 1.1) 10^3/T \quad (3)$$

in which the error is the standard deviation.

The partial pressures of each species and the total pressure of the gaseous mixture in equilibrium with the olivine sample have been plotted vs. temperature in Fig. 5. An analysis of the results points out the following: the partial

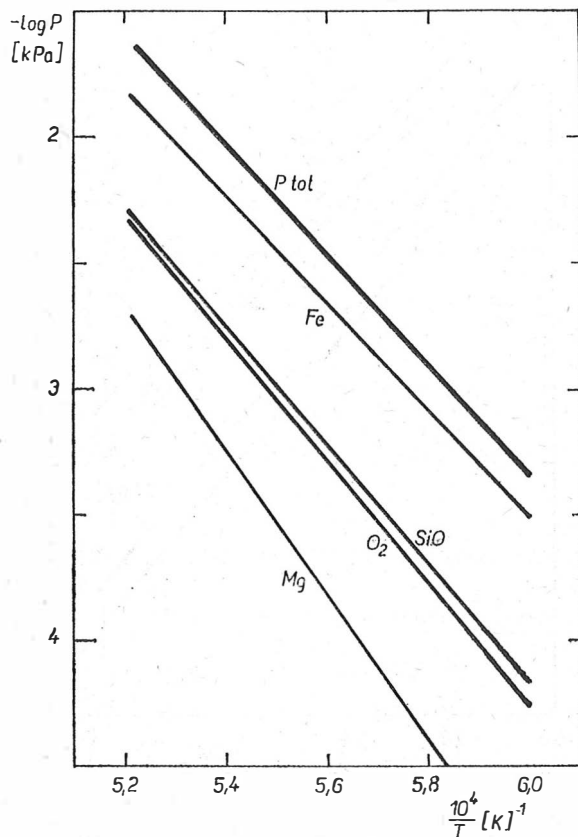
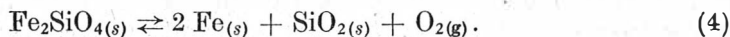


Fig. 5. Partial pressures of gaseous phase components, and total pressure vs. temperature.

pressure of iron in the mixture is comparable with the vapour pressure of pure metal (7), (Fig. 6). The conclusion is that this element vaporizes from olivine with almost unitary activity. This is not surprising considering the results obtained in the vaporization of fayalite (8) pure and mixed with other components in some basalts, for which the following evaporation process was proposed:



The partial pressure of the SiO species is also comparable with that observed over pure cristobalite (9), (Fig. 6). This observation is in agreement with the previous vaporization scheme, i. e. eq. (4), in which a SiO₂ phase is formed. Finally all the data obtained at temperatures below the melting point of the sample show a good reproducibility of the tensimetric values, both for the Fe and the SiO, even for small concentrations of fayalite in the olivine sample. Such behaviour clearly excludes a superficial impoverishment of the sample

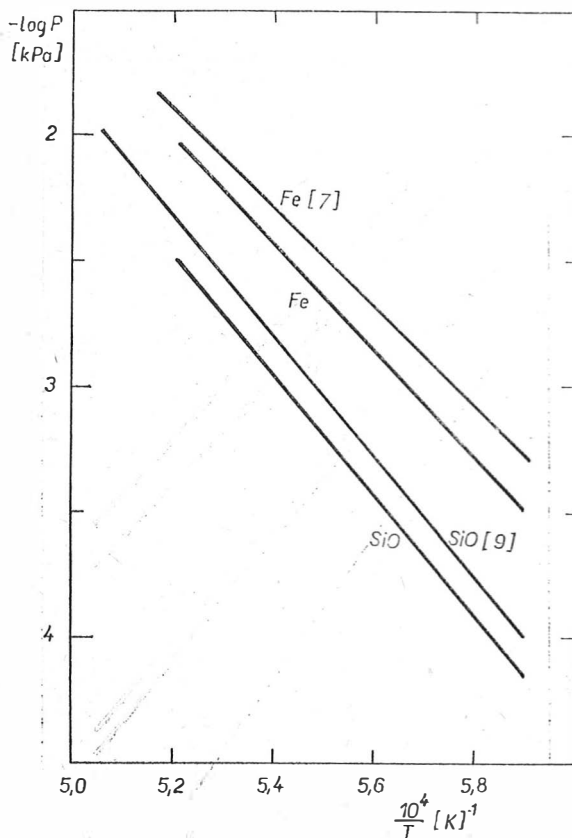


Fig. 6. A comparison of the temperature dependence of Fe and SiO partial pressures established in the present study, with published partial pressure values for these components over pure Fe and SiO₂.

and suggests the presence of a diffusion transport of the iron within the olivine crystal having kinetics almost comparable to the evaporation kinetics of pure iron.

Therefore it can be deduced that for olivine samples richer in fayalite the same evaporation process should be found and that this process identifies itself with the evaporation process of pure fayalite because the contribution of the magnesium partial pressure is almost negligible (3 %) with respect to the total pressure, at least in the temperature range in question.

CONCLUSIONS

Fe^+ , SiO^+ and Mg^+ — ions were the only species identified in gaseous phase vaporizing the olivine sample in thoria and zirconia crucibles at the temperatures 1673—1925 K. Using rhenium crucible, also oxygen was found in gaseous phase. The temperature dependence of partial pressures of the species can be described by Clausius-Clapeyron equations. The mean values of partial molar sublimation enthalpies were calculated to be 420.3, 460.5, 548.5, 473.1 kJ/mole for Fe, SiO, Mg and O_2 respectively. Evaporation of the olivine sample occurs probably according to the same mechanism as in the vaporization of pure fayalite.

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STUDIUM VYPAŘOVACÍHO PROCESU OLIVÍNU HMOTOVOU SPEKTROMETRIÍ

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Součástí výzkumu měsíčních hornin je studium vypařovacího procesu jejich složek. Pro studium vypařování olivínu byl vybrán vzorek obsahující 10 % fayalitu. K identifikaci plynných složek a ke stanovení jejich tenze par bylo použito hmotového spektrometru Bendix 3015. Vypařování vzorku nastávalo v Knudsenových celách, které byly zhotoveny z různých materiálů.

Při použití cely z kyslíčnicku hlinitého byla pozorována intenzivní interakce vzorku olivínu s materiálem kelímku, která činila výsledky měření tenze par složek plynné fáze natolik nespolehlivými, že nebyly brány v úvahu.

V teplotním intervalu 1680—1920 K byly za použití cely z kyslíčnicku thoričitého identifikovány v plynné fázi ionty Fe^+ , SiO^+ a Mg^+ , pomocí rovnice (1) vypočteny jejich parciální tlaky a z nalezené teplotní závislosti určeny hodnoty parciální molární entalpie sublimace (viz tabulka I). Obdobné výsledky byly získány při použití cely z kyslíčnicku zirkoničitého.

Při vypařování v platinové cele byl vedle dříve uvedených složek identifikován v plynné fázi i kyslík. Vzhledem k nízké hodnotě bodu tání platiny nebylo možno získat dostatečný počet spolehlivých výsledků pro sestavení teplotní závislosti parciálních tlaků jednotlivých složek.

Pro další studium byla proto použita cela z rhenia. V teplotním intervalu 1699—1920 K byly identifikovány v plynné fázi stejné ionty jako v případě platinové cely. Při vyšších teplotách (1920—2100 K) byly v plynné fázi dále nalezeny oxidy rhenia (ReO_2^+ , ReO_3^+).

Hodnoty parciálních tlaků složek plynné fáze, získané za použití různých cel, jsou navzájem v uspokojivém souladu. Závislost parciálních tlaků složek plynné fáze na teplotě je dána rovnicemi (2) a (3) a jejich grafické znázornění je na obr. 5. Z obr. 6 je patrné, že tenze par nad čistým železem a nad čistým kyslíčkem křemičitým jsou srovnatelné s hodnotami parciálních tlaků iontů Fe^+ a SiO^+ , které byly zjištěny v této práci. Toto zjištění odpovídá předpokládanému mechanismu vypařování fayalitu, které podle rovnice (4) probíhá za rozkladu na Fe , O_2 a SiO_2 . Příspěvek parciálního tlaku hořečnaté složky je oproti celkovému tlaku par zanedbatelný. Je tedy možno alespoň ve zkoumaném teplotním intervalu interpretovat vypařování vzorku olivínu stejně, jako vypařování čistého fayalitu.

Obr. 1. Závislost iontové intenzity na hodnotě ionizujícího napětí.

Obr. 2. Vypařování za použití cely z kysličníku thoričitého — průběh závislosti $\log(I+T)$ na $1/T$.

Obr. 3. Vypařování za použití cely z kysličníku zirkoničitého — průběh závislosti $\log(I+T)$ na $1/T$.

Obr. 4. Vypařování za použití cely z rhenia — průběh závislosti $\log(I+T)$ na $1/T$.

Obr. 5. Závislost parciálních tlaků složek plynné fáze a celkového tlaku na teplotě.

Obr. 6. Srovnání teplotní závislosti naměřených hodnot parciálních tlaků Fe a SiO s publikovanými hodnotami tlaku těchto složek nad čistým Fe , resp. SiO_2 .

ИССЛЕДОВАНИЕ ИСПАРИТЕЛЬНОГО ПРОЦЕССА ОЛИВИНА С ПОМОЩЬЮ МАСС-СПЕКТРОМЕТРИИ

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Целью предлагаемой работы является исследование испарительного процесса отдельных компонентов лунной породы. Для исследования испарения оливина подобрали пробу, содержащую 10 % fayalита. Для идентификации газообразных компонентов и для определения их упругости паров использовали масс-спектрометр Bendix 3015. Испарение протекает в ячейках Кнудсена, приготовленных из разных материалов.

Используя ячейку из окиси алюминия, наблюдали интенсивные взаимодействия пробы оливина с материалом тигля, которые оказывали влияние на результаты измерения упругости паров до той степени, что они оказывались ненадежными и нельзя было их учитывать.

В температурном интервале 1680—1920 K, применяя ячейки из окиси тория, идентифицировали в газообразной фазе ионы Fe^+ , SiO^+ и Mg^+ , с помощью уравнения (1) рассчитали их парциальные давления и на основании найденной температурной зависимости установили величины парциальной молярной энтальпии сублимации (см. табл. 1). Подобные результаты получались с применением ячейки из окиси циркония.

При испарении в платиновой ячейке кроме ранее установленных компонентов идентифицировали в газообразной фазе кислород. Вследствие низкой величины точки плавления платины нельзя было получить достаточное количество надежных результатов для выведения температурной зависимости парциальных давлений отдельных компонентов. Поэтому для дальнейшего исследования применяли ячейку из рения. В температурном интервале 1699—1920 K идентифицировали в газообразной фазе те же ионы, как в случае применения платиновой ячейки. При более высоких температурах (1920—2100 K) в газообразной фазе были найдены окислы рения (ReO_2^+ , ReO_3^+).

Величины парциальных давлений компонентов газообразной фазы, полученные использованием разных ячеек, находятся в хорошем согласии. Зависимость парциальных

давлений компонентов газообразной фазы от температуры дана уравнениями (2) и (3) и их графическое изображение приводится на рис. 5. Из рис. 6 видно, что упругость паров над чистым железом и над чистой двуокисью кремния сопоставима с величинами парциальных давлений ионов Fe^+ и SiO^+ , нами установленными и приводимыми в предлагаемой работе. Это установление соответствует предполагаемому механизму испарения фаялита, которое согласно уравнению (4) протекает с разложением на Fe , O_2 и SiO^+ . Повышение парциального давления магниевого компонента по сравнению с общим давлением паров можно неучитывать. Следовательно, таким образом, хотя и только в исследуемом температурном интервале, можно проводить интерпретацию испарения пробы оливина тем же способом, как испарение чистого фаялита.

Рис. 1. Зависимость интенсивности ионов от величины ионизационного потенциала.

Рис. 2. Испарение с применением ячейки из окиси тория — ход зависимости $\log(I+T)$ от $1/T$.

Рис. 3. Испарение с применением ячейки из окиси циркония — ход зависимости $\log(I+T)$ от $1/T$.

Рис. 4. Испарение с применением ячейки из рения — ход зависимости $\log(I+T)$ от $1/T$.

Рис. 5. Зависимость парциальных давлений компонентов газообразной фазы и общего давления от температуры.

Рис. 6. Сопоставление температурных зависимостей измеряемых величин парциальных давлений Fe и SiO с опубликованными величинами давления приведенных компонентов над чистым Fe , или SiO_2 .