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GEOLOGICAL APPLICATIONS OF IONIZATION LTE MODEL IN
LASER PROBE MASS SPECTROMETRY

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Abstract

Recently, the laser plasma ionization process of the laser Probe Mass Spectrograph permitted one to obtain quantitative information on the fluid inclusions and trace distributions in ores. Indeed laser ionization provides the physical conditions for a substantial application in the Local Thermodynamical Equilibrium (LTE) model. Other geological information in the case of micro-analysis on the quartz, fluorite, and zircon has also been obtained.

Introduction

In 1973, a review paper, Keil and Snetsinger (1973) treated the possibility of extending in geology the applications of laser probe mass spectrometry (LPMS) which had until then been limited to the study of the gas distribution in meteorites (Megrue, 1967, 1969) and in coal (Vastola et al., 1967). More recently, Eloy and Lebel (1978) have published analytical results from individual micro-fluid inclusions (for diameter <10 μ m), giving separate information on the fluids and on the solid walls.

Indeed, laser probe mass spectrometry uses the interaction of a pulsed laser beam focused on a sample surface, as the ion source allowing (Bykovskii et al., 1978) : 1) the localization of the sampling volume, 2) the erosion of the ores without contamination because no treatment of the samples is required, 3) simultaneous analysis of all chemical elements.

This ionization process permits a high versatility in different material analysis : for example, insulator, biological or mineral samples, solid, liquid or gaseous phases ; in addition the laser ionization provides generally a limited dispersion between the elementary ionization yields when the created plasma is not disturbed by additional ionization processes (for instance : auxiliary electron bombardment device or unexpected electrical discharges).

Basically, the physical features of the laser-material interaction have a direct consequence on the analytical capabilities of this method : indeed, as reported by Conzemius and Capellen (1980), strong differences appeared between relative sensitivity coefficients (RSC) experimentally obtained from different materials or by different authors. Consequently, if the ionization yields of elements inside the laser plasma are theoretically governed by classical laws such as those of Saha (1921), Eggert (1919) and Saha (1922), all attempts to apply such formulae for correction calculations have failed since the first application by Honig (1963).

In this paper, we will show that it is possible to establish a calculation method in order to get a good correlation between

Key words : Laser probe mass spectrograph, geological micro-analysis, fluid microinclusions, matrix analysis, quantitative analysis local thermal equilibrium.

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experimentally obtained and expected values. The conditions to be fulfilled are : 1) the plasma laser around the sample is in local thermal equilibrium (LTE), 2) the ionic composition is not destroyed by an extracting field between the sample and the first source slit.

Firstly, we summarized the attempts to obtain quantitative results from mass spectra provided by laser ionization.

Short survey of correction calculation attempts

Preliminary attempts in laser mass spectrometry

Firstly, Honig (1963) considered the laser exclusively as a heating process and consequently ion production as a thermoionic emission. Therefore, he proposed the use of the Langmuir-Saha formula (Honig, 1969) :

$$N^+/N^0 = \exp [e (W-IP)/k T] \quad (1a)$$

$$= \exp [11606 (W-IP) / T] \quad (1b)$$

where T is the temperature of hot surface, in K, N^+ the number of positive ions, N the number of neutral, W the work function of surface in V., IP the ionization potential in V., e the electronic charge, 1.6021×10^{-19} coulomb, k Boltzmann's constant, 1.3804×10^{-23} joule/K.

But J.F. Ready (1971) was not so optimistic. He wrote "this equation was derived for equilibrium conditions, but it has often been applied to the non-equilibrium case of removal of material from a metallic surface by laser heating. The Langmuir-Saha equation must be applied with caution in such circumstances".

Valkovic (1975) wrote "One serious limitation of the laser source at the present state of development is the difficulty of obtaining quantitative results". At the same time, Eloy and Stefani (1975) were studying experimental RSC's in different matrices. After a long series of experiments this compilation did not lead to a general correction method based on the knowledge of relative elemental sensitivities.

Devyatykh et al. (1976) and Dietze and Zahn (1972) tried to obtain an empirical formula. Recently, Kovalev et al. (1978) applied a correction factor estimated from:

$$\begin{aligned} \Delta Q &: \text{heat of sublimation} \\ \phi &: \text{ionization potential} \\ \sigma &: \text{ionization cross-section} \\ \epsilon_0/\epsilon_i &: \text{coefficient of relative sensitivity (RSC)} \\ \epsilon_0/\epsilon_i &= \Delta Q_0 \phi_i^\sigma \sigma_0 / \Delta Q_i \phi_i^\sigma \sigma_i \quad (2) \end{aligned}$$

Of course, Conzemius and Capellen (1980) observed marked differences between the

reported RSC's values from different materials and different authors. Busygin (1977) noted "a rather high dependence of relative ion yield on the diameter of the focal spot".

Lastly, Haas et al. (1981) reported an attempt to apply the local thermodynamic equilibrium model (LTE model) in using the law of mass action of Guldberg-Waage to calculate the dissociation yields of compounds into the plasma. This approach supposes a previous knowledge of all possible compounds in the sample ; that is not generally the case.

Effectively, the physical properties (chemical bonds) of the sample determine the yields of vaporized atoms (Eloy, 1965) and the thermodynamic features of the laser plasma (thermal homogeneity, stability and directivity : Tonon, 1973). But the main part of the laser energy contributes to provide the ionization energy. Therefore the main parameter of the total ion emission yield and consequently of the ion extraction is the ionization rate of laser plasma which depends on both electronic temperature and density of plasma. In this respect we have considered a new approach to apply a theoretical model of laser ionization for a quantitative determination (Deloule and Eloy, 1981b).

Local thermal equilibrium (LTE) model

When we compare the successive interpretations of the laser ionization with respect to the physical model established for ion bombardment, spark source and discharge plasma (Franzen and Schuy, 1967), we note a strong difference between the conceptions of the correction procedures. Thus, up to now, the users of laser mass spectroscopy (Kovalev et al., 1978 ; Haas et al., 1981) come up against a very complicated association of physical phenomena without resolving the analytical problem.

In the case of secondary ion mass spectroscopy (SIMS) applications, we observe however the same opposition between two methods : empirical and theoretical approaches (Shimizu et al., 1975). In this field, the review of every known study on theoretical conversions of ion intensities to elementary concentrations is very instructive. Among these different attempts, one emphasizes : 1) the use of empirical sensitivity factors (Mc Hugh, 1970), 2) the quantum mechanical model of surface ionization advanced by Schroeder et al. (1973), 3) the LTE approach of Andersen and Hinthorne (1973) carried out by the Carisma program, 4) the simplified LTE program of Simons et al. (1976).

Andersen and Hinthorne (1973) assumed the secondary ion emission was produced by a plasma in local thermal equilibrium and from Simons et al., (1976) the estimated electronic temperature (Te) and density (Ne) appeared to be correlated according to the curves seen on figure 1 (Newbury et al., 1976; Lovering, 1975).

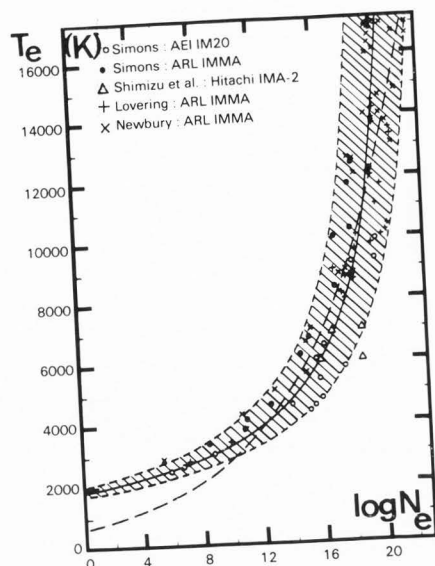


Figure 1. Correlation of T_e and N_e values determined from various LTE computer programs applied to the SIMS analysis and reported by Simons et al. (1976).

This range of estimated electronic temperature and electronic density ($T_e < 8000$ K) corresponds to strong variations of secondary ionization yields with respect to the difference of temperature, and it is now accepted, the LTE model is not based on physical arguments but on empirical ones (Suba and Stopka, 1982) (Newbury, 1979).

New approach for analytical corrections in the case of ionization by laser plasma creation

Main physical features

Previously, Eloy (1980) studied the features of the laser material interaction in order to obtain a laser micro-plasma in local thermal equilibrium. In spite of the affirmation of Kovalev et al. (1978, p.109) "as a result of the work, at the plasma formation threshold a small output of ions and instability in the ion formation were observed", but in agreement with the work of Leising (1973), Deloule and Eloy (1981a) have displayed the analytical capabilities of a superheated micro-plasma in local thermal equilibrium, obtained with 10^{-13} g. of the solid material. The choices of a short laser time duration (3 ns.) and restrictive conditions of laser flux focalization are the main physical conditions of these high ionization effects. As a matter of fact, during our analytical improvements in the field of the laser interaction, we have established the constancy in the collected ions quantity in spite of simultaneous decreases of laser energy and laser time duration (Chamel and Eloy, 1983). The ion yield was improved by these simultaneous

reductions, in correlation with a two phase description of the laser interaction, Deloule and Eloy (1981a) :

i) In a first phase, the energy absorbed by the target is due to the collective excitation of the electrons induced by the electrical field of the laser photons (Leising, 1973, Tonon, 1973). There are transitions between different free states of the electrons which absorb the energy and transmit them to the atoms by collision. The creation of a cloud of free electrons brought about by these transitions lasts about 2×10^{10} s., the time duration required to start the vaporization of the target.

ii) Then, the light energy is absorbed by the free electrons in the plasma, transmitted either to the ions by collision or to the solid by thermal diffusion. For example, in the case of an aluminum target and for a laser time duration ≈ 30 ns., the yield of laser energy transmitted to the plasma is on the order of 10% (Leising 1973). Afterwards the vaporization process is governed by the laws of heat propagation. The absorption of energy is localized in 2 zones (see table 1), the boundary of the opaque vapour where there is heating of the sample, the plasma where occurs the ionization of the species. (figure 2)

Table 1. Different physical properties of phases in the laser-material interaction

	1 dense medium	2 opaque vapour	3 transparent vapour
state	solid	vapour	plasma
phenomena	thermal conductivity vaporization into the solid	ionization	expansion
light interaction	no light	no light	internal absorption

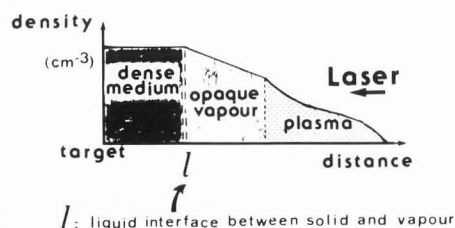


Figure 2. Density profile of laser plasma versus the distance to the target inside its expansion zone.

From our own observations, the use of a laser time duration shorter than 10 ns., partly reduces the contribution of the laser energy

absorption to the vaporization phenomena : the loss of thermal energy by conductivity is highly decreasing in the dense medium (phase 1, figure 2).

In consequence, as the electronic density decreases very rapidly by the expansion of the plasma zone (which also decreases the efficiency of the laser plasma-interaction) and as the laser is focused on the initial surface of the sample (which decreases the flux of provided energy for the plasma region far away from the sample surface), it can be seen that the ion creation zone is stopped at the opaque vapour-plasma boundary (Leising, 1973).

Because of the velocity of the laser plasma (\approx Km/s.) and without auxiliary ionization, we will consider that in the second step there is neither recombination nor reequilibrium of the system between this field free zone and the ion extraction optics, if an auxiliary ionization does not occur.

As a consequence, the main properties of this plasma are : 1) high degree of charge , 2) conservation of initial charge state during the plasma expansion (Tonon, 1972), 3) anisotropic angular distribution of the ionic emission (Langer et al. 1966) (Perez, 1971).

Ionization corrections by the Saha-Eggert equation

The conditions required for a LTE plasma (Venugopalan, 1970) are fulfilled in the LPMS II instrument (figure 3), by the ion source design and the procedure, (Eloy, 1980; Eloy et al.; 1983, Chamel and Eloy, 1983).

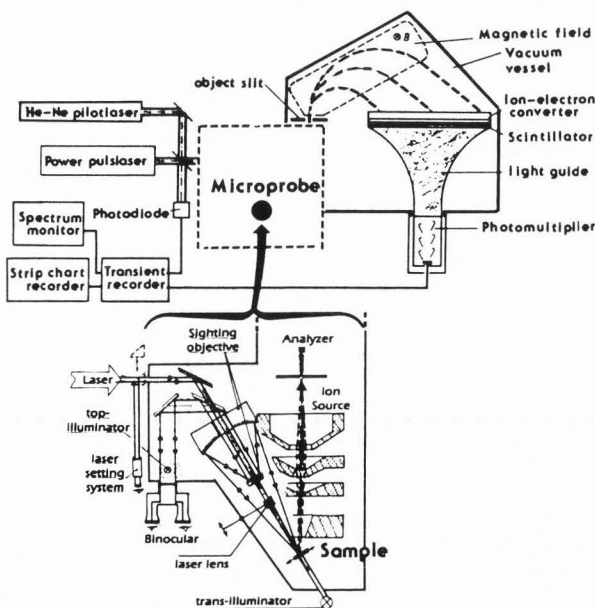


Figure 3. Schematic view of the laser probe mass spectrograph II (LPMS II).

The mass spectra are representative of this plasma (figure 4).

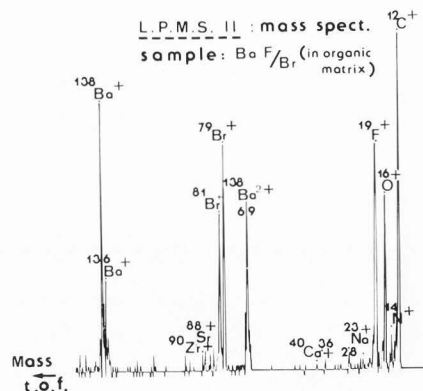


Figure 4. Example of LPMS II mass spectrum obtained with a sample of BaF/Br embedded in organic matrix.

In this case, we can apply the Saha equation (Saha, 1921) to determine the distribution of each atomic and ionic species in different states of charge :

$$\frac{N_{(z+1)}}{N_z} = \frac{2(2\pi m_e k T_e)^{3/2}}{h^3 N_e} \cdot \frac{U_{(z+1)}}{U_z} \exp\left(\frac{-E_z}{kT}\right) \quad (3)$$

k = Boltzmann's constant

U_z = partition function of ion with charge z

N_z = number of ions with charge z

E_z = ionization energy of z-charged state

m_e = electron mass

h = Planck's constant

This equation allows the distribution of each atomic and ionic species (negative or positive ions) in different states of charge (z) to be studied versus electronic temperature and density for some samples (CaF₂, SiO₂, C₂O₆Ca Mg). From calculated curves (previously reported : Dumas Milne Edwards and Joffre, 1981), four ranges of electronic temperature (T_e) with strong different features can be distinguished : 1) $T_f < T_e < 6,000$ K : high contribution of the negative ions and neutral atoms ; yields for the singly charged positive ions are low and strongly dependent on the temperature (variation on the order of 10^3 to 10^4) (with T_f = fusion temperature of solid), 2) $6,000$ K $< T_e < 10,000$ K : strong variation of the contribution in both negative and positive ions between the different chemical elements ; high contribution of neutral atoms, 3) $10,000$ K $< T_e < 20,000$ K : negligible contribution of the negative ions ; high contribution of the singly charged

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positive ions with only slight variations of ions yields; weak yields of (2+) and (3+) ions, 4) 20,000 K <math>K < T_e</math>: highly ionized plasma state (multicharged ions exclusively).

From this study of LTE plasma, the 3rd range of electronic temperature (: 10,000 K <math>K < T_e < 20,000</math> K) appears to be the best one for chemical analysis: rather unselective ion yields of high value allow all chemical elements to be recorded as positive ions on the mass spectra. A typical example is given in figure 4 (sample: BaF/Br embedded in an organic matrix): the peak heights C^+ , O^+ as well as F^+ and Br^+ are roughly representative of the element concentrations.

Now, because we produce a highly ionized plasma with high electronic density states, the more appropriate expression is the Saha-Eggert equation (Venugopalan, 1970): in the formula (3) $\exp^{-E_Z/kT}$ becomes

$$\exp\left[\frac{-(E_Z - \Delta E_Z)}{kT}\right], \text{ where } \Delta E_Z \text{ is the "Unsold"}$$

correction factor (Unsold, 1955, p. 375) or "Debye-Hückel" correction factor (Drawin et al. 1965).

This ΔE_Z term takes the high ionic density into account, in the case of a short Debye radius.

Knowing the relative abundance of the main elements, the Saha-Eggert equation permits one to calculate the electronic temperature and densities of laser plasma in the analytical conditions. These obtained values permit one to calculate the correction factors for all other elements simultaneously detected (Eloy, 1984; Chamel and Eloy, 1983). Since, three years, numerous verifications of this correction method have been made and proved its obvious application (Eloy, 1984).

From different analytical applications of this correction method (Eloy, 1984) to the LPMS mass spectra, we have estimated the plasma features for laser energies ranging between 1.8 and 12 μJ : table 2 shows the different temperatures (T_e) and electronic densities (N_e) obtained for various solid samples.

Table 2. Plasma features (with LPMS) calculated by the Saha-Eggert law (LTE model)

Samples	stoichia	temper. T_e (K)	dens. N_e (e/cm^3)	$W_{\text{las.}}$ μJ .
Cd-Te	50-50	7,000	$10^{20.75}$	3
Hg-Te	50-50	11,000	$10^{20.75}$	9
Cd-Hg-Te	1-3-4	6,000	$10^{20.25}$	4
Si-As	100-.05	17,500	10^{16}	1.8
Mg-F ₂	333-66.6	18,500	$10^{18.25}$	8
Ba-F ₂	333-66.6	16,000	$10^{18.75}$	6
Ba-F/Br	10-5-5	14,500	$10^{19.5}$	7
polyest.+Cs	100-.01	10,500	$10^{18.75}$	12
polyest.+Co	100-.003	9,000	$10^{19.75}$	11

Another application of the LTE model for the quantitative interpretation of the LAMMA spectra has been reported by Haas et al. (1981), combining the law of mass action for molecule dissociation and the Saha-Eggert equation for ionization and taking into account the oxygen concentration as an additional parameter. The electronic temperature of 8000 K and the electronic density of $2.10^{17} e/\text{cm}^3$ estimated from Al, Ba, Ca and Si concentrations in NBS glass standard (K 309 and K 491) lead to the assumption that, in the instrument, the features of the laser plasma belong to the second range of temperature as defined above. This could explain the difficulties in applying the LTE model (Denoyer et al. 1982).

Geological applications of LPMS

Among the geological applications of the chemical analysis techniques, the study of microcrystallites (or precipitated crystals) or fluids enclosed in inclusions or in inter-crystalline zones, is of interest to understand the genesis of ore deposits. Obviously, the field of applications can be extended by microanalytical methods allowing solid or fluid inclusions to be individually characterized, and in addition, the laser microprobe offers particular properties (Bykovskii et al. 1978): 1) the erosion of the host mineral to liberate a micro-inclusion saves the neighbouring ones, illustrated by the figure 5, 2) the laser interaction with solid generating a liquid interface (figure 2), the situation is favorable to ionise the fluids liberated from the inclusion cavities.

To take advantage of the LPMS technique, the computer program (ELOGET)* developed from the LTE model to obtain a quantitative analysis, has been applied to geological results. In a first attempt, the correlation between the temperature and the density, of the laser plasma theoretically defined by Venugopalan (1970), has been checked against different geological standards, as shown in figure 5.

Samples: $\text{SiO}_2, \text{F}_2\text{Ca}, \text{CaMgC}_2\text{O}_6$

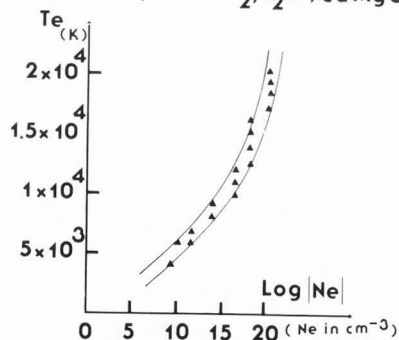


Figure 5. Correlation of T_e (electronic temperature) and N_e (electronic density) values determined from LTE computer program applied to the laser probe analysis by the LPMS.

* product of the author (unpublished but available on request)

Control of the LTE model validity for the LPMS instrument by use of geological standard

With the crystals

i) Dolomite ($\text{CaMg}(\text{CO}_3)_2$). In table 3, (Deloule and Eloy, (1981a), the calculated ratios for the components of a dolomite crystal firstly demonstrate the validity of the LTE model corrections.

Table 3. Calculated ratios for components of a dolomite crystal

Ratios	Expected	Experimental*	Corrected
$\frac{\text{Ca}}{\text{Mg}}$	1	1.428	1.079 ± 0.05
$\frac{\text{O}}{\text{C}}$	3	0.82	2.975 ± 0.05
$\frac{\text{Ca+Mg}}{\text{C}}$	1	3.3	0.986 ± 0.10

* averages of four mass spectra.

ii) Zirconia ($\text{ZrO}_2 + 2\% \text{HfO}_2$) - In figure 6a, the temperature deduced from the stoichiometric values ($\text{Zr} = 1, \text{O} = 2$), is plotted versus depth of the laser sampling inside the solid crystal.

Using the same analytical results and one value for the temperature (16,500 K), the calculated ratio Zr/O appears to be dependent on the erosion depth, (step = 500 Å) as shown in figure 6b. The variation of the standard deviation, σ , could be explained by the evolution of the surface shape of crater, shot after shot : 1) in surface the variations are increased by the influence of the surface rugosity, 2) in depth the variations are due to the small diameter (sizes $\leq 10 \mu\text{m}$) with respect to the depth.

With fluid inclusions in ores. For fluid inclusion analysis in geological samples using the LPMS, a specific procedure is required in order to control the laser erosion up to the cavity and then the ionization of the fluid components. Among the mass spectra collected laser shot by laser shot and stored in a computer memory unit, only some of them recorded during vacuum gauge oscillations correspond to fluids liberated from the inclusion. Indeed, the laser erosion does not release the enclosed fluids during a single shot but rather thins down the thickness of the inclusion wall resulting in weak fluid leakages by multiple cracks. It is the reason why the liberated gases or the liquids appreciably change the vacuum in the ion source, without disturbing the ion collection. In addition, this process induces the decomposition of the inclusion cavity, the migration of fluids and salts through the wall, and precipitation of the salts into the cavity. Consequently, the

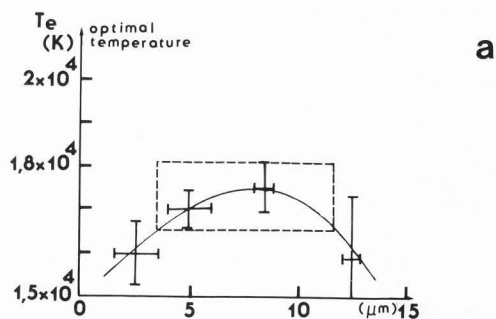


Figure 6a - Variation of the optimal plasma temperature for Zirconia deduced from the stoichiometric value of $\text{Zr} = 1$ and $\text{O} = 2$ versus laser erosion depth.

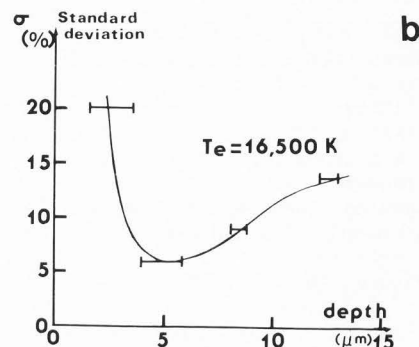


Figure 6b. Variation of the standard deviation for one value of temperature (16,500 K) versus laser erosion depth.

collected mass spectra recorded each second, by the LPMS allows the analysis of the composition of fluids extracted from the cavity before the salts precipitated into the cavity.

We cite some chemical analyses obtained for fluid inclusions enclosed in several different host-materials :

i) Fluorite (CaF_2 from Burc, Tarn (France) (see figure 7)

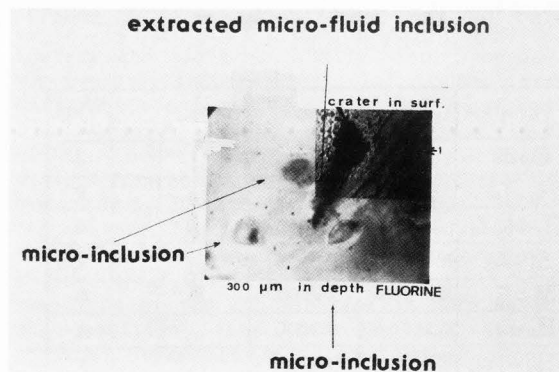


Figure 7. Photo of a laser crater and fluid inclusion cavities inside a fluorite sample.

10 μm
H

Geological applications of LTE model using LPMS

In 1981, Deloule and Eloy have determined the ratios Na/K from individual inclusions, assuming $(Na + K)/Cl = 1$ (see table 4). The results agree with the average values from chemical analysis of solutions prepared by crushing and washing parts of the same sample, reported by Deloule (1981) in the range 4.3 to 7.

Table 4. Analytical results of 3 fluid inclusions in a fluorite crystal MC 40 A and relevant electronic temperature T_e (K)

Inclusion n°	(Na/K)	T_e
3	6.85	43,900
4	5.02	29,100
5	6.25	27,600

ii) Quartz (SiO_2 from Calanda (Swiss Alps)). The ratio Na/K published by Poty et al. (1974), for the fluids was stated as spread between 5 and 20. The LPMS analysis gives two values for this ratio : 3.7 ± 2.4 and 2.4 ± 0.3 .

Quantitative analysis by LPMS in geological samples

Solid crystals

i) Dolomite. The dolomite crystals are known as being : $Ca Mg (CO_3)_2$ with the stoichiometric composition : C = 2, O = 6, Ca = 1, Mg = 1. But, Goldsmith and Graf (1958) showed from X-ray studies, the presence of overstructure depending on the atomic ratio Mg/Ca.

Three different samples of dolomite have been studied : 1) dolomite of a shabka (Cheid) in Tunisia (Deloule and Eloy, 1982) : mineral of triassic formation ($T : 200^\circ C$ and pressure 1-2 Kbar), 2) dolomite of Zag et Tir in Tunisia : mineral of Tunisian diapir with hydrothermal genesis (Perthuisot et al., 1978), 3) dolomite of Shaba (Zaire) : Roan serial of Shaba (sedimentary preconcentration minerals of uranium and classified as : grey "clay-talc" ores).

With the LPMS, the stoichiometric composition of the two dolomites from Tunisia was studied by applying the LTE model of correction (Saha-Eggert equation). The near vicinity of a fluid inclusion induces in the first sample (shabka, Tunisia) local differences in the Ca/Mg atomic ratio with regard to the expected stoichiometric composition (see table 5).

Recent studies of the second sample from Tunisia (Zag et Tir) support this observation as shown in figure 8. In a particular zone inside the crystal the ratio Ca/Mg varies from 0.5 to 4, whereas the average value determined by atomic absorption is 1.087.

ii) Zircon from Tamanrasset (Sahara). Last but not least, the LPMS technique has been applied to individual zircon grains,

Table 5. Application of the Saha corrections. Sample dolomite from a shabka (Tunisia), LPMS analysis

Ratio	$\frac{Ca}{Mg}$	O/C	$\frac{C}{Ca}$	$\frac{O}{Mg}$	$\frac{O}{Ca}$	$\frac{C}{Mg}$
expect.	1	3	2	6	6	2
exp.	4.7	2.6	0.054	0.65	0.14	0.25
corr.	1.4	2.9	1.8	7.3	5.2	2.5
accuracy	+40	-4	-11	+21	-14	+26
plate:	1443	expo:8	$T_e = 20000_K$ $N_e = 10^{19}/cm^3$			

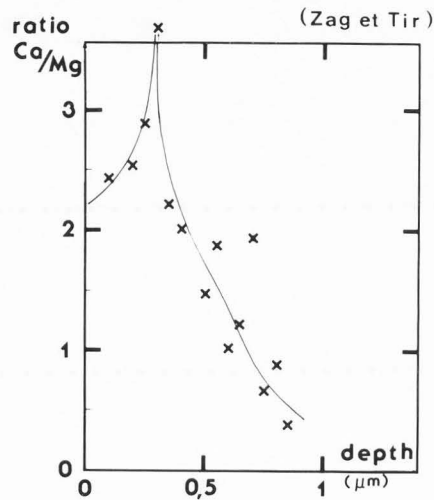


Figure 8. Variation of the Ca/Mg ratio inside a dolomite crystal (Zag et Tir, Tunisia).

40 to 80 μm in diameter (Eloy and Kosztolanyi, 1985, étude de la composition chimique des zircons du granite d'Anfeg (Algérie) à l'aide de méthodes micro-analytiques "Chemical composition study of Anfeg's granit zircons (Algeria) with the aid of microanalytical methods", *Bullet. Soc. Geol., France*, in press). For the first time, the stratigraphical variations of the main components, SiO_2 and ZrO_2 , in the external layers, have been demonstrated with a spatial resolution of 200 to 500 \AA (figure 9), allowing the impurity concentrations to be quantitatively evaluated for each spectrum (figure 10).

Among the new results, we note : 1) correlation between U and Hf (see figure 11), 2) concentration profile for the uranium in the external layer (figure 12) : this variation was expected but not previously observed by geologists.

Fluid inclusion studies. This is the most original application of this laser-ionization LTE model to geological analysis.

We studied three different host minerals : 1) quartz (of Calanda), 2) halite (of Keuper), 3) dolomite (of Shaba)

i) Quartz (Calanda). In the preliminary studies of fluid inclusions using the photoplate

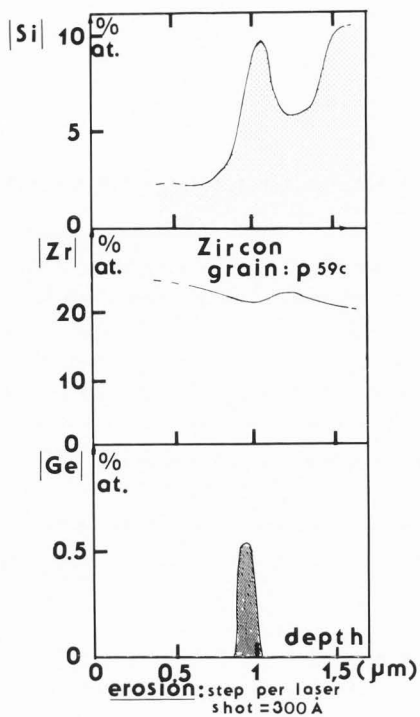


Figure 9. Stratigraphical variation of Si, Zr and Ge in the external layers of a zircon grain (Tamanrasset)

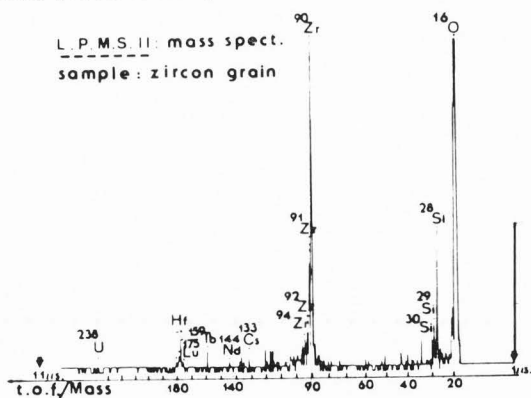


Figure 10. Example of an LPMS mass spectrum obtained with a zircon grain (Tamanrasset)

detection, the analytical informations from 5 to 10 shots were integrated on the same exposure (Deloule and Eloy, 1981a), (see figure 13) and unexplained differences were observed between the sampling times (related to the number of laser shots) of chemical species K^+ and Na^+ .

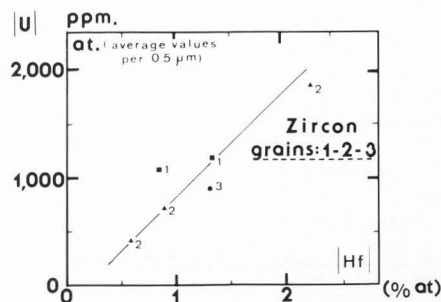


Figure 11. Correlation between uranium and hafnium concentrations in the external layers of a zircon grain (Tamanrasset)

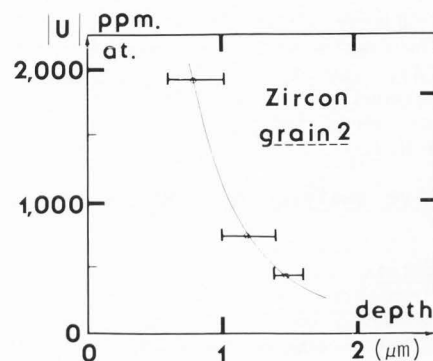


Figure 12. Concentration profile of uranium in the external layers of a zircon grain (Tamanrasset)

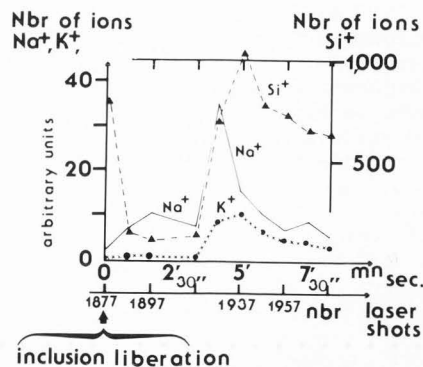


Figure 13. Different sampling times of the elements during the liberation of a fluid inclusion enclosed in Calanda quartz (result of LPMS I).

ii) Keuper halite (Cl Na) from Varangeville salt mine (France). This Keuper halite sample originated in a salt formation resulting from brine evaporation. The composition

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of the brine is given by Debessy et al. (1983) :

- Na = 109,558 mg/l
- K = 3,985 mg/l
- Ca = 480 mg/l
- Mg = 9,984 mg/l
- SO₄²⁻ = 14,590 mg/l

Using the LPMS II devices equipped with the "time of flight" (TOF) separation, mass spectra are recorded each second during the liberation of fluid inclusions and stored on line in a computer memory (5 Megabytes). In delayed time, the device allows us to study slowly and individually the mass spectra stored for each laser shot, examples of which are plotted in figure 14, and eventually to process the data by the ELOGET program.

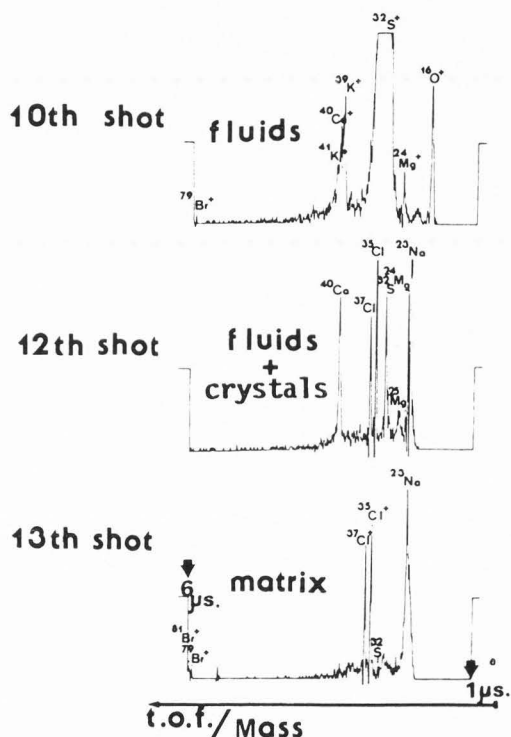


Figure 14. Three successive mass spectra recorded during the liberation of a fluid inclusion enclosed in Keuper halite (result of LPMS II)

For instance, the 10th mass spectrum shows a broad peak of ³²S⁺, characteristic of a high abundance of SO₄²⁻, but the lack of resolution forbids concentration calculations. Such calculations are possible on the following ones (12th and 13th), and the results are presented as an example of analytical treatment (table 6).

Indeed to calculate the corrected results of fluid analysis from electronic temperature and density on each laser plasma, it is

Table 6. Application of the Saha-Eggert correction. Sample : Keuper halite

Fluid inclusion : F.I. n°1					
N° of spectra	12		13		
Sampling phases	F.I.+residu. crystals		matrix+F.I. crystals		
Stoichiometric hypothesis	Σ cations = Σ anions		Σ cations = Σ anions		
Te (K) calculated	11,900		11,200		
log N _e (e/cm ⁻³)	17		17.5		
atomic relative concentration (% at.)	O	5.3	0.5	0.02	
	Na	41.6	16.1	7.1	42.1
	Mg	3.6	15.	19.2	1.5
	S	1.3	14.9	6.1	2.5
	Cl	47.2	37.8	10.2	46.2
	K	0.9	0.5	0.2	0.15
	Ca	0.1	15.1	57.3	5.
	Br				2.5
S/Ca	13.3	1		0.5	

necessary to introduce at least, a known stoichiometry for two elements.

Then different stoichiometric assumptions have to be studied.

In table 6, we present the results calculated for two possible stoichiometric hypotheses based on :

- host material : Cl Na : Cl = 1 and Na = 1
- or inclusion components : electric neutrality of salts i.e., Σ anions = Σ cations

The latter assumption (Σ cations = Σ anions) appears to be convenient to estimate the real elementary concentration (see table 6) comparison between the brine composition with respect to the corrected concentrations).

In the case sample, the main interest of LPMS apparatus is to detect simultaneously all elements involved in the halite inclusions.

Thus, we can also observe the accumulation of certain species, Ca and Br, in the wall of inclusions because of the high sampling rate of the laser.

Moreover, the treatment of this analysis of a micro-fluid inclusion shows the slight decrease of the values of estimated electronic temperature and density at the time of the liberation of aqueous fluid, (down to T = 11,000 K). It is the consequence of both strong enhancement of sampling volume induced by the fluid liberation and lack of laser ionization energy.

iii) In dolomite (Roan serial of shaba, Zaire) n° KB 48. The geological samples were studied by Audéoud (1982) as being sedimentary preconcentration minerals of uranium and classified as grey RAT "clay - talc ores" ("roches argilo-talqueuses" = RAT).

The fluid inclusions were previously studied by Raman MOLE microprobe and by thermometric optical microscopy. The trapping temperature and pressure of inclusions are respectively 350°C and 1.2 Kbars. These studies showed the accumulation of different chlorides

- CaCl_2 associated with fluids (H_2O and CO_2)
- likely with MgCl_2 , CaCO_3 , NaCl and KCl .

The LPMS mass spectra obtained on a fluid inclusion confirm the presence of sulphur salts and chlorides in the fluid. We present some elementary profiles versus erosion depth on figure 15 (the arrow indicates the mass-spectrum recorded simultaneously with the first deviation of vacuum gauge).

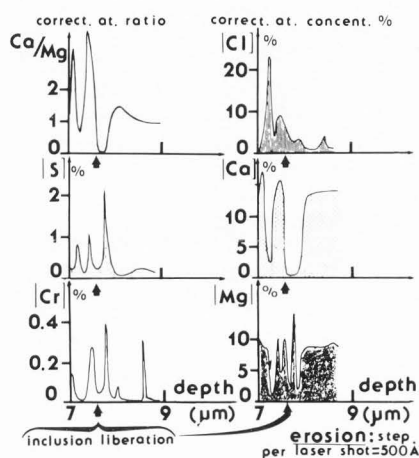


Figure 15. Elementary profiles versus erosion depth (dolomite crystal of Shaba, Zaire) in the case of Ca, Mg, Cl, S and Cr.

The LPMS results bring the following new information : 1) the presence of NaCl and KCl , is checked and their measured concentration, 2) Cr, Mn and Pare detected in the fluids, 3) the evolution of the Ca/Mg ratio in the vicinity of micro-inclusion walls as confirmed as previously detected with another dolomite sample (Zag et Tir).

The interpretation of the calculated atomic concentrations yields an estimate of the evolution of the molar fractions (see figure 16) of each expected salts.

Moreover this study permits one the following observations in the inclusion : 1) the most important salt is MgCl_2 , 2) the accumulation of CaCl_2 in the walls of the micro-inclusion.

We can verify the correlation between the appearance of H_2O and the position of the arrow indicating the first deviation of the vacuum gauge.

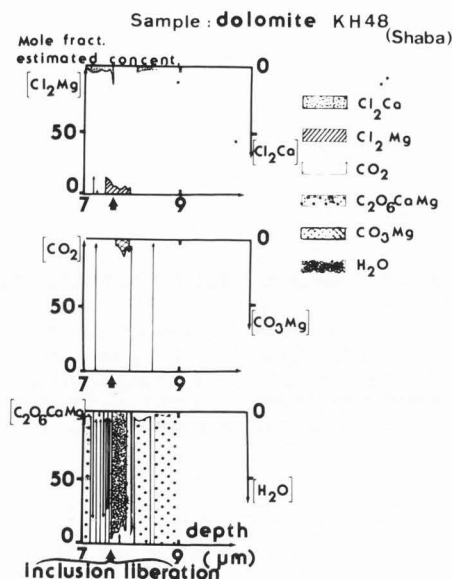


Figure 16. Estimated molar fraction for the expected salts enclosed the dolomite sample versus depth.

As a consequence of the observed drop in the electronic temperature of plasma simultaneously with the liberation of fluids, the ionization yields are reduced. For this reason, the usual thresholds of sensitivity obtained with the solids are not available. The fall of sensitivity is evaluated to a factor 10 for the same laser energy conditions as the solid samples.

In conclusion, if the increasing interest of geologists for LPMS is supported by the wide range of analytical applications, namely distribution of elements in microsamples and characterization of fluid inclusions, the features of this technique involve problems for quantification as presented in this paper.

Basically, the use of the Saha-Eggert equation to correct the experimental data, requires in the ion source plasma, a local thermal equilibrium which agrees with the theory of the laser solid interaction and in the calculations, the concentration ratio of two main elements. In practice, these conditions can be only partially fulfilled, due to heterogeneities in geological crystals, or to the time dependent analysis of fluid inclusions. So the versatile computer program (ELOGET) has to be used with care, particularly to separate the analytical information of the fluid inclusion from that of the cavity walls.

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Discussion with Reviewers

J.A. Minkin : How does LPMS differ from LAMMA ?

Authors : In a previous publication Chamel and Eloy (1983) presented a comparison between LAMMA and LPMS. To summarize, 1) the patented ion source of the LPMS was specifically designed for solid analysis with the laser absorption in reflexion mode, 2) LAMMA is a "classical time-of-flight" mass spectrometer whereas the LPMS is a magnetic mass spectrograph modified for "time-of-flight" detection, 3) the time duration of the laser-material interaction and vaporization phenomena are reduced by a factor of approximately 10 in the LPMS ion source with respect to the LAMMA system. The consequence of this is that at present the laser erosion of the LPMS alone allows a depth resolution of 500 Å in the study of stratigraphical profiles. It is the LPMS alone which applies as standard routine the LTE model of corrections to experimental results.

J.A. Minkin : Are there particular geological applications for which one instrument is more suitable than the other ?

Author : The LPMS alone can record and store each second, a mass spectrum to determine the relative concentration of matrix elements and more especially, it can record analytical information on the fluid inclusions and cavities.

J.A. Minkin : What is the minimum size of an inclusion which can be analyzed by LPMS ?

Author : The optimum sizes analyzed by the LPMS range between 1 to 20 µm in diameter.

J.A. Minkin : What is the minimum concentration of a given element which can be detected ?

Author : the minimum detected concentration is approximately on average :

- 10⁻¹⁷ g. in a solid sample

- 10⁻¹⁵ g. in a fluid inclusion

Reviewer 2 : The "status of the LTE model in the SIMS community is totally misrepresented. Please comment.

Author : To comment on such a development in the SIMS LTE Model is not within the scope of this paper (the LTE model application in laser probe mass spectrometry), so we have intentionally limited the discussion on the LTE Model but additional references are available in the paper.

Reviewer 2 : .. an independent observation or calculation or something concerning electron density and temperature of the plasma has to be presented.

Author : In this paper, it is impossible to describe and present a summary of the results obtained on all laser plasma temperature and density measurements. Tonon (1973) and Leising (1973) have offered numerous publications on this subject. Our work is the application of their experimental results.

Reviewer 2 : .. table 3 clearly shows that ion intensities are not directly representative of the chemical composition of the sample..

Author : We think that the reviewer has misunderstood the words "measured" and "calculated" because it is clearly evident that this work presents a correction method, based on the LTE model which obtains representative values by taking into account the experimental intensities and the ionization parameters. There does not exist any one physical reason why the measured and expected values are the same. Indeed these differences exist because the ionization and ion extraction yields strongly depend on partition functions and ionization potentials of each ionic species.

Reviewer 2 : A variation of Ca/Mg as a function of depth (figure 8) requires an extensive account because the solid solution range of dolomite is very limited in both directions toward calcite and magnesite and the observed variation is not permissible if this sample is dolomite.

Author : The variations of Ca/Mg presented were observed for the first example, near the cleavage plane of a dolomite crystal. For the second example the variations were measured during sampling in the vicinity of a fluid cavity. In such cases, we consider a very particular sample of a dolomite crystal and are able to explain this uncommonly observed variation of Ca/Mg ratios. The previous measurements of stoichiometric compositions (Deloule and Eloy, 1981a) have enabled us to ensure that the sample is not misrepresented after many laser shots.

Reviewer 2 : Figure 10 clearly shows that the observed intensities are not representative of the isotopic compositions of elements. For instance, $^{28}\text{Si}/^{29}\text{Si}$ does not look like 19.6. $^{90}\text{Zr}/^{91}\text{Zr}$ looks fairly different from what is expected from the natural abundances and so does $^{91}\text{Zr}/^{92}\text{Zr}$.

Author : Two authors have also observed the same effects with another laser microprobe (LAMMA) : see Simons', (1983/1984) Isotopic analysis with the laser microscope mass analyzer. Int. J. of Mass Spectrom. Ion Phys. 55, 15-30 ; and Denoyer et al. (1982). Simons

measured and explained this effect well, by a percentage of missing codes of analogue-digital converter (A/D converter) in the transient recorder Biomation which was used in the measurements. Indeed "a more significant source of error in the isotopic measurements results from the dynamic response of the A/D converter to a time-varying input signal" during the storage of the mass spectra recorded by the ion detector. "Missing codes occur when certain output code levels are never activated for input signals with high slew rates" (the consequence is a lack of bytes in the transient recorder. With the LPMS we use the same transient recorder and Simons' explanation is in accordance with the fact that the lack of line intensities appears more frequently after a high line intensity (a matrix line for example). A suitably calibrated curve of the detection signals takes into account this effect and introduces a corrective factor to convert the line intensities to number of ions.