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Communication présentée à : 2. International Congress on Nuclear Microprobes

Melbourne (AU)
5-9 Feb 1990

HYDROGEN STUDY IN MELT INCLUSIONS TRAPPED IN QUARTZ WITH NUCLEAR MICROPROBE

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ABSTRACT

Elastic recoil spectrometry induced by 3 MeV helium-4 microbeam has been used to determine hydrogen distribution within melt inclusions trapped in quartz. These minerals were selected from different geological environments : Guadeloupe (West Indies), Pantelleria Island (South Sicily - Italy) and San Pietro (South Sardinia - Italy). Bulk hydrogen contents are calculated (H assumed to be in H_2O form). The knowledge of hydrogen distribution assists both in a better understanding and in the establishment of volcanic dynamism hypotheses. Finally, fluid hydrogen rich inclusions are evidenced and H concentration profile is simulated and reported for the first time in glass inclusion.

1. INTRODUCTION

The knowledge of volatile behavior in magma during its ascent towards the surface is important because it gives informations about the processes by which magma tends to reach chemical and physical equilibrium with its environment before eruption. Morever, volatiles play an important role on triggering and governing the extent and the nature of eruptive processes. Because lavas loose most of their volatiles during eruption processes, analyses of trapped melt inclusions are a useful tool for understanding preeruptive physical and chemical conditions.

Numerous authors have demonstrated that magma trapped in crystallization lacks (melts inclusions) of lava minerals permits to measure volatile dissolved element contents in magma in pre-eruptive conditions. Water is the overcoming volatile component of acid magmas, its quantitative determination has been achieved just recently with ion micro-probe [1, 2, 3] and by IR spectrometry [4]. Not many values have been measured, they are all around H_2O 4 wt% : 1) Inyo Obsidian Dome : 4 ± 1 % [2] ; 2) Long Valley : 4.1 ± 1.2 % [2] ; 3) Taupo : 4.5 ± 0.8 % [3] ; 4) Pantelleria : 4.3 ± 0.2 % [1]. We choose to approach the water problem in acid magmas by the hydrogen quantity determination with the nuclear microprobe (DAM - Bruyères-le-Châtel - France), using the elastic recoil of protons [5, 6]. This method gave us promising results in a recent work [7]. Interactions between 3 MeV helium-4 microbeam and melt inclusion as target have been exploited. Recoil protons were detected in transmission geometry. The analyzed depth varies from 2 to 4 μm. Hydrogen has been assumed in H_2O form. In this paper, water contents are calculated in inclusions contained in pumice fall quartz crystals : peralkaline melts for Pantelleria, comenditics (San Pietro) and metaluminous rhyolites (Guadeloupe). The results are compared to those previously published for material of similar compositions. Some important remarks can be made and permit to strenghten the data already acquired on these materials. The method employed to quantify the hydrogen presence, particularly the simulation code, allows the study of the H distribution within a fluid inclusion.

2. BRIEF DESCRIPTION OF THE METHODOLOGY

2.1. Elastic recoil of protons in transmission geometry

The equations governing the energy of particles in elastic recoil of protons are fully described in the kinematic of elastic collision [8]. The interaction geometry is characterized by the relation between the scattering angle and the recoil angle according to the conservation principle of energy and impulsion [9].

For transmission geometry (figure 1), the energy of the recoil proton is maximum and a slow variation of θ around this position has a very slight influence on the recoil proton energy values.

When it is possible to prepare thin targets (Eo = 3 MeV ; thickness $\leqslant$ 30 μm), transmission is the more adequate geometry for our purposes. We reached 4 micrometers of analyzed depth in transmission mode instead of 0.4 micrometer in reflexion geometry [7]. More, the first geometry is supple and most of all, less caution is needed for the alignment of the sample surface with respect to the incident direction.

2.2. Interpretation of recoil spectrum and simulation code

The interpretation of recoil spectrum allows the hydrogen depth profiling. All the parameters required to induce in this step are largely described in recent papers [5, 6]. The absolute character of this method permits to study complex samples for which it is difficult to obtain a standard matrix. The relative quantities of the components of the target must be perfectly known.

The computer program "GABY" had to be used in order to automate the different processes (energy loss, energy spreading, algorithms and complex numerical treatment). The simulation code allows the experimental data to be interpreted. More details are available in these proceedings in J. TIRIRA and *al.* [10].

3. EXPERIMENTAL

3.1. The Bruyères-le-Châtel nuclear microprobe

All the measurements are achieved in the analysis chamber of the french AEC nuclear microprobe. The ^{4}He beam is delivered by a 4 MV VAN DE GRAAFF accelerator. The beam line is equipped with an adjustable object aperture and a magnetic quadruplet (Harwell system) [11]. The vacuum is maintained around 2 x 10^{-6} torr using a turbomolecular pump so that surface contamination of the samples can be reduced. The analyzed area is not bigger than the incident beam spot size (100 μm^2 typically) and the current is between 0.5-0.7 nA.

A current chopper placed just before the quadrupoles and a faraday cup mounted in the analysis chamber allow the number of incident helium ions to be monitored.

In the case of transmission geometry, the recoil protons - at 0° angle detection - are recorded with a surface barrier detector (200 mm^2, 100 μm) covered by a 2 mm collimator.

The distance between the focussing plane and the detector is 93 mm and the solid angle $\Delta\Omega$ depends on the beam spot size (for 20 μm, $\Delta\Omega$ = 1.45 ± 0.02 x 10^{-3} sr). The incident ^{4}He energy is fixed to 3 MeV.

3.2. Target preparation and sampling

Target preparation

The melt inclusion size is typically between 50 and 300 μm with (see figure 2).

A piece of each mineral containing glassy inclusions was isolated from the rocks. A section of 100 μm thickness was thinned down to about 25 μm by Al_2O_3 polishing, then stuck on a hole (ϕ : 500 μm) in the center of the target holder. The melt inclusions were obviously placed on this hole to make possible the transmission observation.

A 100 ± 10 nm gold layer was deposited on the surface sample to enhance the thermal and electric charge transport. The figure 3 a.b shows the damages observed on San Pietro and Pantelleria glasses, when the surface has not been prepared with a sufficient gold layer (70 nm). In this case, the helium microbeam current intensity was fixed at 2 nA.

We note that the damages are less important on Pantelleria inclusion (less hydrated than San Pietro glass) for similar conditions.

Sampling

Three volcanic glasses trapped only in quartz crystal of pumice falls were selected according to their composition and their geological context. We choose quenched material like pumice falls to avoid post entrapment crystallization on the walls of the cavity, that can occur during slow cooling (for instance in lava flow) and to avoid post entrapment exsolved vapour giving low hydrogen contents for inclusion residual melt. All inclusions are single phase (only glass), at room temperature, without any gaz bubble.

Montagna Grande (Pantelleria, 9000-15000 years old) [12] and San Pietro (Sardinia, 14 million years) are peralkaline glasses. Montagna grande is a typical pantellerite glass characterized by low aluminium, high iron and alkali ($\Sigma Na_2O + K_2O > 10$ wt%) contents. San Pietro is comenditic in composition with moderate iron, high aluminium and alkali ($\Sigma Na_2O + K_2O > 8,8$ wt%) contents [13]. These rocks are located in distension zone. Usually peralkaline rocks are dry or low hydrated melts [14]. The first data on water contents in Pantelleria lavas are recent [1], the H quantity determination has never been achieved up to now on the other materials.

Quartz melt inclusions from Guadeloupe (West Indies, 250000 years old) come from a calcalkaline suite of a subduction zone [15]. A systematic study of Guadeloupe glassy inclusions from different pumice level minerals exhibits crystallization temperatures between 950 and 810°C, and minimum P_{H_2O} between 1.8 and 2.5 Kb [16]. All the inclusions from the above formations have been studied thermometrically with heating stage technique. The appearance of shrinkage bubble before the $\alpha \dashrightarrow \beta$ quartz transition, then the homogenization of cavities filling up between 750° and 820° fit well with the behaviour of an high alkali and hydrated melt. The heating stage nu. reversibility, the unchanged glass composition before and after the thermal treatment, as well as after a longtime (3 days to 1 week at 750°C) proves the host mineral tightness.

A semi quantitative estimation of volatile element contents (essentially H_2O) is given by the deficit of oxide sum, analyzed with electron microprobe. The analyses (table 1) have been carried at 15 KV, 10 nA with a defocusing probe (ϕ : 15-20 μm). Sodium and silicium are firstly analyzed acid to minimize the Na migration.

The analyses have been controlled with two acid glass standard. For each inclusion, the number of analyzed points is superior to 10. The homogeneity has been tested on several inclusions. We note (table 1) that the deficits vary from 3.7 wt% to 8.8 wt%.

Table 1 : Composition of the glasses (wt%) trapped in quartz of three different origins. Electron microprobe analysis : CAMEBAX*
* Centre d'Analyses CAMPARIS - Université Pierre et Marie Curie - Paris (France)

	Montagna Grande (Pantelleria) (14 points)	San Pietro (Sardinia) (9 points)	Guadeloupe (West Indies) (17 points)
SiO_2	68.94 ± 0.82	70.65 ± 1.36	71.73 ± 1.09
TiO_2	0.34 ± 0.06	0.12 ± 0.10	d.l.
Al_2O_3	7.42 ± 0.20	10.00 ± 0.27	11.56 ± 0.14
FeO	7.33 ± 0.27	2.78 ± 0.32	1.07 ± 0.19
MnO	0.28 ± 0.08	d.l.	d.l.
MgO	0.05 ± 0.02	0.06 ± 0.02	d.l.
CaO	0.33 ± 0.06	d.l.	0.79 ± 0.13
Na_2O	6.42 ± 0.27	4.66 ± 0.22	3.14 ± 0.17
K_2O	4.22 ± 0.09	4.17 ± 0.20	3.18 ± 0.2
Cl	0.89 ± 0.07	0.45 ± 0.03	0.25 ± 0.06
S	0.04 ± 0.01	d.l.	d.l.
Total	96.26	92.83	91.68
Deficit	3.74	7.17	8.32
Th°C (Crystallization)	748°C [17]	780°C [16]	820°C [13]

d.l. : detection limit

4. RESULTS AND DISCUSSION

4.1. Melt inclusions

The table 2 gives the main results calculated on the three volcanic glasses, when the hydrogen distribution seems relatively homogeneous as the example of figure 4.

Table 2 : Atomic hydrogen density, water contents and analyzed depth in Pantelleria, San Pietro and Guadeloupe inclusions by elastic recoil of protons

Origin	Atomic H content (x 10^{22} atoms/cm^3)	Water content (wt%)	Analyzed depth (μm)	Number of analyzed points
Montagna Grande (Pantelleria)	Inclusion 1			
	0.85 ± 0.08	5.1 ± 0.5	1.7	2
	0.57 ± 0.05	3.4 ± 0.3	1.5	
	Inclusion 2			
	0.66 ± 0.06	4.1 ± 0.4	3.7	6
	0.69 ± 0.06	4.2 ± 0.4	3.4	
	0.71 ± 0.06	4.3 ± 0.4	3.4	
	0.73 ± 0.07	4.4 ± 0.4	3.4	
	0.69 ± 0.06	4.1 ± 0.4	3.4	
	0.73 ± 0.07	4.4 ± 0.4	3.4	
	Inclusion 3			
	0.73 ± 0.07	4.4 ± 0.4	2.3	3
	0.73 ± 0.07	4.4 ± 0.4	2.3	
	0.61 ± 0.06	4.1 ± 0.4	2.3	
Average (n = 11)	0.73 ± 0.13	4.3 ± 0.8		
San Pietro	Inclusion 1			
	1.04 ± 0.09	6.2 ± 0.6	3.0	2
	1.15 ± 0.10	6.9 ± 0.6	2.7	
	Inclusion 2			
	1.24 ± 0.11	7.4 ± 0.7	2.3	2
	1.52 ± 0.13	9.1 ± 0.8	2.3	
Average (n = 4)	1.23 ± 0.21	7.4 ± 1.2		
Guadeloupe	Inclusion 1			
	1.41 ± 0.13	8.8 ± 0.8	1.9	2
	1.45 ± 0.13	9.0 ± 0.8	1.8	
	Inclusion 2			
	1.89 ± 0.17	11.8 ± 0.9	1.8	
	Inclusion 3			
	1.60 ± 0.14	10.0 ± 0.9	2.3	
	Inclusion 4			
	1.48 ± 0.13	9.2 ± 0.8	2.3	
	Inclusion 5			
	1.28 ± 0.12	8.0 ± 0.7	1.4	2
	1.31 ± 0.12	8.2 ± 0.7	1.4	
	Inclusion 6			
	1.31 ± 0.12	8.2 ± 0.7	3.75	3
	1.86 ± 0.17	11.6 ± 1.04	4.05	
	1.47 ± 0.13	9.2 ± 0.8	3.75	
Average (n = 10)	1.51 ± 0.21	9.4 ± 1.3		

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FIGURE CAPTIONS

Fig. 1. : Elastic recoil detection in transmis: ion mode

Fig. 2. : Melt inclusions trapped in quartz

Fig. 3.a : Scanning electron microscopy of helium-4 microbeam damages on Pantelleria glass inclusion

1 : glass
2 : beam impact

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Fig. 3.b : Scanning electron microscopy of helium-4 microbeam damages on San Pietro glass inclusion

1 : glass
2 : beam impact

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Fig. 4 : Elastic recoil detection on San Pietro glass inclusion in transmission geometry (solid curve : simulated spectrum ; dots : experimental spectrum ; Eo : 3 MeV ; i : 0,8 nA ; beam diameter : 20 μm ; t : 1800 s)

Fig. 5.a : Evidence for fluid hydrogen rich inclusion in glass (Eo : 3 MeV ; i : 0,7 nA ; beam diameter : 30 μm ; t : 1800 s)

Fig. 5.b : Hydrogen atomic density profile derived from the spectrum fig. 5.a

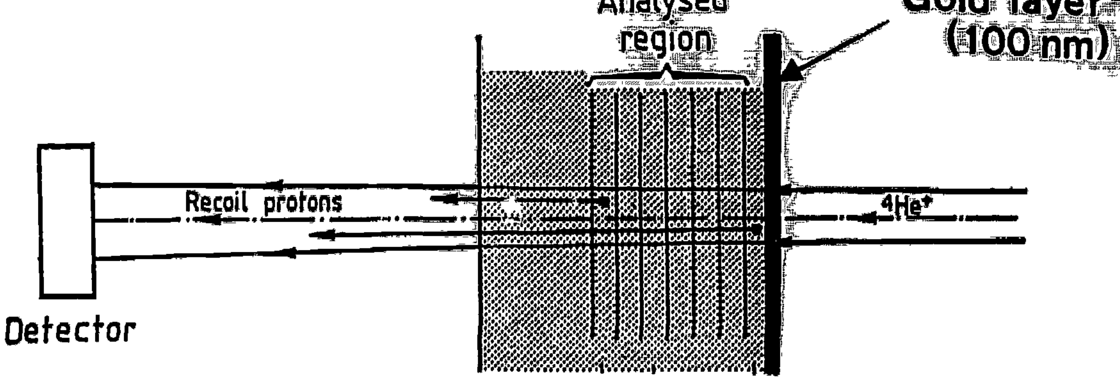

Fig. 1. : Elastic recoil detection in transmission mode

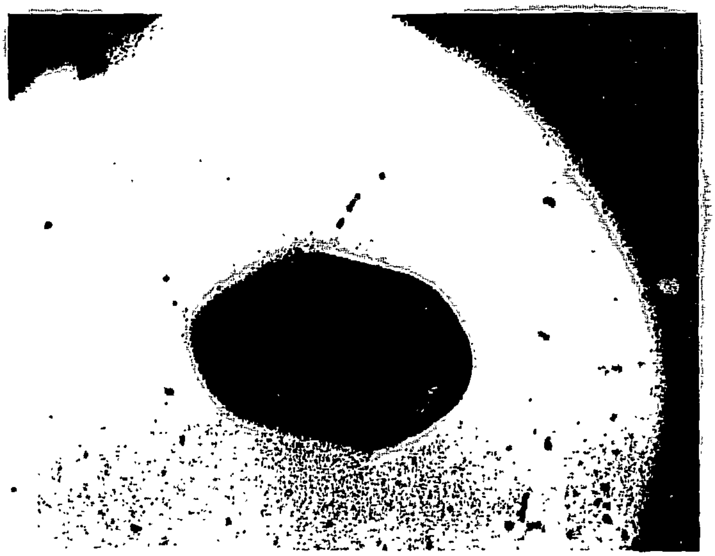

Fig. 2. : Melt inclusions trapped in quartz

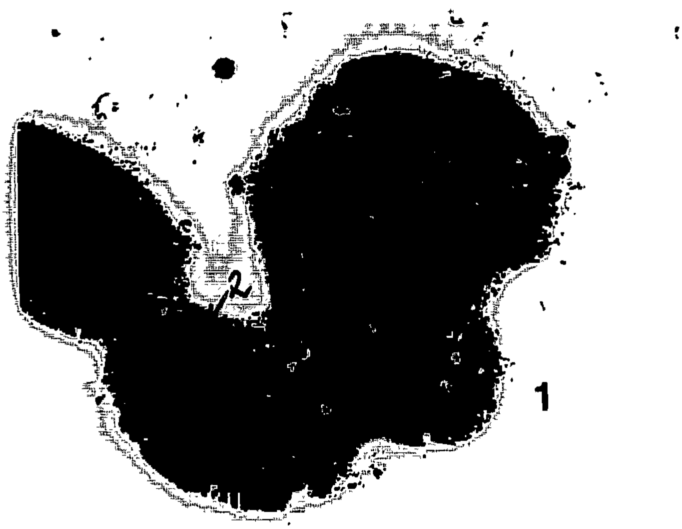

Fig. 3.a : Scanning electron microscopy of helium-4 microbeam damages on Pantelleria glass inclusion

1 : glass
2 : beam impact

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Fig. 3.b : Scanning electron microscopy of helium-4 microbeam damages on San Pietro glass inclusion

1 : glass
2 : beam impact

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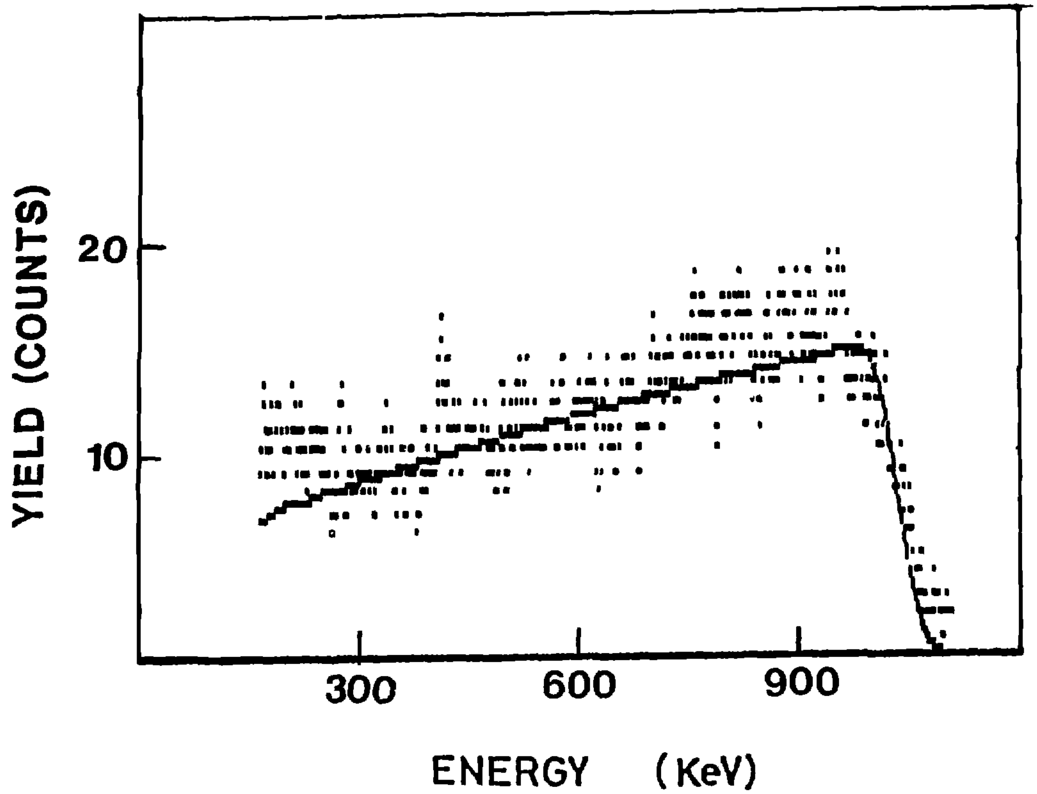

Fig. 4 : Elastic recoil detection on San Pietro glass inclusion in transmission geometry (solid curve : simulated spectrum ; dots : experimental spectrum ; Eo : 3 MeV ; i : 0,8 nA ; beam diameter : 20 μm ; t : 1800 s)

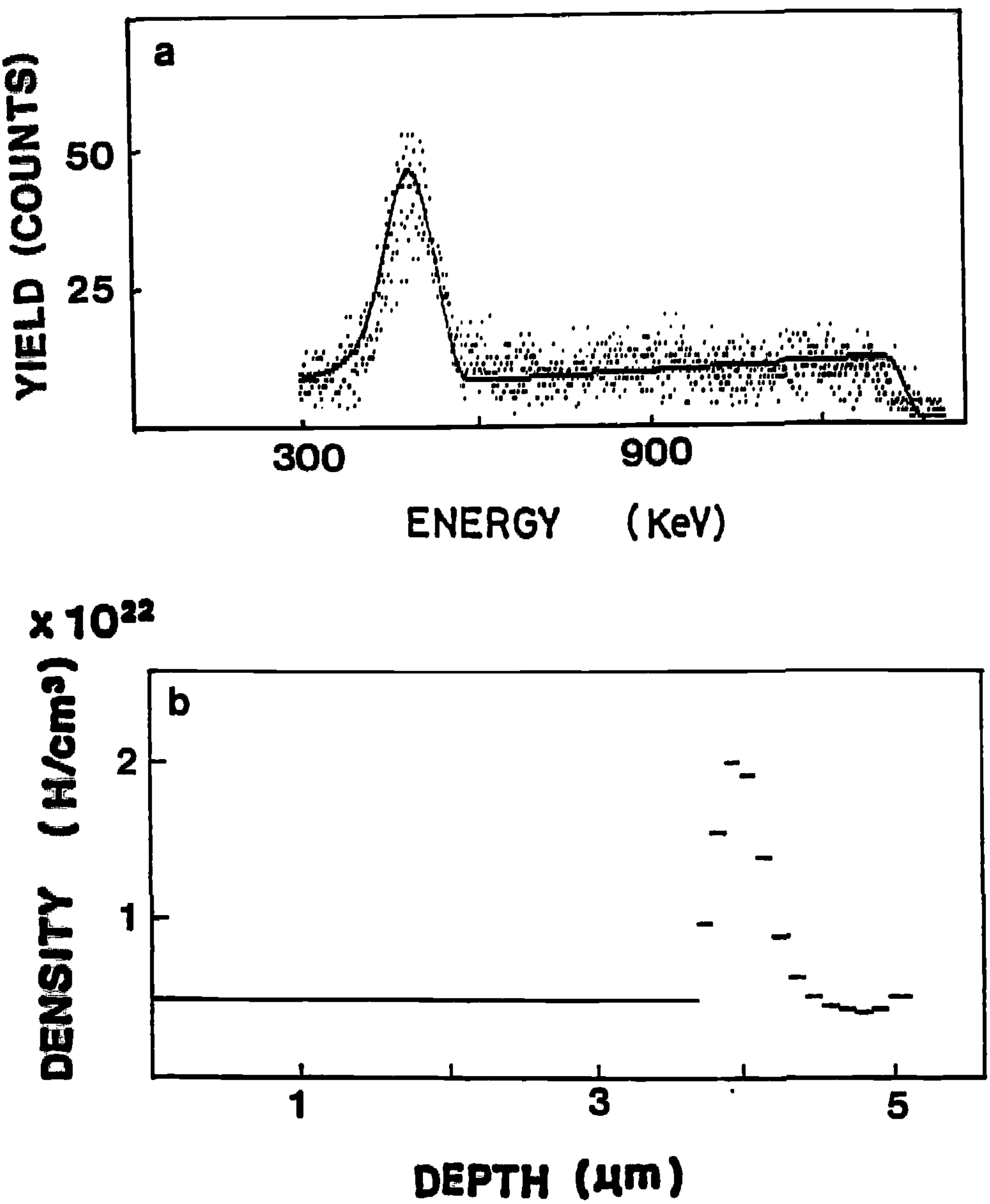

Fig. 5.a : Evidence for fluid hydrogen rich inclusion in glass (Eo : 3 MeV ; i : 0,7 nA ; beam diameter : 30 µm ; t : 1800 s)

Fig. 5.b : Hydrogen atomic density profile derived from the spectrum fig. 5.a

Pantelleria

The calculated water contents obtained with the inclusions of Montagna Grande quartz agree perfectly with those previously published in Kovalenko et *al.* [1] (H_2O : 4.3 ± 0.2 %, this work : 4.3 ± 0.8 %). The hydrogen distribution is homogeneous within a same inclusion (6 analyses in different points for inclusion 2 - table 2) and between several inclusions (inclusions 1, 2, 3). The hydrated character of the pantelleritic magma [1] is perfectly confirmed. This last character plus the alkali and chlorine richness explain the crystallization temperature (T = 750°C) relatively low for this type of magma [17].

San Pietro

We observed important degradations under the helium-4 microbeam on this material (figure 3.b). Two melt inclusions were analyzed in good conditions (without any damage - SEM observation). We measured high water content (7.4 ± 1.2 % - table 2), up to now never reported in peralkaline magmas. These values fit well with the estimated deficit (7.17 % - table 1) by electron microprobe and with low crystallization temperature (780°C - table 1). However, the number of analyzed inclusions is insufficient to conclude to an homogeneity in this material.

Guadeloupe

Pumice quartz are in keeping with a subduction context where the high H_2O pressure influence is emphasized [16] by the presence in the pumices of hydrated minerals like micas and amphiboles. Ten analyses have been made on 6 inclusions, H_2O contents vary from 8.2 % to 11.8 %, with an average of 9.41 ± 1.3 % (table 2). This value is relatively close to the electron microanalysis deficit. A 30 % variation has been obtained within an inclusion (inclusion 6), if the artefact hypothesis can be excluded, we can conclude to an hydrogen heterogeneous distribution in the inclusion. This point of view must be verified. However, if we take account of the lower values (around $H_20 \approx 8$ %), we observe that they are higher than those previously published by american authors [1, 3] by means of ion microprobe ($H_20 \approx 4$ to 5 %),from material of different origin but with a neighbouring composition.

4.2. Fluid inclusion

Figure 5.a shows recoil spectrum from a Montagna Grande (Pantelleria) glass, induced by 3 MeV $^4He^+$ microbeam. One clearly sees that there are two different regions in the spectrum, the first one fat in the high energy range, the second one with one peak in a lower energy range. The corresponding hydrogen atomic density profile, derived from the spectrum is presented in figure 5.b. This profile exhibits a single high concentration

peak located at below 3.9 μm the surface, with a 0.3 μm width. The average hydrogen concentration in the first region is about times 5 lower than in the second region.

The high hydrogen content in the Pantelleria glass proves the presence of fluid inclusion. Finally, the study had to be carried out as part of the analyse of the fluid inclusions and will be extended so that these results can be further interpreted.

5. CONCLUSION

In this work, we study hydrogen content in different melt inclusions. The hydrated character of the pantelleritic magma is confirmed. In San Pietro and Guadeloupe glasses, we measured high water content, these results agree well with estimated value (thermometric studies and electron microprobe analysis), and they were unknown up the now.

The hydrogen profile in fluid inclusion is shown. This determination has been carried out without any modification or element volatilization of the inclusion.

The hydrogen study has to be extended with more inclusion analyses so that these results can assist on the establishment of physical and chemical pre-eruptive conditions.

ACKNOWLEDGEMENTS

The authors are indebted the Christian MOREL and Jean-Claude MARIANI (DAM-SPTN - BRUYERES-LE-CHATEL) for providing stable helium-4 microbeam, to Patrick TROCELLIER for its assistance, to Michelle HALOCHE for her collaboration.