

THE INDIVIDUAL ANALYSIS OF FLUID INCLUSIONS IN MINERALS USING LASER ABLATION INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (LA-ICP-MS): AN EVALUATION

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(7 figures, 5 tables)

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ABSTRACT. During the last decade, the possible application of laser ablation inductively coupled plasma – mass spectrometry (LA-ICP-MS) as a quantitative technique for the analysis of individual fluid inclusions has been intensely studied. The quantitative ability of this technique is, however, complicated by several fractionation processes that operate during ablation, transport and analysis in the ICP-MS. In the present study, a number of these fractionation effects were studied and the quantitative ability of LA-ICP-MS analysis of fluid inclusions in natural quartz is evaluated. Using NIST SRM 612 and 614 as reference materials, it is shown that the fractionation during transport is minimised when the sample cell is flushed with He, in contrast with the set-up where Ar is used. Calcium has been successfully applied as an internal standard to calibrate the REE in NIST-glasses. The use of Ca to calibrate other lithophile and chalcophile elements, such as K, Zn, Cu and Pb, can however be questioned. It is shown that the technique is capable of semi-quantitatively characterising different fluid inclusion populations in natural quartz, which demonstrates its importance as a tool for palaeofluidflow modelling. However, during LA-ICP-MS analysis of fluid inclusions in natural quartz, elements are reprecipitated in a glassy phase, as shown by SEM-EDX analysis of the sample surface after ablation. This process could result in a fractionation and may account for the poor precision of the analysis.

KEYWORDS: LA-ICP-MS analysis, fluid inclusions, fractionation, SEM-EDX analysis

1. Introduction

Fluids play a major role in many geological processes. Their role may be physical, e.g. when they influence stress fields and heat fluxes, or chemical when they supply and drain components for mineral growth, dissolution or transformation. During the growth of a mineral, part of the fluid can be trapped as primary fluid inclusions in the crystals. Such an inclusion generally has a volume as small as 10^{-15}m^3 and can be filled with complex mixtures of solid, liquid or gaseous phases of variable composition (Roedder, 1984). They represent direct evidence of the fluids that were once present in the Earth's crust.

As analytical ability increased in time, more than 35 methods for the semi-quantitative or quantitative analysis of fluid inclusions have been proposed or tested (e.g. Shepherd & Rankin, 1998). Bulk analytical methods commonly involve the analysis of solutes released by crushing or decrepitation (destructive techniques). This may only give valuable information if a single generation of relatively homogeneous fluid inclusions is present (e.g. Banks *et al.*, 1991; Heijlen *et al.*, 2001). In most cases, however, the presence of different fluid in-

clusion generations or types does not allow a valuable interpretation. Non-destructive methods for the analysis of individual fluid inclusions, such as proton-induced X-ray or gamma-ray emission (PIXE and PIGE) and synchrotron X-ray fluorescence microanalysis (SXFMA), have been developed during the last decade (Anderson *et al.*, 1989; Heinrich *et al.*, 1992; Mavrogenes *et al.* 1995). However, these methods, which include extremely complex and expensive instruments, need complicated corrections for fluorescence absorption when fluid inclusions are located well below the sample surface. The combination of the high spatial resolution of a laser beam for sampling and the high sensitivity of an inductively coupled plasma mass spectrometer (ICP-MS) for elemental analysis, as first proposed by Gray (1985) has major advantages due to the simultaneous, multi-element analysis of individual fluid inclusions at relatively low cost. Several successful, quantitative analyses of inclusions in various host minerals have been published during the last years (Moissette *et al.*, 1996; McCandless *et al.*, 1997; Audétat *et al.*, 1998; Günther *et al.*, 1998; Shepherd *et al.*, 1998; Schäfer *et al.*, 1999).

Elemental analysis of sample released by laser ablation with ICP-MS does not give direct concentrations because of the variable amount of matter entrained in the ICP-MS. Therefore, measured signals of the elements of interest are ratioed against an element present in a known concentration (internal standard). This internal standard should have similar ablation characteristics and, ideally, a comparable atomic mass as the elements being determined. In solid sampling, however, the choice of an internal standard is limited by its natural occurrence in the sample. Often, a major element is chosen in order to minimise the counting error. The intensity ratios of the elements of interest to the internal standard are calibrated to obtain response ratios (counts per second/ppm) using an external standard where the elements are present in known concentrations. Commercially available NIST-glasses are frequently used for this purpose although also liquids, pressed pellets and Li B O -glasses have been evaluated for their applicability as external standard (Perkins *et al.*, 1991; Pearce *et al.*, 1992; Günther *et al.*, 1997; Odegard & Hamester, 1997). In most published LA-ICP-MS analyses of minerals and fluid inclusions, only one external calibration standard, containing all elements of interest, is used. The assumption of a linear response over an often large concentration range is made as well as of similar response ratios for external standard and the sample. However, it has been shown that fractionation can occur during sample ablation (Fryer *et al.*, 1995; Jeffries *et al.*, 1996; Longrich *et al.*, 1996; Chen, 1999) and during transport of the ablated material (Thompson *et al.*, 1990; Chenery *et al.*, 1992; Outridge *et al.*, 1996, 1997). Moreover, the composition of the matrix influences the plasma conditions and thus also the ionisation of the elements in the plasma (Chan *et al.*, 2000). Therefore, in this study, experiments were set up to check for:

- (a) the effect of fractionation during transport,
- (b) the influence of the atmosphere in the ablation chamber by using Ar- and He-carrier gasses,
- (c) the linearity in response, using 2 standard glasses with a similar matrix (NIST612 and NIST614).

In these experiments, Ca was used as an internal standard because of its possible use for the standardisation of fluid inclusion signals. Then, the quantitative analysis of fluid inclusions in quartz was evaluated with the instrumentation and the calibration strategy outlined above. Because of its

transparency, chemical simplicity and natural abundance, quartz is the preferred host mineral for fluid inclusion studies (Roedder, 1984). This paper aims to give an overview of the analytical capability of the technique as well as of the practical problems and limitations that may arise during LA-ICP-MS analysis of fluid inclusions in natural quartz.

2. Methodology

2.1. Laser ablation unit

In the earliest stages of the development of laser ablation for analysing solid samples by ICP-MS, a ruby and a Nd:YAG laser operating at their fundamental wavelength of 694 and 1064nm, respectively, were used (Gray, 1985; Arrowsmith, 1987). During the early nineties, the frequency-quadrupled Nd:YAG laser ($\lambda = 266\text{nm}$) was favoured, because of the more efficient absorption by most minerals and the higher spatial resolution that can be obtained using UV-radiation. In this study a commercial LSX200 Laser Ablation System (Cetac Technologies, Inc.) was used. The LSX200 comprises a frequency-quadrupled Nd:YAG laser, an ablation cell mounted on a motorised, software controlled stage and a binocular microscope or CCD-camera to view the sample. The output laser beam has a homogeneous energy distribution, i.e. the so-called 'flat topped beam profile'. It is capable of delivering a maximal pulse energy of 5 mJ on the sample (<6ns pulse duration) at a repetition rate, which can be varied between 1 and 20 Hz. The spotsize can be chosen between 10 and 300 μm .

The sample is placed in an ablation cell, which is flushed with an inert carrier gas. The adaptable sample cell has a maximal volume of $\sim 100\text{ cm}^3$. The ablated material is transported through tygon tubing and a number of valves to the mixing device, or directly to the plasma torch (Fig. 1). When He was used as the carrier gas, it was mixed in the mixing device with a flow of Ar before the ablated material was transported to the plasma. If only Ar was used in the experiments, the mixing device was removed from the flow path. The laser parameters used are given in Table 1.

ICP-MS (HP4500)	Measurements on NIST612/NIST614		Fluid inclusion analysis	
	Ar-only	He-Ar	He-Ar	He-Ar
carrier gas flow (l/min)	Ar 1.35	1.1	1.1	1.1
auxiliary gas flow (l/min)	He -	0.4	0.4	0.4
plasma gas flow (l/min)			1.0	
RF-power (W)			14.9	
mass resolution (AMU)		~0.7	1300	~0.3
analysis method		Spectrum Analysis		Time Resolved Analysis
measured isotopes		${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{25}\text{Mg}$, ${}^{27}\text{Al}$, ${}^{39}\text{K}$, ${}^{42}\text{Ca}$, ${}^{55}\text{Mn}$, ${}^{57}\text{Fe}$, ${}^{62}\text{Ni}$, ${}^{65}\text{Cu}$, ${}^{66}\text{Zn}$, ${}^{88}\text{Sr}$, ${}^{89}\text{Y}$, ${}^{93}\text{Nb}$, ${}^{140}\text{Ce}$, ${}^{146}\text{Nd}$, ${}^{147}\text{Sm}$, ${}^{153}\text{Eu}$, ${}^{165}\text{Ho}$, ${}^{169}\text{Tm}$, ${}^{175}\text{Lu}$, ${}^{208}\text{Pb}$		${}^7\text{Li}$, ${}^{23}\text{Na}$, ${}^{25}\text{Mg}$, ${}^{27}\text{Al}$, ${}^{39}\text{K}$, ${}^{42}\text{Ca}$, ${}^{55}\text{Mn}$, ${}^{57}\text{Fe}$, ${}^{62}\text{Ni}$, ${}^{65}\text{Cu}$, ${}^{66}\text{Zn}$, ${}^{85}\text{Rb}$, ${}^{88}\text{Sr}$
number of points per peak		3		1
dwell time (ms)		1		30
repetitions		10		
LASER (Cetac LSX200)		Single Line Scan	Single Line Scan	Fluid inclusions Single Point
wavelength (nm)			266	
pulse duration (ns)			<6	
repetition rate (Hz)			5	
output energy (mJ)		5		1-5
spot size (μm)		300		100
scan speed ($\mu\text{m/s}$)		10		-

Table 1. Experimental conditions of the laser ablation unit and the ICP-MS.

2.2. ICP-MS

The LSX200 was used in combination with a Hewlett Packard 4500 ICP-MS. This instrument has a typical sensitivity of ~25000 cps/ppm for Li and Tl and ~35000 cps/ppm for Y and Rh when analysing solutions. For the same type of analysis, the detection limits are <1ng/l for most elements. The sensitivity using laser ablation sample introduction was optimised by ablating a NIST612 glass where ^{59}Co , ^{139}La and ^{232}Th were monitored. The ^{248}Th to ^{232}Th ratio was < 1%. The tune parameters used are summarised in Table 1.

2.3. Calibration and external standards

If the response ratios are identical for analysis of the sample and the standard material, the concentration of an element can be calculated using the following equation (Ludden *et al.*, 1995):

$$(C_X)_{\text{sample}} = (C_{\text{IS}})_{\text{sample}} \cdot \frac{\{I_X/I_{\text{IS}}\}_{\text{sample}} \cdot (C_X)_{\text{standard}}}{\{I_X/I_{\text{IS}}\}_{\text{standard}} \cdot (C_{\text{IS}})_{\text{standard}}}$$

where I are the measured intensities of analytes in the sample and the external standard, C is the concentration and the indices X and IS refer to, respectively, the elements of interest and the internal standard. The NIST612 and NIST614 reference materials consist of a glass matrix with a nominal concentration of 72 wt% SiO_2 , 14

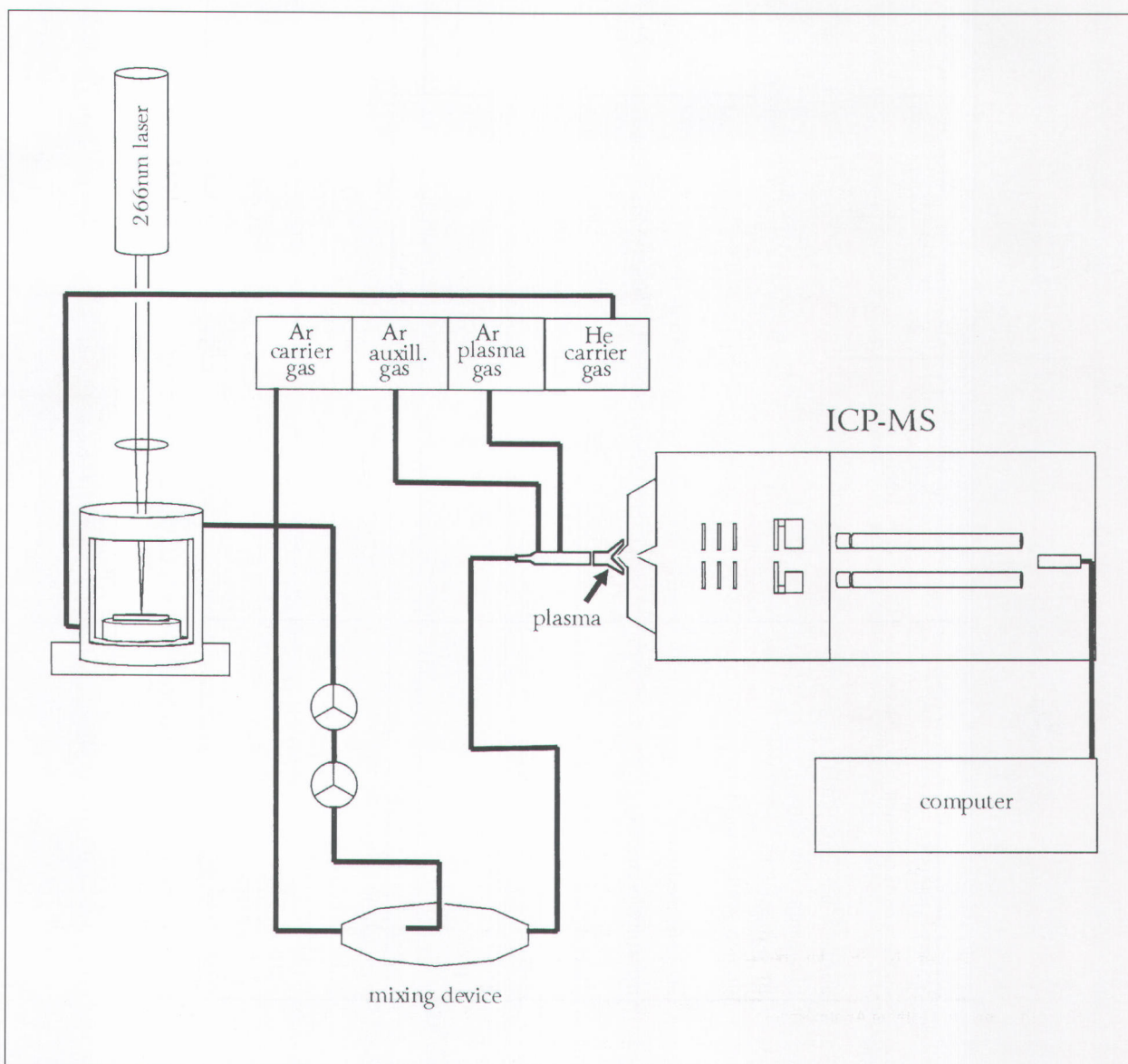


Figure 1. Schematic view of the instrumental set-up for ablation in Ar- and He-atmosphere.

wt% Na₂O, 12 wt% CaO and 2 wt% MgO. 61 elements are added at nominal concentrations of 50 and 1 ppm, respectively. Only the concentration of 8 elements is certified in these glasses (Ag, Sr, Th, Pb, Rb, U and Fe, Ni or Cu, K for the NIST612 or 614, respectively). The NIST612 glass was analysed for its major and minor element content by a large number of analytical techniques at various research institutions. A summary of all published data is given in Pearce *et al.* (1997). These authors give 'preferred concentration values' for 57 trace elements in the glass. The NIST614 glass is, however, much less studied. Analyses using solution ICP-MS were reported by Hollocher & Ruiz (1995) and Lahaye *et al.* (1997), Secondary Ion Mass Spectrometry (SIMS) by Horn *et al.* (1997) and LA-ICP-MS by Norman *et al.* (1996), Horn *et al.* (1997) and Lahaye *et al.* (1997).

3. Results and interpretations

3.1. Fractionation during transport

Studies by Thompson *et al.* (1992) and Outridge *et al.* (1996, 1997) showed that fractionation could occur during transport of the ablated material to the plasma, through a selective loss of particles enriched in some elements. In the Cetac LSX200 laser ablation unit, the ablated material is transported by the carrier gas through 2 valves and then to the ICP-MS (Fig. 1). This circuit involves an increase of the tube length of 0.5m, compared to a set-up where the material is transported from the ablation chamber directly to the mixing device or to the plasma (depending on the carrier gas). Moreover, it can be expected that most material loss occurs during the complex pas-

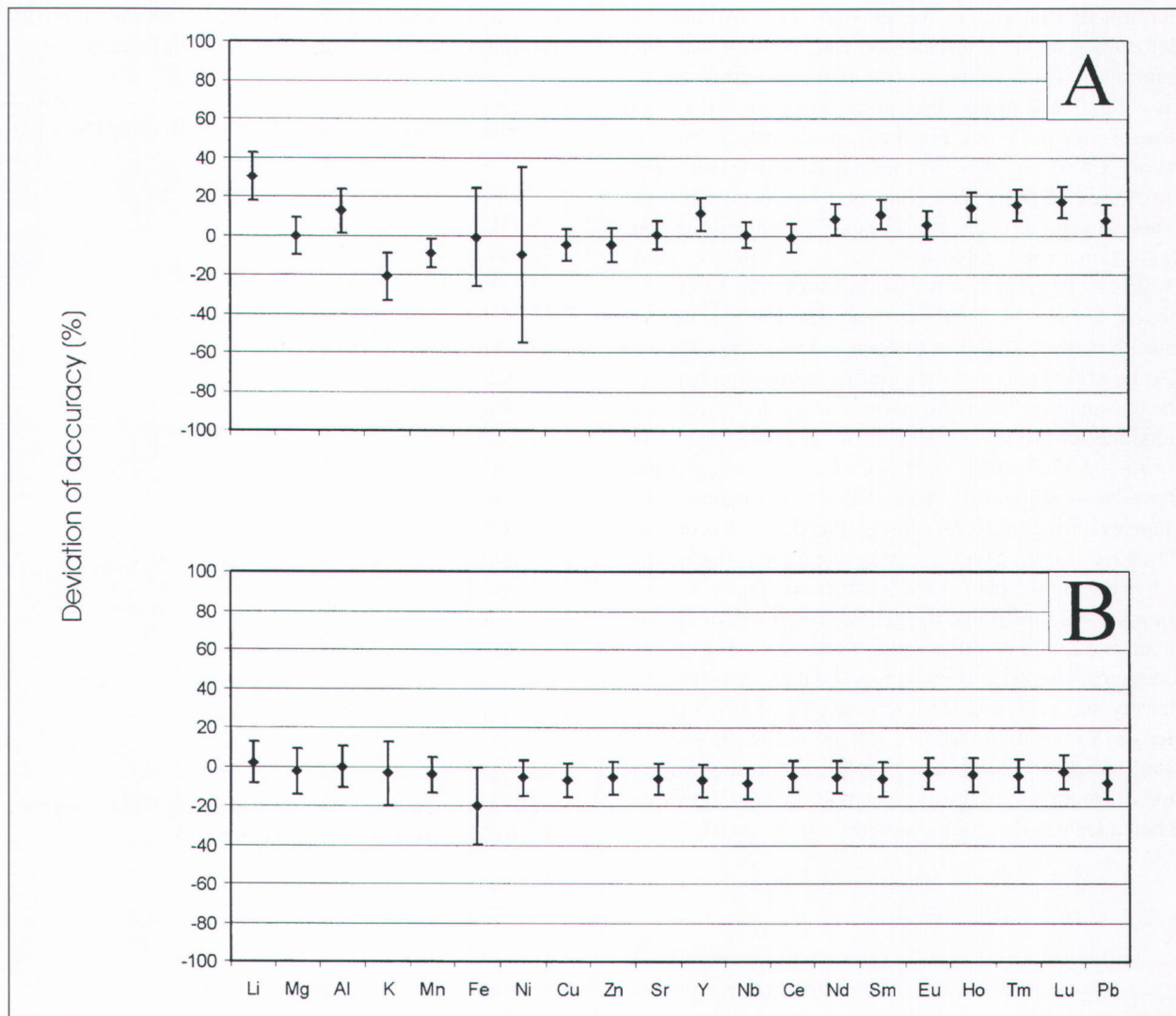


Figure 2 A. Deviation in accuracy of the analysis of a NIST612-glass with 'long flow path' in Ar-atmosphere, calibrated with the response ratios determined from analysis of the same material using the 'short flow path'.

B. Deviation of accuracy calculated for a similar experiment as in A, but ablation occurred in a He-atmosphere and a mixed He-Ar set-up was used.

sage through the valves. Therefore, it was checked if the incorporation of the valves in the transport path had an influence on the measured response ratios. If the valves were bypassed, the transport path from the sample cell outlet to the plasma (with or without mixing device) was ~ 2m (Fig. 1).

The particle size distribution of the transported material depends on the used carrier gas (Günther & Heinrich, 1999a). Since higher sensitivities and lower limits of detection were reported when ablation occurred in a He-atmosphere and the material was transported by a mixed He-Ar gas flow (Günther & Heinrich, 1999a), the above experiments were carried out using both a mixed He-Ar gas and Ar gas only. In practice, the laser was focused on the surface of the external standard material and a line scan was performed by moving the sample cell in the XY-plane during ablation. In this way, the ablation rate was kept constant, resulting in a fairly continuous introduction of material in the plasma. The influence of defocusing of the laserbeam on fractionation was then minimised. Analyses were done using a spectrum analysis with 10 repetitions, three points per peak and a dwell time of 1ms per point. For the quantification of the elements, Ca was used as the internal standard. The analysis of the NIST612 glass with the 'short transport path' (valves excluded) was used for calibration and the concentration in the glass with the 'long transport path' (valves incorporated) was calculated. Li, Mg, Al, K, Mn, Fe, Ni, Cu, Zn, Sr, Y, Nb, Ce, Nd, Sm, Eu, Ho, Tm, Lu and Pb were analysed in the glass. As shown in Figure 2A, most elements show a significant deviation between the two analyses when the instrumentation was tuned for maximal sensitivity using Ar carrier gas only (up to 30% for Li and ~20% for K and the REE). This indicates that the relative amount of these elements compared to Ca changes during transport through the valves. In contrast, when He is used as transporting agent from the sample cell to the mixing device and the instrumentation is tuned for maximal sensitivity, the general accuracy for the elements measured is much better, except for Fe (Fig. 2B). Günther & Heinrich (1999a) proposed that due to its lower density and viscosity, He might be a more efficient carrier gas for smaller particles that are not easily precipitated during transport. This might explain the diminution of fractionation during transport through the valves when a He gas flow in the sample cell was used.

3.2. Linearity during transport

The analysed concentrations of the 20 elements in a NIST614 glass, with NIST612 and Ca used as external and internal standards, respectively, are given in Table 2. In these experiments the glasses were ablated in a He-atmosphere. As previous experiments showed that fractionation during transport using this instrumental set-up was not significant, the valves were incorporated in the transport path for practical simplicity. The results are generally in good agreement with other reported analyses of this material (Fig. 3). However, large deviations from published data exist for K, Ni, Cu, Zn and Pb. It should be noted that, in previous studies, these elements (with the exception of Pb) were not measured on the NIST614 glass by LA-ICP-MS. However, they are very important for the study of fluid inclusions in mineral deposits in order to elucidate fluid-rock interaction and depositional processes (Roedder & Bodnar, 1997). The above observations will be discussed in conjunction with the analyses of fluid inclusions in natural quartz.

element	concentration	SD (n = 10)	RSD (n = 10)
Li	1.3	0.2	17
Mg	42	17	40
K	72	9	13
Mn	1.6	0.1	9
Fe	20	8	40
Ni	4.1	0.9	22
Cu	7	2	30
Zn	5.4	0.9	16
Sr	52	5	9
Y	0.86	0.09	11
Nb	0.92	0.09	10
Ce	0.9	0.1	12
Nd	0.8	0.1	14
Sm	0.8	0.1	18
Eu	0.83	0.09	11
Ho	0.75	0.07	9
Tm	0.75	0.08	11
Lu	0.77	0.09	12
Pb	3.7	0.4	11

Table 2. Concentrations analysed in the NIST614-glass. NIST612 was used as the external standard.

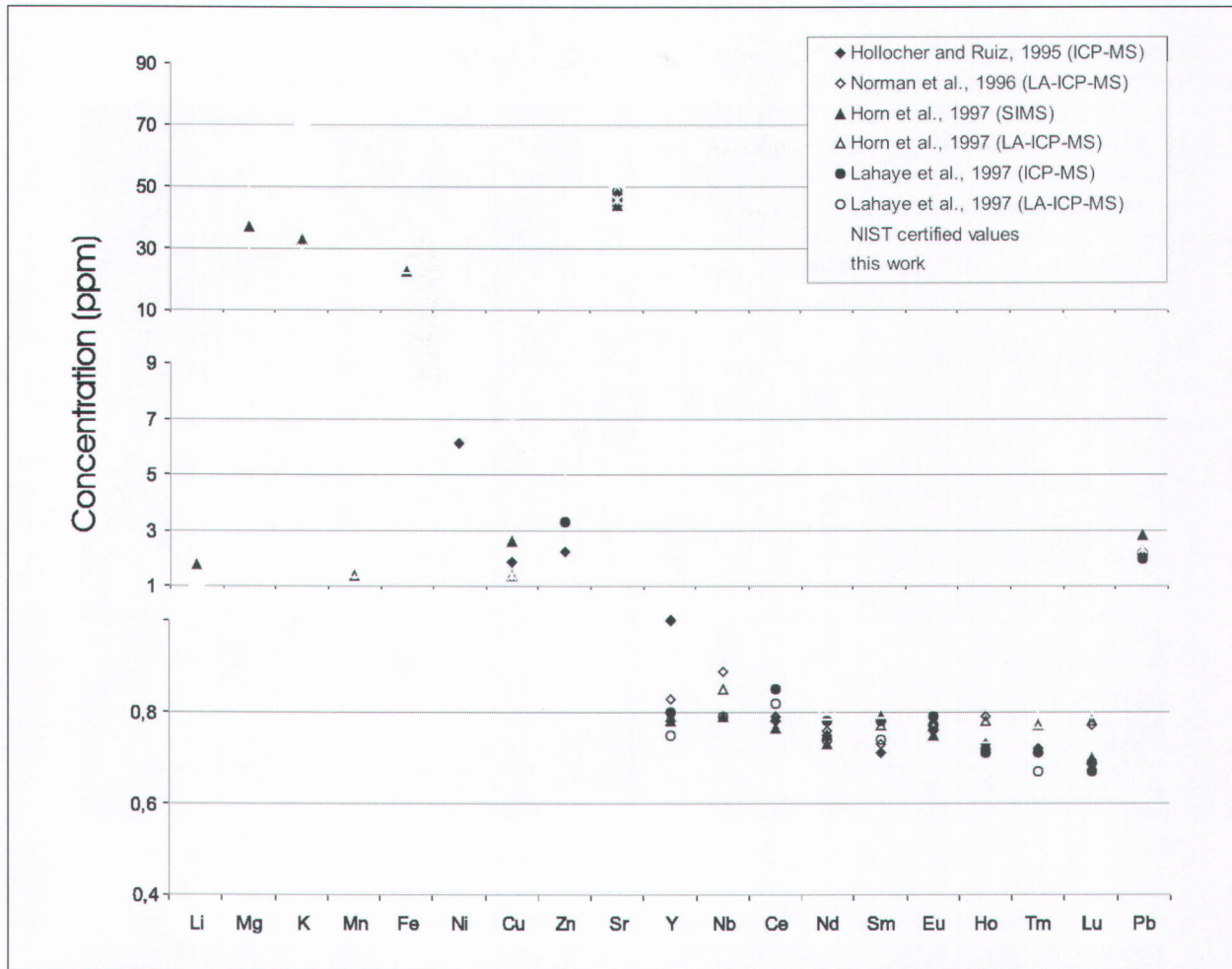


Figure 3. Analysed concentrations of a number of elements in the NIST614-glass in comparison with other values reported in literature. The analytical techniques used are between brackets. Bars represent 1 standard deviation.

3.3. Fluid inclusion analysis

3.3.1. Sample material

Quartz samples from a pegmatite in Minas Geraes (Brasil), containing large inclusions (50-100 μm), were used in the fluid inclusion study. All inclusions are present along secondary (pseudosecondary?) trails. Primary inclusions in growth zones or isolated in the crystals have not been identified. During cryogenic experiments, all of the inclusions show a similar melting behaviour, but a different melting temperature. The temperature of first melting ranges between -63.1 and -50.8°C . Three populations can be distinguished based on the final melting temperature of ice ($T_{m_{ice}}$; Fig. 4). Population I and II display a tight grouping, with $T_{m_{ice}}$ -values ranging from -25.9 to -23.7°C and from -20.4 to -18.6°C , respectively. Population III shows a larger spread. $T_{m_{ice}}$ varies between -15.2 and -6.0°C . These final melting temperatures of ice correspond to salinities ranging between 23.3 and 22.3 eq. wt% CaCl_2 for population I, 20.8 and 19.8 eq. wt% CaCl_2 for population II and 17.9 and 10.2 eq. wt% CaCl_2 for population III

(according to Oakes et al., 1990). In contrast to the common practice of addressing salinities as eq. wt% NaCl , we prefer to report all salinities as eq. wt% CaCl_2 , in order to maintain a consistency among the data since $T_{m_{ice}}$ -values $< -21.2^\circ\text{C}$ cannot be expressed as eq. wt% NaCl . From each of the different populations, several inclusions were selected for LA-ICP-MS analysis.

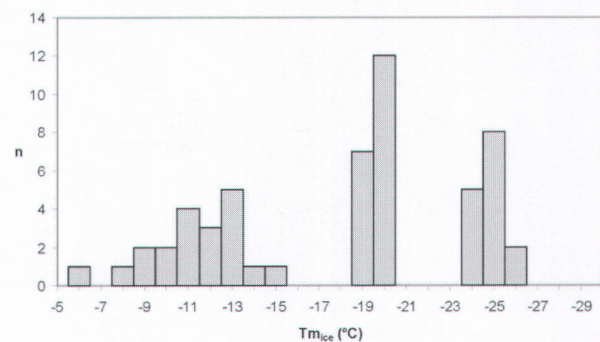


Figure 4. $T_{m_{ice}}$ values of the fluid inclusions in the quartz samples investigated.

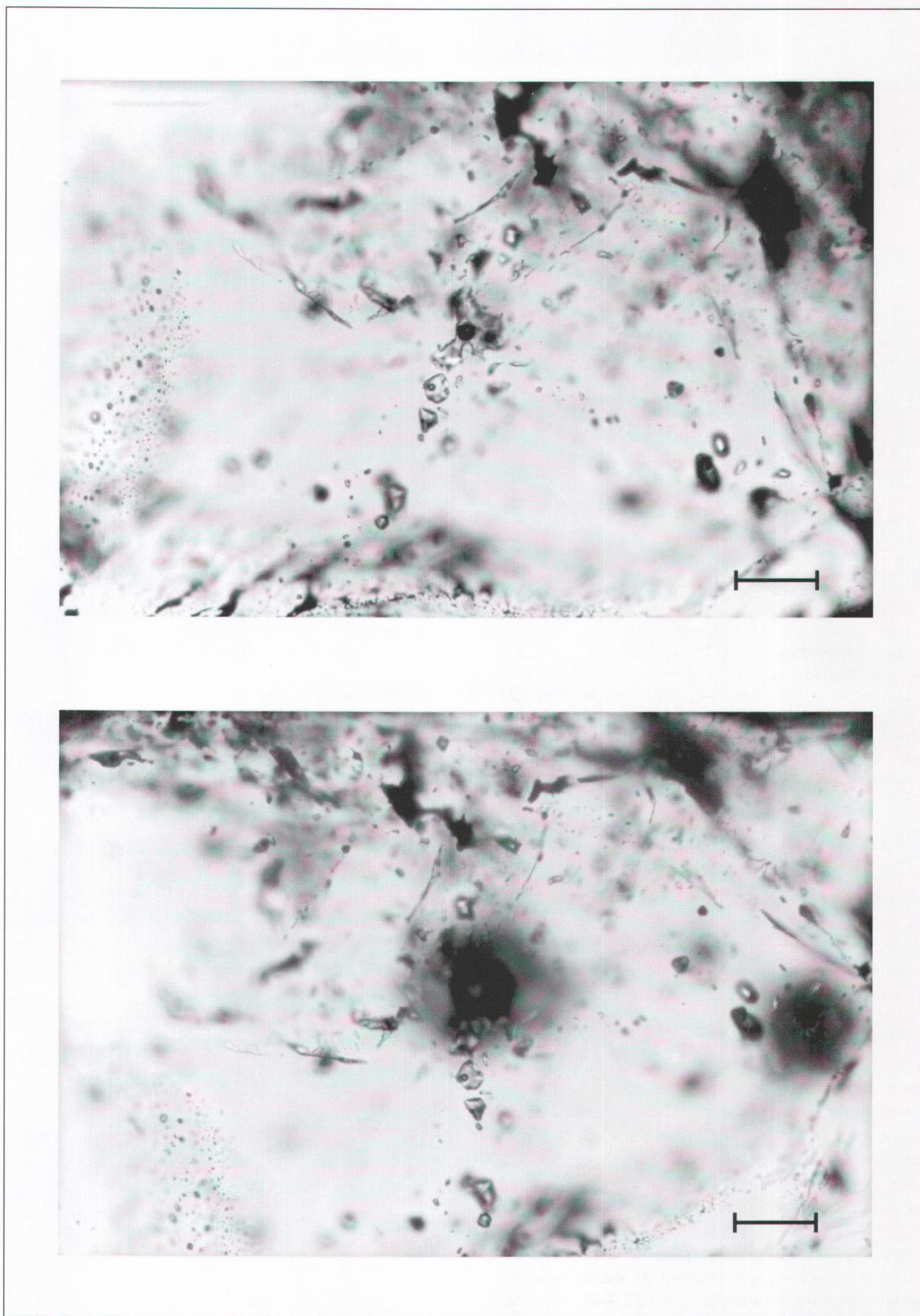


Figure 5. Photographs of a typical fluid inclusion in the quartz samples before and after ablation. Scale bar is 100 μm .

3.3.2. Procedure

The ablation of fluid inclusions produces transient signals as material is entrained in the ICP-MS during a short time. Therefore, measurements were made in Time Resolved Analysis. In this way, the elements of interest can be monitored in real time and drilling progress can be followed. The first 60 seconds were used to measure the background before analysis. Then the laser started firing. Analysis of the fluid inclusions was performed in a He-atmosphere. While ablation of the NIST-glasses with the LSX200 produces nice, flat-bottom shaped pits, even when using spotsizes as small as 10µm (Günther & Heinrich, 1999b), the ablation of quartz wafers often resulted in spallation of the material and a large crater was produced (Fig 5). With a spotsize ≤ 50 µm, ablation could not be guaranteed. If ablation occurred, it often was so violent that no usable signal was obtained. Best controllable ablation was achieved with a spotsize of 100µm or larger and with a gradual increase of the laser fluence during ablation.

Because Na is mono-isotopic, high concentrations of this element can saturate the electronmultiplier. Günther *et al.* (1998), using an Elan 6000 ICP-MS (Perkin-Elmer), therefore deminished the mass resolution for Na from 0.7 to 0.3 AMU, while keeping the resolution for the other elements at 0.7 AMU to ensure optimum sensitivity. Changing the mass resolution for one element only is not possible with the HP4500. In our analysis, Na was also measured and the mass resolution for all elements was set at ~ 0.3 AMU which of course decreases the overall sensitivity. The limits of detection (LOD), calculated from the ablation of the NIST612 glass, do not seem to increase significantly for most elements measured (Table 3). This indicates that the background decreases simultaneously.

Element	LOD (ppm) AMU ~ 0.3	LOD(ppm) AMU ~ 0.7
Li	14	1
Na	60	n.m.
Mg	2	0,26
K	44	n.m.
Ca	103	119
Mn	0,26	0,22
Fe	6	12
Ni	0,4	0,29
Cu	0,3	0,304
Zn	0,5	0,88
Rb	0,13	0,157
Sr	0,03	0,047

n.m. = not measured

Table 3. Limits of detection (LOD) for a number of elements when the resolution is set at ~ 0.7 and ~ 0.3 AMU, as determined from analysis of NIST612.

3.3.3. Results

The intensity ratio to Ca versus the Cl/Ca intensity ratio for some cations analysed in the different fluid inclusions are graphically shown in Fig. 6 and summarised in Table 4. As can be seen from Fig. 6, no distinction can be made between the measured signals of the inclusions of population I and II. Inclusions of population III show, however, clearly higher Na, K, Sr and Cl ratios to Ca than those of the former two populations. Relative standard deviations (RSD) of the intensity ratios to Ca are generally large. Only the Cl/Ca has a RSD $< 30\%$. For some elements, the RSD can reach approximately 100% for analyses of fluid inclusions of one population (e.g. Li, Mg, Ni, Br and Rb).

Calculated mean concentration ratios, using the response ratios from spectrum analyses of the NIST612 glass that were performed between successive fluid inclusion measurements, show that the fluids are dominated by Ca, Na and Li which can be expected for the fluid inclusions in these pegmatites (Morteani *et al.*, 2000). Cl is also a major element in the fluids but its signal can, unfortunately, not be calibrated because the chlorine concentration in the NIST-glasses is unknown. The mean Na/Ca ratio is 0.5 for population I, 0.8 for population II and 1.9 for population III. The mean Li/Ca ratio is 0.2, 0.4 and 0.7, respectively. All other cations analysed have ratios to Ca smaller than 0.1 (Table 5).

3.4. SEM-EDX analysis of the sample surface after ablation

SEM-inspection of the wafer surface after analysis of the fluid inclusions showed that the ablation resulted in a large amount of particles on the wafer surface that could not be transported to the ICP-MS (Fig. 7A, B). When subjected to a qualitative Energy Dispersive X-ray analysis (EDX), most of these particles seemed to be pure quartz fragments, which contained no detectable amounts of elements other than silica and oxygen (Fig. 7C). Their morphology suggests that they resulted from the acoustic shockwaves during ablation (Chan & Russo, 1991). However, more rounded particles, which seemed to have been precipitated out of a molten state, were enriched in Na, Al, K, Ca, Fe, Zn and Rb (e.g. Fig. 7D). The presence of these elements in the particles was highly variable. For example, in some particles only Ca could be detected. Li could not be detected with EDX because of its interference with oxygen. The quartz itself does not contain concentrations of these elements that are detectable with EDX. Therefore, the only sources of these elements are the fluids in the inclusions.

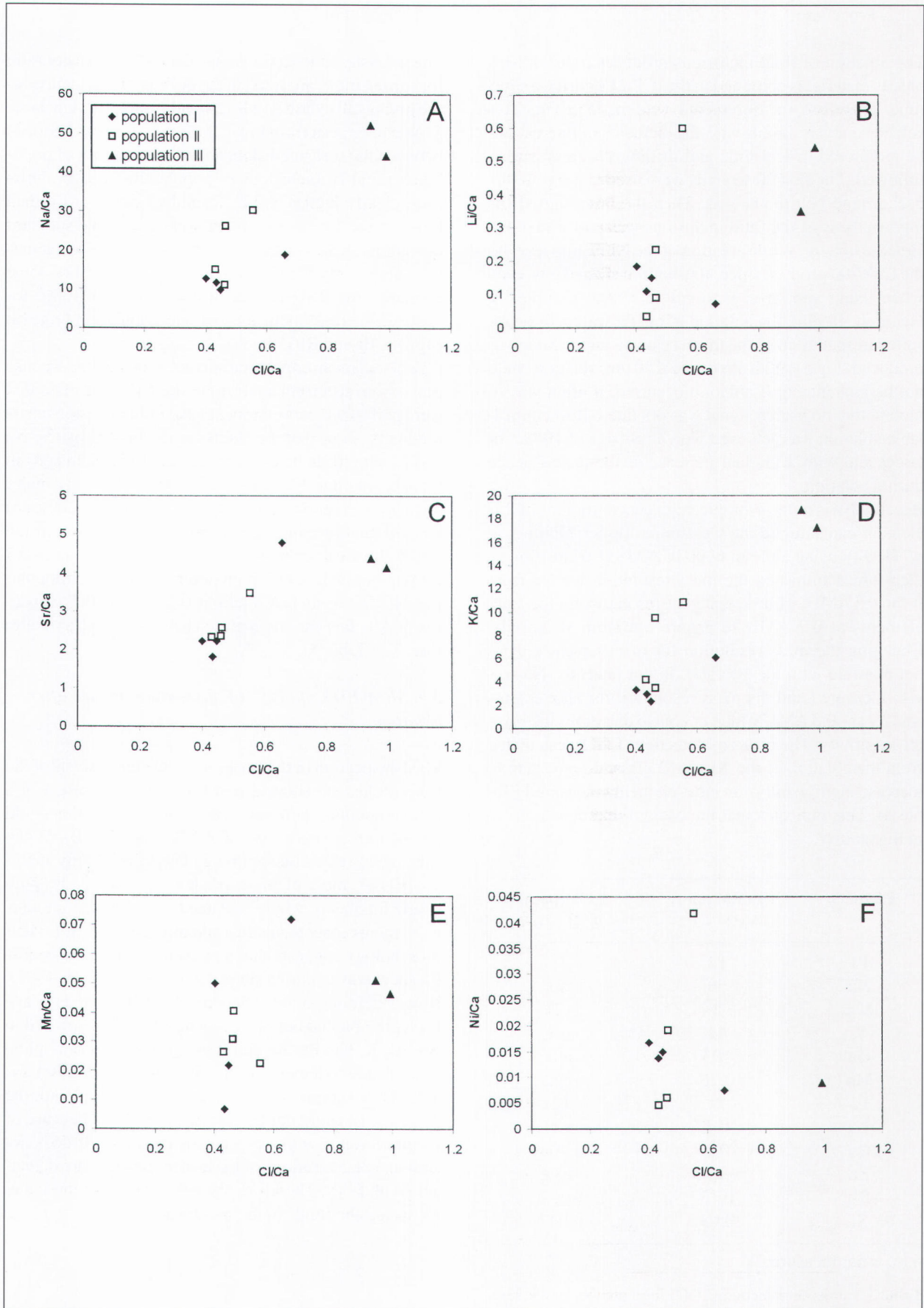


Figure 6. Intensity ratios to Ca of a number of elements analysed in the fluid inclusions in quartz.

inclusion	Intensity ratios to Ca													T _{m,ice} (°C)	
	Li	Na	Mg	Cl	K	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr		
Group I	1	0,151	9,7	0,031	0,45	2,3	0,022	0,010	0,015	0,003	-	0,026	0,034	2,2	-24,2
	2	0,072	18,8	0,003	0,66	6,1	0,072	0,009	0,007	-	-	0,027	0,208	4,8	-24,1
	3	0,110	11,8	-	0,43	2,9	0,007	-	0,014	-	-	0,015	0,037	1,8	-23,8
	4	0,185	12,9	0,005	0,40	3,3	0,050	-	0,017	0,003	-	0,019	0,034	2,2	-25,3
	mean	0,13	13	0,01	0,5	4	0,04	-	0,013	-	-	0,022	0,08	3	
	RSD	38	29	120	24	46	77	-	31	-	-	27	111	49	
Group II	5	0,236	26,3	-	0,46	9,5	0,041	0,019	0,019	-	-	-	0,130	2,6	-20,0
	6	0,035	15,2	0,005	0,43	4,2	0,026	-	0,005	-	-	0,013	0,042	2,3	-19,1
	7	0,600	30,2	0,015	0,55	10,8	0,023	-	0,042	0,005	0,004	0,099	0,204	3,5	-20,0
	8	0,090	11,1	-	0,46	3,5	0,031	-	0,006	-	-	0,016	0,065	2,4	-19,2
	mean	0,2	21	-	0,48	7	0,030	-	0,02	-	-	0,04	0,11	2,7	
	RSD	106	44	-	11	53	26	-	96	-	-	114	66	20	
Group III	9	0,540	44,1	-	0,10	17,2	0,046	-	0,009	-	-	0,074	0,348	4,1	-10,7
	10	0,350	52,2	-	0,90	18,7	0,051	-	-	-	-	0,070	0,192	4,4	-8,1

Table 4. Intensity ratios to Ca of the elements analysed in the fluid inclusions.

inclusion	Calculated, molar concentration ratios to Ca													
	Li	Na	Mg	Cl	K	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr	
Group I	1	0,2	0,4	0,004	-	0,006	0,0001	0,0031	0,0003	0,00005	-	-	0,0001	0,007
	2	0,1	0,8	0,000	-	0,015	0,0004	0,0026	0,0002	-	-	-	0,0005	0,015
	3	0,2	0,5	-	-	0,007	0,0000	-	0,0003	-	-	-	0,0001	0,006
	4	0,3	0,5	0,001	-	0,008	0,0003	-	0,0004	0,00005	-	-	0,0001	0,007
	mean	0,2	0,5	0,002	-	0,009	0,0002	0,003	0,0003	0,00005	-	-	0,0002	0,009
	RSD	38	29	123	-	46	77	-	31	-	-	-	100	49
Group II	5	0,4	1,0	-	-	0,024	0,0002	0,0057	0,0004	-	-	-	0,0003	0,008
	6	0,1	0,6	0,001	-	0,010	0,0002	-	0,0001	-	-	-	0,0001	0,008
	7	0,9	1,2	0,002	-	0,027	0,0001	-	0,0009	0,00008	0,0002	-	0,0005	0,011
	8	0,1	0,4	-	-	0,009	0,0002	-	0,0001	-	-	-	0,0002	0,008
	mean	0,4	0,8	0,001	-	0,017	0,0002	-	0,0004	-	-	-	0,0003	0,009
	RSD	106	43	-	-	53	26	-	96	-	-	-	66	20
Group III	9	0,8	1,8	-	-	0,042	0,0003	-	0,0002	-	-	-	0,0008	0,013
	10	0,5	2,1	-	-	0,046	0,0003	-	-	-	-	-	0,0004	0,014
	mean	0,7	1,9	-	-	0,044	0,0003	-	-	-	-	-	0,0006	0,014

Table 5. Concentration ratios to Ca of the elements analysed in the fluid inclusions. NIST612 was used as the external standard.

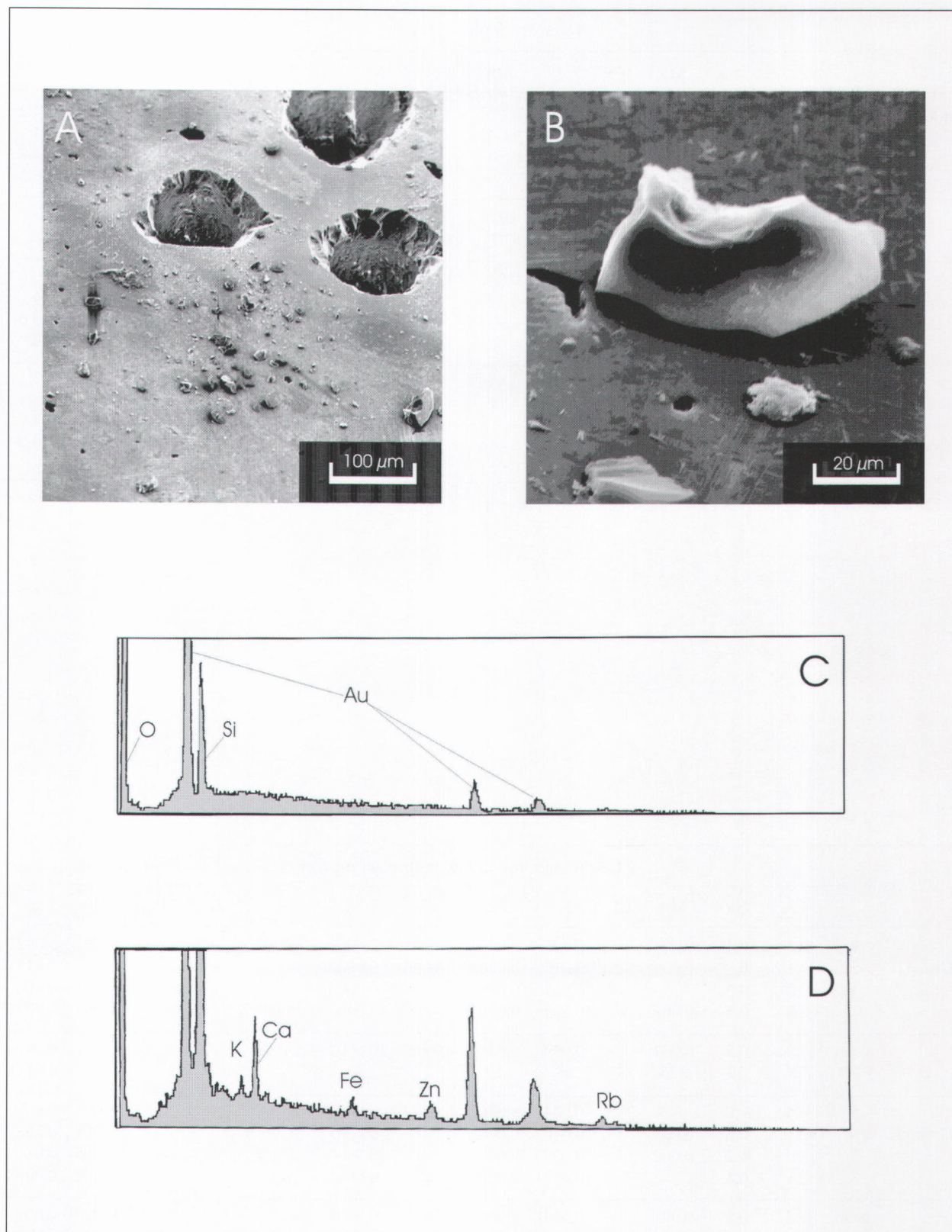


Figure 7 A. SEM-image of a quartz wafer after ablation of fluid inclusions. Large craters and a lot of liberated material that remained on the sample surface can be observed.

B. Detail of A, showing a large particle with a conchoidal fracture (1) and a smaller, more rounded one (2). The latter seems to have formed out of a molten state.

C. SEM-EDX analysis of particle 1 in B. No elements other than O and Si could be detected. Au peaks are due to the coating with gold.

D. SEM-EDX analysis of particle 2 in B. K, Ca, Fe, Zn and Rb could clearly be detected.

4. Discussion

The results of the analysis of the NIST614 glass, calibrated with the NIST612, indicate that the response ratios to Ca vary over a concentration range. In their study of LA-ICP-MS analysis of solid materials, Morrison *et al.* (1995) showed that for a variety of different matrices the REE had a similar behaviour and could be successfully calibrated using Y as an internal standard. Contrastingly, the large ion lithophile elements (LILE, e.g. Rb, Ba and Cs), the high field strength elements (HFSE, e.g. U, Th, Zr, Nb, Hf, Ta, W) and the chalcophile and siderophile elements (e.g. Ga, Ni, Cu, Zn, As, Mo, Pb) showed strong deviations in accuracy for most matrices if Y was used as the internal standard. A roughly similar grouping was made by Longerich *et al.* (1996) in a study of time-dependent fractionation effects during single-spot analyses of a NIST612 glass. They concluded that large number of elements correlate well with Ca (among which Y, Sr, Ba, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), however, others had a distinctly different behaviour (e.g. Zn, Cu and Pb). Unfortunately, in none of these studies Na nor K was analysed. In conclusion, they demonstrated that Ca can be successfully applied as an internal standard to quantify the REE and some divalent alkaline earth's (Mg, Sr), but not for the calibration of LILE, some siderophile and the chalcophile elements.

While the use of a 'flat-topped' 266nm laser enables a very controllable ablation of glass standard materials, the ablation of quartz using this type of laser is much more difficult. In contrast to previous researchers (e.g. Shepherd & Chenery, 1995; McCandless *et al.*, 1997) who used a 266nm laser with a non-homogenised, Gaussian energy distribution, where energy peaks might initiate ablation, our experience shows that improvement of the beam quality by homogenising the energy distribution (as is the case in the LSX200) seriously complicates the practical aspects of quartz ablation. It results in an increase of the minimum spotsize that can be used. In order to avoid excessive fracturing of quartz, the starting energy, the rate of energy increase during ablation, the repetition rate, etc., have to be thoroughly investigated before analysis.

Taking these aspects into account, the LA-ICP-MS analysis enables the discrimination between different fluid inclusion populations in the quartz samples investigated. The fluid inclusions of population III clearly display a relatively lower Ca and higher Li, Na, K and Sr content than those of population I and II. As noted by Shepherd & Chenery (1995) this offers the possibility for recognising temporal variations in fluid chemistry, necessary for ore-deposit or diagenetic modelling.

While previous research confirmed the applicability of the NIST-standard material 612 to calibrate the obtained

signals (Shepherd & Chenery, 1995; Moissette *et al.*, 1996; Günther *et al.*, 1997, 1998), the above experiments on the NIST-glasses highlight the importance of matrix-matching, especially with respect to the concentration of the analytes in the external standard and the sample, and of the choice of the internal standard. Regrettably, the accuracy of our measurements can not be evaluated unless the inclusions are analysed by an independent technique.

Part of the variance in the intensity ratios measured in the fluid inclusions in the pegmatitic quartz can be the result of the natural inhomogeneity between the inclusions analysed. However, the presence of glass particles enriched in some elements on the surface of the wafers after ablation of the inclusions, even when ablating in a He-atmosphere, indicates that the variance could also be the result of a fractionation during analysis. The formation of particles that were preferentially enriched in a variety of elements was observed during ablation of metals, sulphide minerals and NIST-glasses (Thompson *et al.*, 1990; Chenery *et al.*, 1992; Outridge *et al.*, 1996, 1997), which demonstrates the importance of this phenomenon as a possible fractionation process.

5. Conclusions

LA-ICP-MS analysis of natural fluid inclusions in quartz demonstrates the semi-quantitative ability of the technique to characterise different fluid inclusion populations. This makes the technique a powerful tool in palaeofluidflow modelling. However, the precision and accuracy of fluid inclusion analysis by ICP-MS should be further investigated. Experiments of different NIST standard reference materials with similar matrix but varying trace-element concentrations, question the applicability of Ca as an internal standard to quantify precisely elements such as K, Zn, Pb and Cu, which are of major importance in fluid inclusion studies. Previous investigations indicate that during LA-ICP-MS analysis, elements tend to group together according to their chemical nature. An incorrect choice of the internal standard can therefore result in a significant deviation of accuracy. For the quantification of LA-ICP-MS analysis of fluid inclusions, however, one is limited by the natural occurrence of major elements in the inclusions because these are the only elements that can be measured by an independent technique, such as microthermometry.

During ablation of the inclusions, part of the elements reprecipitate in a glass phase which remains on the sample surface as demonstrated by SEM-EDX analysis of the samples analysed.

In order to improve precision and accuracy, an evaluation of other elements, ideally Cl, as internal standards is required. In the case of Cl, this also implies the use of other external standard materials as the NIST-glasses, because the Cl concentration and its homogeneity in the

glasses are unknown. Improvement of LA-ICP-MS ('flat-topped' 266nm laser) as a quantitative technique for fluid inclusion analysis also depends on the further insight in the mechanisms of selective reprecipitation of elements in a glass phase during ablation.

6. Acknowledgements

This manuscript benefited from the helpful review by J. Touret. The research is supported by the Fund for Scientific Research Flanders (Belgium) grant G030097N. We would like to thank J. Hertogen for adapting the LA-ICP-MS to the use of helium and H. Nijs for carefully preparing the doubly polished wafers. The research of W. Heijlen is financed by the Flemish Institute for the Promotion of Scientific-technological Research in the Industry (IWT).

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Manuscript received on 18.1.2001 and accepted for publication on 4.4.2001