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Analytical strategies for LA-HR-ICP-MS analysis of quartz: results from collaboration between Monash University and NGU

NGU
Norges geologiske undersøkelse
Geological Survey of Norway
Geological Survey of Norway
N-7441 Trondheim, Norway
Tel.: 47 73 90 40 11
Telefax 47 73 92 16 20

REPORT

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Title:
Analytical strategies for LA-HR-ICP-MS analysis of quartz: results from collaboration between Monash University and NGU

Authors:
Larsen R.B. & Lahaye Y.

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Summary:

- Laser ablation analysis of quartz was facilitated by a UV-laser system adapted to a High Resolution Inductively Coupled Mass Spectrometer at Monash University, Australia
- In a complete analytical package meeting the requirements from most of the industry concerned with high purity quartz, the following elements must be included: Al, B, Ca, Cr, Cu, Fe, Ge, K, Li, Mg, Mn, Na, P, Pb, Rb, Ti and U.
- The method developed at Monash obtained promising results for Al, B, Ge, Li, Fe, Pb, Rb, and U from this list and also for Be, Ba, Nb, Y, Zr and Th. LOD's for some elements, particularly Al, Li, Cu, Mn and B are too high but fine tuning of the instrument and better matrix matching external standards at NGU have already improved LOD's for these elements considerably. Li and B can be analysed with even better LOD's if specific cones reserved for quartz analysis only.
- Ge can be analysed in LR-mode if Ge^{74} is analysed rather than Ge^{72}. Mg, Sc, Ti, Cr, Fe can be analysed in MR-mode and K in HR-mode. A method that analyse these isotopes in MR and HR mode is currently being tested at NGU with good results. P can not be analysed because it its high ionisation potential and alternative isotopes do not exist. Na can not be analysed because atmospheric air which is soaked in to the carrier gas induces LOD's higher than 100 ppm. However, for most quartz it may be assumed that the following equation, expressing the molar concentration of structurally bound Al, Li and Na in igneous quartz and most hydrothermal quartz, is valid (e.g. Dennen, 1966)

$$[Al] = [Li] + [Na] \quad \text{(in mol\%)}$$

Accordingly, the concentration of Na may be approximated if the concentration of Al and Li is known. This approach may suffice for many applications.

The method is recommended when the concentration of structural impurities (and sub-microscopic inclusion), before acid leach, is required. After acid leach, LA-analysis may still be applied on grain mounts although, if a pure quartz concentrate is available, conventinal solution HR-ICP-MS is more beneficial

Keywords: LA-HR-ICP-MS	Quartz	Trace elements
Analytical method		

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TABLES

1. INTRODUCTION

In 1996 NGU initiated the project "High Purity Quartz in Norway". The goals of the project are to define the geological conditions that facilitate the genesis of high purity quartz (HPQ) in igneous geological settings and to develop an analytical method for rapid and precise analyses of quartz.

The present report summarises the preliminary results regarding the development of an analytical method based on direct laser ablation sampling of quartz wafers at Monash University, Victorian Institute of Earth and Planetary Sciences (VIEPS), Australia.

Monash University maintains a state of the art LA-HR-ICP-MS facility, i.e. a facility designed for laser ablation sampling of solid specimens and simultaneous analysis of the sample material by a highly sensitive single collector mass spectrometer. Collaboration with VIEPS was implemented with the goal of maximising progress with similar instrumentation at NGU.

2. GENERAL OUTLINE OF THE LA-HR-ICP-MS TECHNIQUE

The LA-HR-ICP-MS method is a cutting edge analytical technique that in its present form was introduced only three years ago and currently is trialed on geological samples all over the Earth science community. This technique aim at estimating the trace element distribution in solid material (e.g. rocksamples) with detection limits down towards 1 ppb and for certain elements, even much lower. The novel concept is to use a laser beam operating at the ultra violet (UV) wavelength (266 nm) to release microscopic samples from a rock surface. Because of the high energy of UV-light, the part of the sample that is bombarded by the laser-beam is partially melted and detached (i.e. ablated) from the sample surface in an explosive process that throw melt and dust in to an argon-gass current sweeping through the sample chamber. Susequently the ablated sample, which is suspended in the argon gass, is transported towards a magnetic mass spectrometer where the chemical composition is estimated. On the way to the mass spectrometer the sample passes through a torch system that generates an argon plasma, i.e. a very high temperature medium maintaining a tempertaure of ca. 10 000 °C. By passing this temperature regime the sample partially or fully decomposes to form positively charged ions (e.g. Ti^{4+}, Si^{4+} K^{+}). In continuing inside the mass spectrometer, the ions will enter a strong magnetic field that bend the individual ions according to their energy, mass and charge hence different ions are bend along distinctive trajectories throughout the magnetic field. After having passed through the magnetic field, a narrow slit is adjusted so that only one specific trajectory, equivalent to the path followed by the desired ion (e.g. Ti^{4+}), will line up with the slit. The ions that are allowed through the slit will subsequently collide with a detector system that measure the number of collisions per time unit, i.e. counts/second. One of the novel features with the mass spectrometer at NGU is its ability to rapidly sweep over large parts of the periodic table (Li^{7} to U^{238}) and rapidly to change between Low-, Medium- and High Resolution (respectively LR, MR and HR). In LR mode, the width (i.e. atomic mass range) over which a particular isotope is measured is quite wide which facilitate very low detection limits (down to the ppt level for some isotopes) and high precision. However, certain compunds having near equal masses may interfere with the measurements and distort the final result. Distortion of the result may be avoided by narrowing the mass range over which the measurement is performed and depending on the size and proximity of the interfering compund, the measurement may be done in MR of HR mode. These options, although drastically reducing the sensitivity of the measurement, facilitates estimation of difficult isotopes such as for example K, Ca, S and As that rarely can be quantified with conventional mass spectrometric techniques.

The laser system which is used for the ablation of the samples operates with a typical beam diameter of 10-100 µm a pulse energy of <30 mJ, and with a frequency of max 10 Hz (i.e. 10 shots/second) with a shot-duration of <10 ns. Either, laser sampling is performed in a single spot or in an area (raster) where the laser beam moves along a predefined grid and the final result reflects the average composition over the area.

Absorbtion of UV-laser light varies greatly from one sample to the next hence the volume of material which is ablated can not be predicted. Therefore, Quantification of an element in the sample requires that the concentration of one element is known already. This element is called the internal standard and is typically a major element in the mineral that either is known stoichiometrically as for examples Si in quartz or is estimated by another analytical method. The concentration of an unknown element in the sampled is then compared to the intensity of the same element in a standard in which the concentration of course is known. Given these informations the unknown concentration may be quantified according to a wellknown eqution. Quantification of Ti in quartz, forexample, where Si is used as an internal standard is expressed in the following way

$$\mathbf{C}Ti_{sample}=[\mathbf{C}Ti_{standard}/(\mathbf{I}Ti_{standard}/\mathbf{I}Si_{standard})]*[\mathbf{I}Ti_{sample}/\mathbf{I}Si_{sample}]*[\mathbf{C}Si_{sample}/\mathbf{C}Si_{standard}]$$

Where **C** is concentration in ppm and **I** is intensity in counts/second.

3. BACKGROUND

Traditionally when analysing quartz from igneous rocks it is required to go through the following principal steps before chemical analysis:

1. Crushing in a cone crusher or similar device
2. Fine grinding
3. Sieving to desired grain size
4. Several flotation steps to separate quartz, feldspar and mica fractions. Alternatively, hand-picking of quartz
5. Magnetic treatment of the quartz fraction
6. Acid leach
7. Calcination
8. Sample digestion prior to chemical analysis that involves several steps including microwave digestion in Teflon bombs, evaporation of digestion containers and dissolution of residue
9. Chemical analysis by AAS, ICP-OES, ICP-MS or other methods

Depending on the specific physical or chemical characteristics of the relevant quartz samples, it may be necessary to include other dressing steps before final analysis.

Besides being time-consuming, expensive and labour intensive, the traditional procedure is also prone to contamination at several of the steps summarised above.

Therefore, at the very beginning of the quartz-project it was decided to develop an *in situ* analytical technique by adopting the LA-HR-ICP-MS for direct sampling and analysis of quartz.

The advantages of LA-HR-ICP-MS analysis of quartz compared to the traditional method include;

- Minimal preparation of the sample, i.e. production of a thick section or a polished rock chip mounted in glue
- Chances of contamination is minimal since grinding and dissolution of the sample are avoided
- The method is rapid and cost-efficient
- In situ LA-analysis provides precise information on the spatial distribution of impurities in quartz
- In contrary to solution ICP-MS the sample is not diluted

These benefits must be weighed against the following disadvantages with the LA-HR-ICP-MS technique

- Laser ablation sampling releases very small quantities of matter; therefore, precision and detection limits are worse than at liquid introduction
- Although the application of UV-laser has reduced the matrix effect considerably (compared to previous IR-lasers), some uncertainties in quantifying the signal remains. Matrix effects reduces the accuracy and the transient nature of the signal influences the presision
- Because the quartz was not exposed to acid leaching before analysis some of the structural impurities and sub-microscopic inclusions, that are partially removed during acid leach are included in the final analysis

Advantages and disadvantages with the LA-HR-ICP-MS method will be further elaborated in the text and in a coming report based on results of the LA-method that is currently being refined at NGU.

4. INSTRUMENTATION

The advantage of the Finnigan MAT *ELEMENT* HR-ICP-MS instrument over conventional quadrupole ICP-MS instruments is the application of a double focusing magnetic sector mass spectrometer that operates at three predefined nominal resolution i.e. 300 M/ΔM (Low Resolution or LR), 3000 M/ΔM (Medium Resolution or MR) and 8000 M/ΔM (High Resolution or HR). In the end, these characteristics together with several other specific features (e.g. Lahaye, 1997) significantly improve the Limit Of Detection (LOD) and precision, and dramatically increase the range of isotopes that may be analysed because interferences with other isotopes are fully resolved at MR or HR settings. The instrument allows for rapid switching from LR to HR settings during the individual analytical runs and the detector system provides for both digital and analogue counting which can be used separately or in combination. The instrument is equipped with an RF generator type ICP20P operating at 27 MHz, the plasma torch is of the Fassal type and standard sample and high performance Ni-skimmer cones were used. See also Table 1.

Table 1: Instrument settings and acquisition parameters

Laser Source	**Merchantek LUV266, Q-switched Nd:YAG**
Wavelength	266 nm
Repetition Rate	4 Hz
Energy	0.1 mJ
Crater Size	80 µm
Methods	Single spot and raster (ca. 800 x 400 µm)
Mass Spectrometer	**Finnigan MAT ELEMENT HR-ICP-MS**
Resolution	300
Cool Gas Flow	13.00
Auxilary Gas Flow	1.10
Sample Gas Flow	1.20
Cone	High performance Ni
Sample Time	10 ms
Mass Window	22 %
Scan Type	EScan
Segment Duration	40 ms
Samples/Peak	15
Acquisition Points	3

The laser system is a MERCHANTEK LUV266 Q-switched Nd:YAG solid state laser with the fundamental wavelength at 1064 nm quadrupled to the Ultra Violet wavelength at 266 nm which is the wavelength during standard operating conditions. Laser ablation is performed in single spots or in a raster where a predefined area is ablated, or along predefined lines and the laser spot diameter may be varied from 10 to 500 µm. Laser pulse duration is typically 4-8 ns and the laser power may be varied from 0.01 to 4 mJ at a repetition rate of maximum 10 Hz.

Additional information on the VIEPS facility may be obtained from Lahaye et al. (1997).

5. ANALYTICAL RATIONALE

During the analysis of quartz at VIEPS, both raster (ca. 800 x 400 µm) and single spot analysis were performed on doubly polished quartz wafers with a nominal thickness of 250 µm. Single spot and raster analyses were conducted with a repetition rate of 4 HZ, a laser energy of 0.1 mJ and with a laser diameter of 80 µm. Other instrument settings appear from Table 1. Analyses were conducted at both Low and Medium Resolutions although mass-drift in MR and, consequently, in HR modes appeared to be so serious that analysis at HR conditions were discontinued and in MR mode was very time consuming. Mass drift during MR and HR LA-analysis is a common problem encountered at many laboratories and, so far, no laboratories have reported successful LA-analysis at these mass spectrometer settings. However, the NGU LA-HR-ICP-MS facility is currently testing a method that apparently solves the problems with LA-analysis at MR and HR settings (Flem et al., *in prep*) and some isotopes were successfully analysed in MR-mode at VIEPS (see later section).

Quartz from granite pegmatites in Evje-Iveland and Froland, South-Norway, was analysed for 33 isotopes during single spot analysis. However, in the final analytical program and during raster analysis only 21 isotopes were included (Table 2) because various interference phenomena, contamination and relatively high LOD's (compared to the expected concentrations in quartz) prevented the quantification of some of the remaining 16 isotopes. Other isotopes including REE's were present at the sub-ppb level and it was decided to omit them in order to focus on a method including industrially important isotopes only.

Si^{29} was used as the internal standard and NIST612 was used for external standardisation although in some of the runs custom made quartz standards were also used. Of the isotopes

included in the analysis (Table 2) NIST612 is only certified (by NIST) for Al, Si, Ca, Fe, Rb, Sr, Pb, Th, and U. The concentrations of other relevant isotopes (Li, B, Be, Mg, Sc, Ti, Cr, Mn, Cu, Ge, Y, Zr, Nb, Cs, Ba) are compiled from other sources (Pearce et al. 1997). To comprise a complete package of the elements that are commonly encountered as trace impurities in quartz, Na, K and P should also be included in the analytical method. However, Na can not be analysed because atmospheric contamination induces background levels of several hundred ppm Na (see section on results) and solution based analysis also introduced contamination of the mass speactrometer. K and P can only be analysed in High Resolution because of serious interferences with various gas compounds at lower resolutions and mass drift at HR settings efficiently prevented the trial of this option at VIEPS.

Table 2: Isotopes and acquisition conditions. *) industrially important, (Yes) not yet included in NGU-method but may be included if desired.

Isotope	*	Interferences, most important	Resolution at Acquisition	Included in present study at VIEPS	Included at NGU in coming method
Li^{7}	•	None	LR	Yes	Yes
Be^{9}		None	LR	Yes	Yes
B^{11}	•	None	LR	No	Yes
Na^{23}	•	Li-O	Can not be analysed	No	No
Mg^{25}	•	Li-O	MR	No	Yes
Al^{27}	•	None	LR	Yes	Yes
Si^{29}	•	None	LR	Yes	Yes
Si^{30}	•	N-O	MR and HR	No	Yes
P^{31}	•	N-O	Can not be analysed	No	No
K^{39}	•	Ar-H	HR	No	Yes
Ca^{44}	•	Si-O	MR	Yes (at LR)	Yes
Ti^{47}	•	Ar-Li	MR	No	Yes
Ti^{48}	•	Ca^{48}	MR	Yes (at LR)	No
Cr^{52}	•	Ar-O, Ar-N	MR	Yes (at LR)	Yes
Mn^{55}	•	None	LR	No	Yes
Fe^{56}	•	Ar-O, Ca-O	MR	No	Yes
Fe^{57}	•	None	LR (Low abundance)	Yes	No
Cu^{63}	•	None	LR	Yes	(Yes)
Ge^{72}	•	Ar-Ar (uncertain)	MR	Yes (at LR)	No
Ge^{74}	•	None	LR	No	Yes
Rb^{85}	•	None	LR	Yes	Yes
Sr^{88}		None	LR	Yes	Yes
Y^{89}		None	LR	Yes	(Yes)
Zr^{90}		None	LR	Yes	(Yes)
Nb^{93}		None	LR	Yes	(Yes)
Cs^{133}		None	LR	Yes	(Yes)
Ba^{137}		None	LR	Yes	No
Ba^{138}		None	LR	No	Yes
Pb^{208}	•	None	LR	Yes	Yes
Th^{232}		None	LR	Yes	Yes
U^{238}	•	None	LR	Yes	Yes

After initial test runs it was realised that Mn and B also had to be excluded from the element list because the best obtainable LOD's were several ppm, hence much above the maximum concentration reported for most quartz samples. Cu was excluded for the same reason in that the average LOD was well above 0.5 ppm.

During both raster and single spot analysis the mass spectrometer performed 50 scans over the included isotopes. During the first 10 scans the background levels of each isotope was measured with the laser switched off. At the tenth scan the laser was switched on and the signal-intensity of each isotope was determined during the remaining 40 scans. Al, Si and Ca

were detected in analogue mode because the high concentration of these isotopes in the external standard would over-saturate the detector if counting mode was switched on. All other isotopes were detected in counting mode. The mass window was set to 22% with 15 samples/peak in order to get 3 channels per peak because this is the most efficient way in gathering laser ablation data with the Finnigan MAT ELEMENT instrument. The sample time was 0.01 s and the settling time was adjusted according to the length of the magnetic jump between each isotope (0.001 s per atomic mass unit and 0.005 s for rest) (Table 1).

After acquisition, the raw data were transferred to a separate PC for data processing. Initial data processing was performed using the custom made software package known as *Schonbein* that currently is only used by VIEPS. The primary application of *Schonbein* is to rapidly select the desired parts of the spectrum for each isotope (background as well as analyte signal) and to rinse the signal for spikes derived from fluid and solid inclusions, micro-fractures, or other erratic fluctuations. Manipulation of the data in *Schonbein* is done in graphic interfaces so that the results of spike removal and data selection can be verified simultaneously. Subsequent statistical data management and calculation of LOD's, precision and analyte concentrations are performed by macros in Excel spreadsheets.

6. RESULTS

A full evaluation of the results is hampered by the absence of well characterised quartz standards during the analysis at VIEPS. Quartz glass standards that are spiked with the desired elements was not obtained before late in the analytical programs and, when tested, it was realised that some of the standards were inhomogeneous and the quartz blank was contaminated. Conventinal glass standards lack several of the isotopes at the ppm level, i.e. they are only present as major elements such as for example Al and Ca. In the statistical management of the data, big differences between sample and standard concentrations of an element greatly increase the uncertainty in quantifying the relevant isotope in the sample. In theory, the standardisation curve from external standard to argon blank should be linear, however, often it is slightly curved at lower concentrations (e.g. Ødegård et al., 1998). This is not least important for quartz where the concentration of many impurities occur in the sub-ppm range.

However, when beginning the project at VIEPS there were several fundamental challenges regarding quartz analysis that remained to be addressed and which indeed were unravelled during the analytical program at VIEPS. In the following sections, these particular problems are addressed and includes the Limit of Detection, interference phenomena and contamination problems. Finally, some of the preliminary results will be summarised.

6.1 Limit of detection

Limits of detection (LOD's), were calculated as three standard deviations above the background level for each isotope. In contrast to solution ICP-MS, the LOD's during LA-analysis are far from stable over time. This is mainly related to fluctuations in ablation yield, matrix effects (which also influences the ablation yield), changes in the level/intensities of interferences and day to day fluctuations in instrument performance. Throughout the entire seven month period comprised by the quartz-project, the LOD fluctuated by 500 %. For example, the LOD for Al during single spot analysis varied from 7.3 to 44.3 ppm and Ti varied from 0.062 to 0.302 ppm (Table 3). Strongly variable LOD's are not a problem as long as maximum concentrations are lower than the desired LOD. However, for many elements, including Al, the maximum LOD during single spot analysis greatly exceeded the requirements.

Table 3: Limits of Detection (LOD) in ppb

In PPB	Ave. single spot	Ave. raster	Min single spot	Min raster	Max single spot	Max raster
Li^{7}	9955	4573	2591	2162	28108	5732
Be^{9}	8977	77381	3501	36579	19202	97003
Mg^{25}	3135	4012	1361	1897	7511	5030
Al^{27}	18708	52366	7292	24754	44283	65645
Ca^{44}	646593	833140	308791	393837	1410873	1044403
Sc^{45}	1048	73	500	35	2313	92
Ti^{48}	136	42	62	20	303	52
Cr^{52}	2075	188	893	89	4963	236
Fe^{57}	160914	9115	52005	4309	506400	11426
Ge^{72}	1557	227	646	107	3587	285
Rb^{85}	482	24	218	11	1103	30
Sr^{88}	226	26	105	12	506	32
Y^{89}	92	8	44	4	203	10
Zr^{90}	107	11	51	5	236	13
Nb^{93}	63	5	29	3	137	7
Cs^{133}	143	14	64	7	324	17
Ba^{137}	591	23	283	11	1329	28
Pb^{207}	494	26	300	12	878	33
Pb^{208}	383	19	234	9	676	24
Th^{232}	14	2	6	2	31	2
U^{238}	14	2	6	2	34	2

The underlying reason for these fluctuations could occasionally be isolated to pinching or other mechanical blocking phenomena of the tubing system an occasionally, fine tuning of the torch improved LOD's. However, more often than not no apparent reason for a particular high LOD could be isolated.

Comparison of LOD's for single spot and raster analysis (Table 3) reveal that micro rastering greatly improves LOD's for masses higher than Al^{27} whereas lighter masses are comparable or worse. That higher masses are better is a result of better counting statistics because the integrated signal is far higher, however, the reasons for higher LOD's for lower atomic is not resolved. Rb, Ba and Pb excel with 20 to 26 times lower LOD whereas the average for all masses is 13 with Ti in the bottom but still with three times lower LOD. With average LOD's lower than 100 ppb for most elements the minimum requirements for analysis of quartz are obtained for these elements. Minimum LOD's (Table 3) imply that fine tuning of the method may improve LOD's to ca. 10 ppb for many elements. Note, however, that several industrially important element with low masses are far above the desired level.

LOD for Fe of 9 ppm for raster and 16 ppm for single spot analysis is a special problem arriving from the fact that the rare isotope, Fe^{57}, had to measured rather than the much more abundant Fe^{56}, because strong interference of gas-compounds (see next section) prevents selection of the later isotope.

6.2 Interference phenomena

Because LA-analysis in MR mode was very time consuming and was not possible in HR mode at VIEPS, P and K had to be omitted already from the beginning because strong

interferences with N-O and Ar-H components invalidated analysis at LR conditions (Table 2). During analysis in LR-mode, however, some elements produced unrealistic concentrations and the underlying reason could be isolated to interference from one of - or a combination of standard, carrier gas and sample.

Mg^{25} The concentration of Mg was too high. It appeared that the preferred isotope, Mg^{25}, interfered with Li-O compounds. Normally Li-O would not be produced in significant concentrations during analysis, however, persistent memory effects from previous runs of $Li_2B_4O_7$ fused glass contaminated the mass spectrometer with Li, hence stabilised Li-O compounds.

P^{31} Strong interference with N-O compounds prevents analysis of this isotope in LR-mode.

K^{39} As previously mentioned, strong interference with Ar-H components produced in the carrier gas prevents analysis of K in LR mode.

Sc^{45} Interference with Si-O and possibly Ar-Li prevents analysis in LR-mode.

Ca^{44} Some interference with Si-O compounds gave too high totals in LR-mode

Ti^{48} Ti-analysis at first looked satisfactory, however on closer inspections the concentrations appeared much lower than expected (Table 4) and it was realised that Ca^{48} in the external standard, although having a very low abundance (0.19 %), provided significant interferences. In effect, the calibration curve for Ti became steeper than reality, hence the apparent concentration in quartz was lower than reality.

Cr^{52} Interference with Ar-O and Ar-N.

Fe^{57} There is no interference with the Fe^{57}, however, the abundance of this isotope is only 2.2 % and, therefore, LOD is very high. Fe^{56}, with an abundance of 91.7 % is much to prefer, however, interference in LR-mode with Ar-O in the carrier gas and, possibly, Ca-O from the external standard, prevented this option at VIEPS.

Ge^{72} Apparently there should have been few problems with this isotope, however, there may be interference with Ar-Ar compounds and it was realised that Ge^{74} is a better option.

Ge^{74} can be analysed in LR-mode, Mg^{25}, Sc^{42}, Ca^{44}, Ti^{47}, Cr^{52}, Fe^{57} in MR-mode and K^{39} in HR-mode. Preliminary analysis of Fe and Ca in MR mode at VIEPS, gave promising results and good precision could be obtained from running matrix matched standards and constructing calibration curves. However, the external standards were not entirely homogeous and the quartz blank was contaminated. Therefore, the final results were inconclusive. Current work at NGU with improved external standards has solved most of the problems encountered at Monash (Flem et al., *in prep*) however, P^{31} that in theory may be analysed in MR-mode, is difficult to properly ionise and only irrelevantly high LOD's can be obtained.

6.3 Contamination

Contamination may be divided into atmospheric contaminations, contaminations by elements inherited from previous analysis and contaminations caused by parts in the mass spectrometer or the laser ablation unit.

Atmospheric air is saturated with Na and, particularly if the mass spectrometer is situated close to the sea, Na can not be analysed unless it is present in hundreds of ppm in the ablated sample. In contrast Pb which may be expected as a common contaminant apparently did not influence the analysis. Other environmental pollutants such as Hg and Cd were not included in the analytical program at Monash. Average LOD for Na over a month was 100-500 ppm.

The high LOD for Al may be an effect of the cleaning procedure used to rinse the cones because aluminium oxide powder normally is used for this purpose.

Inherited contaminants include elements that occurred abundantly in samples that were analysed before quartz and could not be entirely removed when rinsing the mass spectrometer with acid solutions. Most elements will disappear over a day or two but certain elements apparently have a 'sticky' quality so that they attach to various parts of the instrument, primarily the cones. Li and B are particularly problematic, not only after the analysis of $Li_2B_4O_7$ fused glass disks, that of course are very rich in Li and B, but also after solution ICP-MS of aqueous solutions with only a few tens of ppm of Li. Analysis at NGU has already demonstrated the extend of this problem and at VIEPS, we confirmed this fundamental problem and eventually had to discontinue analysis of B isotopes. Use of specific high-quality cones that are dedicated to quartz analysis reduced the background signal for Li and B somewhat, but not sufficiently. Typical detection limits for Li are 5-30 ppm whereas the typical concentration in quartz often is lower. However, the quartz samples from Evje-Iveland appeared to have very high concentrations of Li and, therefore, were included in the final analysis.

Contamination from parts in the mass spectrometer was a minor problem although Ni could not be analysed due to high concentrations of this element in the cones.

6.4 Preliminary results from quartz analysis

Granite pegmatite quartz from 20 localities was analysed. Single spot analysis comprises the average of 6 analyses in one quartz section in order to compensate for inhomogeneities. Only one raster analysis was produced since, covering an area equivalent of 20 or more single spot analysis, rastering compensates for micron-scale inhomogeneities.

Given the problems with interference and contamination outlined above only 15 of the elements included in the original list of 21 isotopes gave significant results. Although Li produced high LOD's, this element is included (Table 4) because many quartz samples contained concentrations that were significantly above LOD.

Otherwise, it may be noted that there are reasonable agreements between raster and spot analysis in the same quartz samples. In most cases, the concentration obtained by raster analysis falls in the range obtained by single spot analysis.

A detailed evaluation of the results is beyond the scope of the present report but will follow in a later communication.

Table 4: Preliminary results from spot and ratser analysis in ppm. *not analysed, lod, limit of detection

PPM	96004	96006	96007	96008	96009	96010	96012	96014	96016	96017
Li raster	15	28	10	11	8	8	30	lod	17	13
Li spot	19	*	*	*	*	*	lod	lod	lod	16
Li range	9-40	*	*	*	*	*	lod	lod	lod	10-22
Be raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Be spot	lod	*	*	*	*	*	lod	lod	lod	lod
Be range	lod	*	*	*	*	*	lod	lod	lod	lod
Al raster	109	123	lod	lod	103	lod	94	lod	lod	lod
Al spot	132	*	*	*	*	*	32	28	23	32
Al range	86-151	*	*	*	*	*	26-36	16-57	13-34	26-36
Ge raster	lod	0.278	lod	lod	lod	0.209	lod	0.204	lod	0.317
Ge spot	1.69	*	*	*	*	*	2.89	3.22	lod	lod
Ge range	1.3-2.4	*	*	*	*	*	2.7-3.3	2.9-3.6	lod	lod
Rb raster	lod	0.033	lod	lod	lod	lod	lod	lod	lod	lod
Rb spot	lod	*	*	*	*	*	lod	lod	lod	lod
Rb range	lod	*	*	*	*	*	lod	lod	lod	lod
Sr raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Sr spot	lod	*	*	*	*	*	lod	lod	lod	lod
Sr range	lod	*	*	*	*	*	lod	lod	lod	lod
Y raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Y spot	lod	*	*	*	*	*	lod	lod	lod	lod
Y range	lod	*	*	*	*	*	lod	lod	lod	lod
Zr raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Zr spot	lod	*	*	*	*	*	lod	lod	lod	lod
Zr range	lod	*	*	*	*	*	lod	lod	lod	lod
Nb raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Nb spot	lod	*	*	*	*	*	lod	lod	lod	lod
Nb range	lod	*	*	*	*	*	lod	lod	lod	lod
Cs raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	0.016
Cs spot	lod	*	*	*	*	*	lod	lod	lod	lod
Cs range	lod	*	*	*	*	*	lod	lod	lod	lod
Ba raster	0.235	lod	lod	lod	0.133	lod	lod	lod	lod	0.140
Ba spot	lod	*	*	*	*	*	2.77	lod	lod	2.01
Ba range	lod	*	*	*	*	*	0.84-3.6	lod	lod	0.7-3.5
Pb^{207} raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Pb^{207} spot	lod	*	*	*	*	*	lod	2.40	lod	lod
Pb^{207} range	lod	*	*	*	*	*	lod	lod	lod	lod
Pb^{208} raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Pb^{208} spot	lod	*	*	*	*	*	lod	lod	lod	lod
Pb^{208} range	lod	*	*	*	*	*	lod	lod	lod	lod
U raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
U spot	0.021	*	*	*	*	*	lod	lod	lod	lod
U range	0.013-0.029	*	*	*	*	*	lod	lod	lod	lod

Table 4 continued

PPM	96019	96022	97023	97026	97030	97032	97036	97041	97045	97052
Li raster	21	17	16	17	11	28	19	21	17	19
Li spot	9	*	lod	5	lod	5	10	lod	25	14
Li range	5-13	*	lod	5	lod	2-8	8-14	lod	20-31	13-16
Be raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Be spot	lod	*	lod	5	lod	lod	32234	20340	lod	lod
Be range	lod	*	lod	3-7	lod	lod	27-39	9-36	lod	lod
Al raster	98	lod	lod	lod	70	135	61	62	75	60
Al spot	93	*	75	36	70	164	285	75	85	58
Al range	86-103	*	27-108	30-46	31-80	144-199	61-565	44-116	61-106	39-72
Ge raster	lod	lod	0.246	0.163	lod	0.369	0.140	0.147	0.136	0.237
Ge spot	lod	*	3.02	1.16	1.11	2.82	1.85	lod	lod	lod
Ge range	lod	*	2.8-3.3	0.7-1.6	0.7-1.5	2.2-3.2	1.5-2.1	lod	lod	lod
Rb raster	lod	lod	lod	lod	0.017	0.039	lod	lod	lod	0.046
Rb spot	lod	*	lod	lod	lod	1.13	lod	lod	lod	lod
Rb range	lod	*	lod	lod	lod	0.9-1.3	lod	lod	lod	lod
Sr raster	lod	lod	0.043	lod	lod	0.048	0.101	lod	lod	lod
Sr spot	lod	*	0.85	0.21	lod	lod	lod	lod	lod	lod
Sr range	lod	*	0.15-1.4	0.1-0.27	lod	lod	lod	lod	lod	lod
Y raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Y spot	lod	*	lod	lod	lod	lod	lod	lod	lod	lod
Y range	lod	*	lod	lod	lod	lod	lod	lod	lod	lod
Zr raster	lod	lod	lod	lod	lod	0.020	0.033	lod	lod	lod
Zr spot	lod	*	0.30	lod	lod	0.13	lod	lod	lod	lod
Zr range	lod	*	0.08-0.6	lod	lod	0.045-0.21	lod	lod	lod	lod
Nb raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Nb spot	lod	*	0.740	lod	lod	lod	lod	lod	lod	lod
Nb range	lod	*	0.033-1.6	lod	lod	lod	lod	lod	lod	lod
Cs raster	0.020	lod	lod	lod	lod	0.016	lod	lod	0.015	lod
Cs spot	0.165	*	lod	lod	lod	0.457	lod	lod	lod	lod
Cs range	0.15-0.2	*	lod	lod	lod	0.17-0.9	lod	lod	lod	lod
Ba raster	lod	lod	0.054	0.053	lod	0.821	2.060	lod	lod	lod
Ba spot	lod	*	25.45	4.91	4.18	14.48	28.20	lod	lod	18.56
Ba range	lod	*	3.5-39	2.7-7.5	0.28-8.4	3.4-26	lod	lod	lod	4.5-32
Pb^{207} raster	lod	lod	lod	lod	lod	0.028	0.181	lod	lod	lod
Pb^{207} spot	lod	*	2.32	0.61	lod	0.86	lod	lod	lod	lod
Pb^{207} range	lod	*	1.0-3.4	0.52-0.73	lod	lod	lod	lod	lod	lod
Pb^{208} raster	lod	lod	lod	lod	lod	0.0294	0.1615	lod	lod	lod
Pb^{208} spot	lod	*	1.63	0.61	lod	0.50	lod	lod	lod	1.30
Pb^{208} range	lod	*	0.27-2.9	0.52-0.92	lod	0.23-0.78	lod	lod	lod	0.69-1.6
U raster	lod	lod	0.0299	lod	lod	0.00709	lod	lod	lod	0.00297
U spot	lod	*	lod	lod	lod	lod	lod	lod	lod	lod
U range	lod	*	lod	lod	lod	lod	lod	lod	lod	lod

Table 4 continued

PPM	97059	97066	97070	97084	97088	97093	97097	97101	97104	97109
Li raster	18	19	22	18	15	22	lod	lod	6	12
Li spot	17	lod	lod	120	107	18	*	*	*	*
Li range	11-23	lod	lod	101-131	106578	11-26	*	*	*	*
Be raster	lod	lod	lod	lod	lod	lod	45.79609	38.28849	lod	lod
Be spot	lod	24	lod	lod	lod	lod	*	*	*	*
Be range	lod	14-40	lod	lod	lod	lod	*	*	*	*
Al raster	lod	83	lod	lod	lod	102	59	75	175	lod
Al spot	43	229	110	lod	lod	97	*	*	*	*
Al range	27-48	107-459	79-137	lod	lod	72-122	*	*	*	*
Ge raster	0.254	0.188	0.270	lod	0.179	0.263	lod	lod	0.239	0.331
Ge spot	2.30	lod	lod	lod	lod	1.76	*	*	*	*
Ge range	2.1-2.5	lod	lod	lod	lod	1.4-2.3	*	*	*	*
Rb raster	lod	0.010	lod	0.024	lod	lod	lod	lod	0.094	lod
Rb spot	lod	lod	lod	lod	lod	lod				
Rb range	lod	lod	lod	lod	lod	lod	*	*	*	*
Sr raster	lod	lod	lod	0.019	0.022	lod	lod	lod	0.056	lod
Sr spot	lod	lod	lod	lod	lod	lod	*	*	*	*
Sr range	lod	lod	lod	lod	lod	lod	*	*	*	*
Y raster	lod	lod	lod	0.007199	lod	lod	lod	lod	lod	lod
Y spot	lod	lod	lod	lod	lod	lod	*	*	*	*
Y range	lod	lod	lod	lod	lod	lod	*	*	*	*
Zr raster	lod	lod	lod	0.008	lod	lod	lod	lod	0.016	lod
Zr spot	lod	lod	lod	lod	lod	lod	*	*	*	*
Zr range	lod	lod	lod	lod	lod	lod	*	*	*	*
Nb raster	lod	lod	lod	lod	lod	lod	lod	lod	lod	lod
Nb spot	lod	0.246	lod	lod	lod	lod	*	*	*	*
Nb range	lod	0.16-0.34	lod	lod	lod	lod	*	*	*	*
Cs raster	lod	lod	lod	lod	lod	lod	lod	lod	0.044	lod
Cs spot	lod	lod	lod	lod	lod	lod	*	*	*	*
Cs range	lod	lod	lod	lod	lod	lod	*	*	*	*
Ba raster	lod	lod	0.015	0.276	0.284	0.074	lod	0.189	0.939	lod
Ba spot	8.92	27.68	lod	lod	5.56	9.96	*	*	*	*
Ba range	5.6-14	12-59	lod	lod	4.4-6.5	4.5-14	*	*	*	*
Pb^{207} raster	lod	lod	lod	lod	0.022	lod	lod	0.048	0.088	lod
Pb^{207} spot	1.04	lod	lod	lod	lod	lod	*	*	*	*
Pb^{207} range	0.81-1.5	lod	lod	lod	lod	lod	*	*	*	*
Pb^{208} raster	lod	lod	lod	0.0169	0.0254	lod	lod	0.0480	0.0905	lod
Pb^{208} spot	1.16	2.01	lod	lod	0.43	0.89	*	*	*	*
Pb^{208} range	0.85-1.7	0.85-4.9	lod	lod	0.31-0.64	0.57-1.2	*	*	*	*
U raster	lod	lod	lod	0.00281	lod	lod	lod	lod	0.0566	lod
U spot	lod	lod	lod	lod	lod	lod	*	*	*	*
U range	lod	lod	lod	lod	lod	lod	*	*	*	*

Table 4 continued

PPM	97120	97130	97130	97132
Li raster	lod	lod	5	lod
Li spot	lod	*	*	*
Li range	lod	*	*	*
Be raster	lod	lod	lod	lod
Be spot	lod	*	*	*
Be range	lod	*	*	*
Al raster	lod	lod	lod	lod
Al spot	lod	*	*	*
Al range	lod	*	*	*
Ge raster	lod	lod	lod	lod
Ge spot	lod	*	*	*
Ge range	lod	*	*	*
Rb raster	lod	lod	lod	lod
Rb spot	lod	*	*	*
Rb range	lod	*	*	*
Sr raster	lod	lod	lod	lod
Sr spot	lod	*	*	*
Sr range	lod	*	*	*
Y raster	lod	lod	lod	lod
Y spot	lod	*	*	*
Y range	lod	*	*	*
Zr raster	lod	lod	lod	lod
Zr spot	lod	*	*	*
Zr range	lod	*	*	*
Nb raster	lod	lod	lod	lod
Nb spot	lod	*	*	*
Nb range	lod	*	*	*
Cs raster	lod	lod	lod	lod
Cs spot	lod	*	*	*
Cs range	lod	*	*	*
Ba raster	lod	lod	0.035	0.027
Ba spot	lod	*	*	*
Ba range	lod	*	*	*
Pb^{207} raster	lod	lod	lod	lod
Pb^{207} spot	lod	*	*	*
Pb^{207} range	lod	*	*	*
Pb^{208} raster	lod	lod	lod	lod
Pb^{208} spot	lod	*	*	*
Pb^{208} range	lod	*	*	*
U raster	lod	lod	lod	0.00210
U spot	0.484	*	*	*
U range	0.23-1.0	*	*	*

7. CONCLUSIONS AND RECOMANDATIONS

- Laser ablation analysis of quartz was facilitated by a UV-laser system adapted to a High Resolution Inductively Coupled Mass Spectrometer at Monash University, Australia
- In a complete analytical package meeting the requirements from most of the industry concerned with high purity quartz, the following elements must be included: Al, B, Ca, Cr, Cu, Fe, Ge, K, Li, Mg, Mn, Na, P, Pb, Rb, Ti and U.
- The method developed at Monash obtained promising results for Al, B, Ge, Li, Fe, Pb, Rb, and U from this list and also for Be, Ba, Nb, Y, Zr and Th. LOD's for some elements, particularly Al, Li, Cu, Mn and B are too high but fine tuning of the instrument and better matrix matched external standards at NGU have already improved LOD's for these elements considerably. Li and B can be analysed with even better LOD's if specific cones are reserved for quartz analysis only.
- Ge can be analysed in LR-mode if Ge^{74} is analysed rather than Ge^{72}. Mg, Sc, Ti, Cr, Fe can be analysed in MR-mode and K in HR-mode. A method that analyses these isotopes in MR and HR mode is currently being tested at NGU with good results. P can not be analysed because of its high ionisation potential and alternative isotopes do not exist. Na can not be analysed because atmospheric air which is soaked in to the carrier gas and inherited contamination from solutions ICP-MS induces LOD's higher than 100 ppm. However, for most quartz it may be assumed that the following equation, expressing the molar concentration of structurally bound Al, Li and Na in igneous quartz and most hydrothermal quartz, is valid (e.g. Dennen, 1966)

  $$[Al] = [Li] + [Na] \quad (\text{in mol\%})$$

  Accordingly, the concentration of Na may be approximated if the concentration of Al and Li is known. This approach may suffice for many applications.

With the results from VIEPS and the current improvements of the method completed at NGU, it may be concluded that standardised LA-analysis of quartz is within reach. A method analysing Al, B, Ba, Be, Cu, Ge, Li, Fe, Pb, Rb, U, Y, Zr, Nb and Th in LR-mode, Mg, Sc, Ti, Cr and Fe in MR-mode and K in HR-mode (Table 2) will probably be most attractive in prospecting for new high purity quartz deposits or when expanding/exploring an existing quarry for its HPQ potential. Avoidance of crushing, flotation, magnetic separation and or handpicking of quartz provides a cost efficient and rapid method.

Accordingly, the method is recommended when the concentration of structural impurities (and sub-microscopic inclusion), before acid leach, is required. After acid leach, LA-analysis may still be applied on grain mounts although, if a pure quartz concentrate is available, conventinal solution HR-ICP-MS is more beneficial.

8. REFERENCES

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