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1	Capabilities of sequential and quasi-simultaneous LA-ICPMS for the multi-element analysis
2	of small quantity of liquids (pl to nl): insights from fluid inclusion analysis
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18 19	Abstract
20	Three configurations of inductively coupled plasma mass spectrometers (ICPMS), namely: a
21	quadrupole (QMS) and a sector-field (SFMS), both equipped with a standard cylindrical
22	ablation cell, and an orthogonal time-of-flight (TOFMS), equipped with a fast washout
23	ablation cell, were coupled with the same 193 nm Excimer laser ablation system in order to
24	evaluate their capabilities for measurement of multiple minor and trace elements in small
25	quantities of liquids (pl to nl), such as fluid inclusions. Analyses were performed with
26	different objects: (i) multi-element solutions sealed in silica capillaries of internal diameter of
27	20 µm serving as synthetic analogues of natural fluid inclusions; (ii) natural two-phase (liquid
28	+ vapour) fluid inclusions with low salinity (ca. 4.8 wt% NaCl eq) and homogeneous
29	compositions, trapped in quartz crystals from the Alps; (iii) natural multi-phase (liquid +
30	vapour + multiple solids) fluid inclusions with high salinity (ca. 13-15 wt% NaCl eq) and
31	homogeneous compositions, trapped in quartz crystals from the Zambian Copperbelt. This

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magnitude compared to OMS and TOFMS, but precision and accuracy are lower due to longer acquisition cycle times. TOFMS presents both advantages of having rapid and quasisimultaneous acquisition for all isotopes from ⁶Li to ²³⁸U in a very short cycle time down to μ s, with higher precisions and lower LODs than for QMS for isotopes with m/Q > 11. Its use, coupled to a fast washout cell, leads to (i) the improvement in the analysis of small-size (< 10 µm) and multi-phase fluid inclusions and (ii) detection of higher number of isotopes compared to QMS and SFMS, which are both limited by the number of measured isotopes from short transient signals of fluid inclusions. Consequently, the tested TOFMS, coupled with a fast washout ablation cell, appears to be a promising instrument for the analysis of natural fluid inclusions by LA-ICPMS, especially for small, multi-phase and/or low salinity fluid inclusions.

47 1. Introduction

The multi-element quantification of minor and trace elements, typically present in concentrations from the ng l^{-1} to g l^{-1} range, in small quantities of liquids (pl to nl) is of a major analytical interest for a large variety of applied fields, for instance in chemistry^{1,2}, $geology^{3-8}$, biology⁹, medicine^{10,11}, climatology¹² or environmental sciences¹³. One current analytical challenge is to improve and to develop strategies for analyses of such small quantities of liquid, whether by: (1) reducing the detectable fluid volume; (2) increasing the number of detectable elements; (3) increasing the sensitivity of the instruments and/or (4) increasing the precision and accuracy of the measurements. For example, a recent research field has been developed on the detection and quantification of nanoparticles carried by liquid microdroplets, in order to study the risks of nanoparticles for the environment and the human health.^{1,14} Such microdroplets have a typical diameter of 30-40 µm and generate very short transient signals when analysed by inductively coupled mass spectrometry, and remain a challenging analytical issue.^{1,14}

One of the most challenging case studies are the geological fluids trapped in natural fluid inclusions. The latter represent droplets of fluids, ranging from pl to nl in volume, and trapped in tiny cavities of typically tens of μ m in diameter during the crystallization of minerals. Natural fluid inclusions can consequently provide direct information about the composition of fluids from which minerals have precipitated and represent therefore invaluable tool for the reconstruction of the geological fluids, which have circulated in the Earth's interior for ca. 4.6

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68 billions years¹⁵. They are of primary interest for a large set of geological research fields, in 69 particular for the study of diagenesis¹⁶, metamorphism^{17,18}, geothermal systems^{19,20}, oil and 70 gas deposits^{21,22} and mineral deposits²³⁻²⁶. Natural geological fluids are characterized by an 71 extremely wide variety of chemical elements, potentially from Li to U, with varying 72 concentration ranges from percent to below $\mu g g^{-1}$, and their analysis represents consequently 73 high analytical challenge.

Due to its high sensitivity, speed and multi-element capabilities, laser ablation coupled to inductively coupled plasma quadrupole mass spectrometers (LA-ICPQMS, hereafter called QMS) has proven²⁷ to be one of the most suitable techniques for the analysis of geological fluids trapped in natural crystals (see review in Pettke et al.⁶). This technique offers several advantages compared to other instrumentations (LIBS, synchrotron-XRF or PIXE for example), like well-controlled ablation of guartz using UV lasers²⁸, the large concentration dynamic range (10⁹ to 10¹¹), the relatively low limits of detection (down to 0.01 μ g g⁻¹)⁶ and fast acquisition times (in the ms range per isotope). At the present time, sequential scanning QMS typically allows registering 20 isotope signals with m/Q from 7 to 238 in less than 260 ms in a single mass scan.⁶ The development of specific quantification strategies to evaluate the elemental concentrations by QMS was also a major cause of the increasing acceptance of LA-ICPMS in fluid inclusion research.^{3-5,29-30}

The signals generated in QMS from this type of tiny samples are usually of relatively low intensity for minor to trace elements and last only for several seconds due to the rapid release of the fluid during the ablation process.²⁸ Unambiguous multi-element detection of such transient signals is not a trivial task when sequential quadrupole mass spectrometers are used and often requires a compromise between the signal duration, acquisition parameters of the mass spectrometer and the number of isotopes to be monitored.^{4-6,31} The current use of QMS is consequently restricted to relatively large-size (> 30 µm) and moderate- to high-salinity (> 5 wt% NaCl eq) fluid inclusions, which contain detectable concentrations of the analytes.⁴⁻⁶ However, this type of fluid inclusions represents a rather limited proportion of the fluid inclusions present in natural samples and are potentially more affected by post-crystallization modifications (e.g. leaking, cracks and/or deformation) than smaller ones. Moreover, even for such samples, the number of isotopes that can be monitored rarely exceeds 20, including majors, minors and trace elements. This can consequently makes a global and representative understanding of the chemical composition of paleofluids difficult. Furthermore, analytical limitations are encountered for small-size (< 10 µm) fluid inclusions as well as for those

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101 containing low trace element contents (< 1 μ g g⁻¹), thus constraining the interpretation of 102 several geological processes related to paleofluids circulations.

Other types of mass spectrometers coupled to laser ablation systems have been tested during the last years, with the aim of improving the quantification of elemental and even isotopic compositions of geological fluids (see review of Pettke *et al.*⁶). Single-collector sector-field mass spectrometers coupled to laser ablation (LA-ICPSFMS, hereafter called SFMS) have achieved about ten times higher sensitivities compared to QMS instrumentation for natural fluid inclusions.³¹ However, QMS and SFMS are both limited by sequential detection, which can deteriorate accuracy and precision of the analysis due to signal aliasing.^{14,32} Moreover, SFMS are also limited by the multiple magnet jumps required to cover the entire mass range from Li to U, which results in longer cycle times compared to QMS, with around 20% longer cycle for 20 isotopes measured. This temporal limitation could appear as a main drawback especially for small fluid inclusions (< 20 μ m), but the recent study by Wälle and Heinrich³¹ concluded that SF expands the accessible fluid inclusion size range to 2 or 3 times smaller volumes or 10 times lower concentrations in larger inclusions.

One application of multi-collector mass spectrometers coupled to laser ablation (LA-MC-ICPMS) was recently successfully proposed for the determination of Pb isotopic ratios in natural fluid inclusions.³³ However, the small volume of fluid trapped is a major limitation for the precise measurement of isotopic ratios. Even with a multi-collection and high sensitivity, the extremely limited duration of the signal and the relatively low concentration allow successful results only for exceptional geological conditions, for example for the Bingham Cu-Mo-Au deposit.³⁴ Even if LA-MC-ICPMS present far lower limits of detection than QMS, they do not allow the acquisition of the whole mass spectra, which is a strong limitation for fluid inclusion studies, especially with the need to measure an internal standard (mainly ²³Na) for the quantification of the fluid compositions.⁴

Detection based on time-of-flight mass spectrometers coupled to laser ablation (LA-ICPTOFMS, hereafter called TOFMS) has been considered highly promising for multi-element analysis of very short transient signals, because it allows quasi-simultaneous measurements of all isotopes.³⁵ This configuration of a mass spectrometer allows overcoming the problem of aliasing for short transient signals and could consequently improve the quantification of fluids trapped in natural minerals.^{14,36,37} First generations of TOFMS with an axial configuration applied to natural fluid inclusions had lower sensitivities, low signal to noise ratio, low dynamic range and higher limits of detection compared to QMS.^{4,39} Nevertheless, previous study on multiphase fluid inclusions from the Mole granite³⁸

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demonstrated the abilities of axial TOFMS for the detection of up to 42 isotopes above the LODs, as well as the discrimination of signals of elements contained in fluid or in solid matrices. Recently, a new prototype of TOFMS with an orthogonal configuration has been developed^{14,36}, which allows quasi-simultaneous detection of the whole mass range, with a high temporal resolution of 30 μ s, a mass resolving power > 1200, a dynamic range of 10⁶ and abundance sensitivity of 10⁻⁵. This instrument was shown to be of particular use for extremely short transient signals (tens of us up to ms range) generated by nanoparticles and microdroplets. Coupling this new TOFMS with laser ablation systems providing low signal dispersion⁴⁰ can lead to increased signal to noise ratios. Other types of simultaneous and quasi-simultaneous mass analysers exist, such as the Mattauch-Herzog sector-field mass spectrometer (MHMS)^{41,42} or the ICPTOFMS Optimass⁴³, respectively. However, no data are currently available from these instruments for the analysis of minor and trace elements in small quantity of liquids.

The aim of the present study is to describe and determine the capabilities of SFMS and TOFMS for the analysis of fluid inclusions and to compare them to QMS, which is the state-of-the-art and the most frequently used instrument for the measurements of fluid inclusions by LA-ICPMS. In this objective, two types of samples have been analysed and the three instruments were evaluated and compared in terms of signal duration, intensity, precision, accuracy (when possible) and limits of detection (LODs). The first set of objects was consisting of sealed 20 um inner diameter silica capillaries, containing multi-element (33 to 37) solutions with different set of concentrations (0.1, 1, 10 and 50 μ g g⁻¹) and with Na fixed at a concentration of ca. 1000 μ g g⁻¹. These capillaries mimic the configurations of small volumes of liquid trapped in a solid matrix, such as natural fluid inclusions, and have already been applied successfully to standardize the fluid inclusion analysis by LA-ICPMS.^{44,45} They allow determining the achievable accuracy of the measurements for different concentrations of trace elements, as they are filled with solutions of known elemental concentrations. They moreover exhibit a much higher reproducibility compared to natural fluid inclusions, due to their fixed geometry and to their constant behaviour during laser ablation. A second set of objects are natural fluid inclusions selected from two origins and trapped within quartz crystals: (i) the first sample (BP-66-210, Alps) contains numerous two-phase (liquid + vapour) and low salinity fluid inclusions, with a homogeneous composition and variable diameters (from 5 to 100 μ m), allowing to test precision and LODs of the three LA-ICPMS configurations for a wide range of fluid volumes; (ii) the second sample (7703-25, Zambia) contains multi-phase (liquid + vapour + solids) and high salinity fluid inclusions, but with a

169 smaller range of diameters (10 to 30 μ m). The presence of several phases, including 170 precipitates, makes the interpretation of the signals obtained for these inclusions with 171 sequential ICPMS more challenging. In this respect, the capabilities of the TOFMS have been 172 tested compared with QMS for the distinction between elements contained in fluid and solids 173 and consequently for a better multi-elemental quantification of complex fluid inclusions.

175 2. Experimental

 2.1. Instrumentation, operating conditions and data processing

All analyses were carried out at the Laboratory of Inorganic Chemistry at ETH Zürich (Switzerland). Three different configurations of LA-ICPMS were used for this study: a quadrupole (OMS) (Elan DRC Plus, PerkinElmer Inc., Ontario, Canada), a sector-field (SFMS) (Element 2, ThermoScientific, Bremen, Germany) and a prototype of time-of-flight (TOFMS) (Tofwerk AG, Thun, Switzerland). This prototype had been developed, by coupling an orthogonal TOF mass analyser (Tofwerk AG, Thun, Switzerland) with the ICP and vacuum interface of a commercial quadrupole-based ICPMS (Elan 6000, PerkinElmer/Sciex, Ontario, Canada) (see Borovinskaya et al.¹⁴ for details). The same laser ablation system, namely a 193 nm GeoLas ArF Excimer (MicroLas, Göttingen, Germany), was coupled to the three ICPMS systems. A standard cylindrical ablation cell with relatively large internal volume was used for both QMS and SFMS configurations, as traditionally used for the analysis of fluid inclusions by sequential instruments.^{4,6,28,31} For the TOFMS, a low dispersion tube cell, developed by Wang et al.⁴⁰, was used, which provides a higher signal to noise ratio per single laser pulse and can reduce the signal duration to less than 30 ms. Its use with a sequential mass spectrometer instrument, like QMS and SFMS, is problematic because signal aliasing will strongly deteriorate the attainable precision.³² However, it is particularly beneficial in the case of TOFMS, by strongly increasing the signal/noise ratio, as shown in recent studies.^{40,46} The cycle time in this paper is resembling the time necessary to produce a single data point in the transient signal. For sequential instruments, such as QMS and SFMS, the cycle time is given by the number of measured isotopes and by the time necessary for the analysis of each isotope (dwell time), plus the time necessary for the change of scanning mass windows (settling time). The Element 2 was configured to achieve lowest possible magnet settling times, reducing the cycle time by about a factor of two compared to the manufacturer

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technical recommendations. For the configuration of TOFMS used, the quasi-simultaneous acquisition of all isotope signals is performed in 30 µs (cycle time). In our experiments, 1000 of these extractions were integrated before every data point was read out to reduce the total amount of data generated.¹⁴ For simplicity, the cycle time for TOFMS in the text will be considered as 30 ms. The reader should, however, keep in mind that every cycle is an average of 1000 TOF extractions. The standard reference material NIST SRM 610 (reference values from Jochum *et al.*⁴⁷) was used as external standard for the calibration of all analyses, and was analysed twice at the beginning and at the end for each set of samples to establish elemental sensitivity and to correct for instrumental drift.²⁹

Operating conditions are given in Table 1, and are different between the measurement of multi-element solution in silica capillaries and the two types of natural fluid inclusions analysed (see 2.2 for sample description). Laser ablation of silica capillaries (see 3.1.) was realised with a frequency of 10 Hz, a laser spot diameter fixed at 32 µm and a theoretical fluence of 124 J cm⁻² per pulse. Laser ablation of fluid inclusions (see 3.2. and 3.3.) was realised with a frequency of 10 Hz and using a stepwise opening procedure, as described in Günther *et al.*³, starting the ablation with a laser spot diameter of 2 μ m and stepwise increasing the spot diameter to the size of the fluid inclusion (from 5 to 90 µm), with a theoretical fluence between 16 and 500 J cm⁻² per pulse. This procedure allows a controlled ablation by reducing the mechanical stress on the quartz surface, which limits the risk of splashing of the fluid.³ LA-ICPMS were optimized for highest sensitivity for an intermediate m/Q range, while maintaining a ThQ/Th < 0.5%, U/Th ~ 1 and $Ba^{2+}/Ba^{+} < 3\%$, as determined on NIST SRM 610. Instrumental background signals (only from the gas blank) were measured for 20 s before each ablation for background correction and calculation of the limits of detection.²⁹ Helium was used as the carrier gas to transport the ablated material from the ablation cell to the ICPMS and argon was added via a laminar flow adapter before the ICP torch.⁴⁸ For the fast washout cell, a combination of argon and helium is used directly in the cell and so no additional make-up gas was used.⁴⁰ To increase the apparent magnet settling time on the Element 2, without increasing the actual magnet settling time, ²²Ne was introduced as a support mass. The earlier magnet settling together with the measurement time spent on ²²Ne helped to stabilise the magnet and improved the precision of the ²³Na intensity (measured using a E-Scan). For consistency, the support mass ²²Ne was also measured on the QMS. Due to a very high background, originating from previous experiments, the quantification of ¹¹B was compromised with the SFMS. Operating conditions for the TOFMS were chosen to maximize the transmission of high m/Q trace element isotopes thus

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compromising the transmission of ions below m/Q = 9 within the notch filter upstream the TOFMS. Therefore, the sensitivity of these ions (including ⁷Li) was insufficient for their detection at the concentrations used. Signal integration and absolute quantification were performed using the software StalQuant, developed at ETH Zürich (see details in Fricker49). The LODs were calculated according to the equation of Longerich et al.²⁹, since it is the most frequently method used in publications dealing with natural and synthetic fluid inclusions. For all analyses of silica capillaries and fluid inclusions, ²³Na was used as the internal standard for the quantification. For fluid inclusions, the Na content was estimated from the wt.% equivalent NaCl as determined by microthermometry.⁵⁰ Signal integration for capillaries and fluid inclusions was set on the basis of the Na total signal duration.

2.2. Materials

Three in-house multi-element solutions containing 33 elements (Li, B, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Sr, Nb, Ag, Cd, In, Sn, Ba, La, Tb, Hf, Ta, W, Pt, Tl, Pb, Bi, U) at concentrations of ca. 0.1, 1 and 10 μ g g⁻¹ each (except Na fixed at ca. 1000 μ g g⁻¹) were prepared in 1% HNO₃ from single- and multi-element standard solutions (Inorganic Ventures, Merck). An in-house multi-element solution containing 37 elements (the 33 elements cited above + Rb, Cs, Ba and Sb) at a concentration of ca. 50 μ g g⁻¹ (except Na which was fixed at ca. 1000 µg g⁻¹) was also prepared. Silica capillaries (Photon Lines SAS, St-Germain-en-Lave, France) with an internal and external diameter of 20 µm and 150 µm respectively, and of ca. 1 cm length were filled with the solutions by capillarity and the ends were tipped with paraffin wax for sealing. An internal diameter of 20 µm was selected to mimic the typical size of natural fluid inclusions analysed by LA-ICPMS. Two types of natural fluid inclusions were selected from two different quartz samples for this study: (i) Two-phase (liquid + vapour) fluid inclusions from a quartz crystal from the French Alps (sample BP-66-210, Mont Blanc Massif, Pointe des Améthystes, see Fabre⁵¹ for description). This sample contains numerous fluid inclusions, which are considered to be homogeneous in composition, as already shown by previous studies^{45,51-53} of fluid inclusions in similar quartz crystals from the Mont Blanc Massif. These fluid inclusions have irregular shape and range from a few microns to 100 µm in diameter (Fig. 1a) and consequently from a few hundred pl to tens of nl in volume. At room temperature they are characterized by a dominant liquid aqueous phase with dissolved salts and a vapour phase of H2O-CO2-N2 as determined by Raman spectroscopy, and no daughter minerals.⁵¹ All fluid inclusions have a relatively homogeneous salinity of 4.8 ± 0.5

wt% NaCl equivalent as determined by microthermometry prior to LA-ICPMS analysis. The characteristics of its fluid inclusions (homogeneity in chemical composition and variability in size) make this sample a perfect experimental case study for the analytical comparison of the three LA-ICPMS setups; (ii) Multi-phase (liquid + vapour + multiple solids) fluid inclusions were selected from a quartz crystal from the western Zambian Copperbelt (sample 7703-25, Kabompo domes, Lolwa occurrence, see Eglinger et al.^{54,55} for description). These fluid inclusions show irregular shape and range from 10 to 30 µm in diameter (Fig. 1b). They contain a dominant aqueous phase with dissolved salts, a vapour phase of $H_2O-N_2-H_2$ determined by Raman spectroscopy and numerous solids previously identified by Raman spectroscopy as calcium chloride hydrates, halite (NaCl), hematite (Fe₂O₃) and calcite (CaCO₃), plus other unidentified solids (Fig. 1b). All fluid inclusions have a high, relatively homogeneous salinity of 53-59 wt% CaCl₂ and 13-15 wt% NaCl equivalent as determined by microthermometry and their detailed composition, as determined by LA-ICPQMS, is given by Eglinger et al.⁵⁴ This sample was used in order to test the capabilities of the TOFMS for analysing complex, multi-phase and high-salinity fluid inclusions compared with the QMS. No analyses were performed with SFMS on this sample.

287 3. Results and discussion

- 289 3.1. Silica capillaries290
- *3.1.1. Signals*

Typical transient LA-ICPMS signals obtained from silica capillaries containing multi-element solutions of ca. 10 μ g g⁻¹ concentration are shown in Fig. 2. The oscillations observed in the transient signals from the TOFMS acquisition (Fig. 2c) corresponds to the 10 Hz frequency of the laser and demonstrates the low aerosol dispersion of the transport system employed with the short cycle time used (30 ms). The signal durations for the capillaries (determined based on the ²³Na signal) are typically longer than 20 s for the high dispersion transport system used for QMS and SFMS, while this is reduced to about 4 s for the tube cell used for TOFMS. With a cycle time of 468 ms for QMS, 887 ms for SFMS and 30 ms for TOFMS, the signal durations correspond to ca. 47, 27 and 133 data points respectively. Peak signal/background ratios for ²³Na are similar for the three setups, with ca. 5×10^3 for QMS, 6×10^2 for SFMS

and 10^3 for TOFMS. For the four tested solutions, the lighter isotopes (⁷Li and ¹¹B) are barely detected by TOFMS due to the optimization setting used for these experiments (see 2.1.). At high concentrations (ca. 50 µg g⁻¹), all elements added to the solutions are detected by QMS, SFMS and TOFMS, except for ¹¹B by SFMS and ⁷Li by TOFMS (due to elevated backgrounds). At low concentrations (ca. 0.1 µg g⁻¹), only isotopes with m/Q > 88 are detected on average by QMS and SFMS, whereas TOFMS detects only isotopes with m/Q > 309 139.

3.1.2. Precision and accuracy

The precision and accuracy were calculated from means and standard deviations for a series of measurements of different silica capillaries (n = 4 to 7) for each solution (0.1, 1, 10, 50 μ g g⁻¹) and for all the isotopes listed in Table 2. The precision is represented by the relative standard deviation (RSD) expressed in % for a series of measurements and is defined by equation (1).

$$819 \quad (1) \qquad RSD_i = \frac{s_i}{m_i} \times 100\%$$

where s_i and m_i are respectively the standard deviation (1 σ) and the mean of the measurements (n = 4 to 7) for one isotope i.

The accuracy is represented by the relative error (RE) expressed in % between the expected concentration of one isotope i in each selected solution (C_i) and the mean concentration calculated from the LA-ICPMS analyses (C_m) of the same solution trapped in different silica capillaries (n = 4 to 7) as defined by equation (2).

328 (2)
$$RE_i = \frac{(C_m - C_i)}{C_i} \times 100\%$$

The value of accuracy is therefore negative if the calculated mean concentration from LA-ICPMS analyses is underestimated and positive if it is overestimated. The precision and accuracy values obtained for the four solutions and for five isotopes (⁷Li, ⁶⁵Cu, ⁸⁸Sr, ¹³⁹La, ²⁰⁹Bi), selected from the low to high atomic masses, are presented in Fig. 3 and Fig. 4 respectively. The full dataset for solutions with 33 elements (at ca. 0.1, 1 and 10 μ g g⁻¹) or 37 elements (at ca. 50 μ g g⁻¹) is given in Table 2. RSD values are typically within 9 to 30% for

OMS and 6 to 60% for SFMS, using the same cylindrical ablation cell, and within 3 to 40% for TOFMS (except ⁷Li) using the fast washout cell, depending on concentrations and detected isotopes (Fig. 3, Table 2). The RSD values of the measured isotopes are not depending on the concentration of the different solutions for the three investigated setups and are not directly correlated with the signal intensity. These findings indicate that the analytical precision is likely dominated by the laser ablation behaviour (non-continuous ablation of liquid) and not by counting statistics. RE values are typically within -40 to 40% for QMS, -50 to 50% for SFMS and -30 to 30% for TOFMS, for all concentrations and isotopes when detected (Fig. 4, Table 2), and generally tend to be higher at low concentration. Anomalously high RSD and RE values are occasionally found for some isotopes such as ⁵⁷Fe (RSD up to 125%, RE up to 170%), ¹¹⁸Sn (RSD up to 122%, RE up to 47%) or ²⁰⁵Tl (RSD up to 67%, RE down to -74%). For isotopes such as ⁵⁷Fe, this can be related to polyatomic interferences of ⁴⁰Ar¹⁶O¹H. For other isotopes such as ¹¹⁸Sn, ¹⁸¹Ta or ²⁰⁵Tl, these variabilities could be either due to a problem of stability of these elements in solution or to a problem during solution preparation. The fact that Ba in the 50 μ g g⁻¹ solution is consistently found at twice the reference values is most likely explained by an error in sample preparation. Consequently, these five elements are not considered in the final evaluation.

3.1.3. Limits of detection

LODs calculated from means of the individual acquisitions (n = 5 to 6) for the OMS, SFMS and TOFMS are presented in Fig. 5 for the solutions at concentration of ca. 10 μ g g⁻¹ and the dataset for all the tested solutions is given in Table 2. The LODs do not depend of the concentration of the different solutions for a same instrument. The observed differences reflect only the variations in fillings of the capillary or the quantity of fluid removed during laser ablation. For the three instruments, LODs decrease of ca. two to three orders of magnitude from low to high atomic mass. The highest LODs are typically within 5 to 30 µg g⁻ ¹ for light isotopes (m/Q \leq 57) for the QMS and SFMS (except for ¹¹B) and within 10 to 20 μ g g⁻¹ for the TOFMS (except for ⁷Li). The lowest LODs are typically within 0.01 and 0.1 μ g g^{-1} for heavy isotopes (m/Q > 139) for the SFMS and TOFMS and between 0.1 to 1 µg g^{-1} for the QMS. For intermediate isotopes with $57 \le m/Q \le 139$, SFMS shows systematically lower LODs than the QMS and SFMS within up to one order of magnitude of ca. 0.05 μ g g⁻¹ for m/Q < 88. QMS and TOFMS have similar LODs within the same order of magnitude of ca. $0.5-3 \ \mu g \ g^{-1}$ and $0.01-0.5 \ \mu g \ g^{-1}$ for light and heavy isotopes respectively, but TOFMS tends to

have slightly lower LODs than OMS for isotopes with m/Q > 111 (Fig. 5, Table 2). Compared to the QMS, LODs are lower for SFMS and TOFMS, and are in the same order of magnitude of ca. 0.01 μ g g⁻¹ for m/Q > 159 for both SFMS and TOFMS.

- 3.2. Two-phase fluid inclusions
 - 3.2.1. Signals

Typical transient LA-ICPMS signals for 25 µm two-phase fluid inclusions from sample BP-66-210 (Mont Blanc Massif, French Alps) are shown in Fig. 6. The signal durations after opening the fluid inclusions mainly depend on the inclusion size (Fig. 7), the salinity being identical for all fluid inclusions. For inclusions of 25 µm in size, the cylindrical ablation cell led to signal durations typically of ca. 26 s with the OMS and 22 s with the SFMS, while the fast washout tube cell reduced the signal length to ca. 9 s. With a cycle time of 273 ms for OMS, 560 ms for SFMS and 30 ms for TOFMS (Table 1), the signal durations correspond to ca. 95, 39 and 300 data points respectively. Within the two-phase fluid inclusions, 9 isotopes (⁷Li, ¹¹B, ²³Na, ²⁵Mg, ³⁵Cl, ⁸⁵Rb, ⁸⁸Sr, ¹³³Cs and ¹³⁷Ba) could be detected with the QMS, 10 isotopes (⁷Li, ²³Na, ³⁵Cl, ⁴⁴Ca, ⁸⁵Rb, ⁸⁸Sr, ¹³³Cs, ¹³⁷Ba, ¹⁸²W and ²⁰⁸Pb) with the SFMS, whereas 14 isotopes (¹¹B, ²³Na, ²⁵Mg, ³⁵Cl, ³⁹K, ⁵⁵Mn, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ¹²¹Sb, ¹³³Cs, ¹³⁷Ba, ¹⁸²W and ²⁰⁸Pb) were detected using the TOFMS. Considering the ratios normalized to ²³Na, only the first seconds of the fluid inclusions signals show constant values (5 s for QMS, 9 s for SFMS and 1.5 s for TOFMS). This corresponds to ca. 96 to 98% of the integrated ²³Na intensity of the fluid inclusions signals and ca. 18, 16 and 52 data points for QMS, SFMS and TOFMS respectively (Fig. 6). Peak signal/background ratios for ²³Na are ca. 10⁴ for OMS, 2 \times 10³ for SFMS and 9 \times 10³ for TOFMS respectively. Peak signal/background ratios for minor and trace elements are in the same order of magnitudes for the three configurations (Fig. 6).

3.2.2. Concentration, standard deviation and precision

The concentrations for the two-phase fluid inclusions analysed (sample BP-66-210, Alps) are presented for the three instruments (QMS, SFMS and TOFMS) and as function of their diameter (in ranges of $< 10 \, \mu m$, 10-25 μm and $> 25 \, \mu m$) in Fig. 8. The calculated mean concentrations, standard deviations (1 σ) and precisions (RSD) for all fluid inclusions are

given in Table 3. The isotopes ³⁵Cl, ⁸⁵Rb, ⁸⁸Sr and ¹³³Cs, ¹³⁷Ba were systematically detected by the three LA-ICPMS configurations and for fluid inclusions $> 10 \text{ }\mu\text{m}$, with a good reproducibility of the measurements. The mean concentrations and standard deviations for the QMS, SFMS and TOFMS are respectively of 4110 ± 7640 , 1100 ± 710 and $19000 \pm 5140 \ \mu g$ g^{-1} for 35 Cl. 210 ± 80, 155 ± 127 and 113 ± 37 µg g^{-1} for 85 Rb, 55 ± 30, 49 ± 36 and 36 ± 10 $\mu g g^{-1}$ for ⁸⁸Sr, 70 ± 35, 62 ± 65 and 35 ± 13 $\mu g g^{-1}$ for ¹³³Cs and 10 ± 20, 6.5 ± 8 and 7.4 ± 5 ug g⁻¹ for ¹³⁷Ba (Table 3). The RSD calculated for all fluid inclusions vary considerably and range within 33 to 200% for QMS (n=35), 10 to 182% for SFMS (n=24) and 23 to 167% for TOFMS (n=40) respectively. For the detected elements, RSDs calculated appear lower for the TOFMS compared to QMS and SFMS respectively, suggesting an improvement in terms of precision achieved by the quasi-simultaneous detection. In all cases, however, the calculated RSDs for fluid inclusions are higher compared to silica capillaries due to their variability in size, shape and depth. Other isotopes are detected sporadically by the three instruments, such as ²⁵Mg, ¹³⁷Ba or ¹⁸²W, and are characterized by higher standard deviations (Table 3). ⁷⁹Br was detected in the fluid inclusions by the three instruments, but was not quantified because of the uncertain reference value for NIST SRM 610 used for calibration.⁴⁷ Additional isotopes, detected by the TOFMS in fluid inclusions > 10 μ m, are ³⁹K, ⁵⁵Mn, ⁷⁵As and ¹²¹Sb, which were not included in the isotope selection for the OMS and SFMS. On the other hand, the isotopes ⁵⁹Co, ⁶⁵Cu or ⁶⁶Zn were not detected by the three instruments due to concentrations below LODs (Table 3).

Small fluid inclusions ($< 10 \mu m$) were also measured with the three instruments, but relatively few data were obtained for this sample set. Nevertheless, results obtained show that TOFMS still detects five isotopes (³⁵Cl, ⁸⁵Rb, ⁸⁸Sr, ¹³³Cs and ²⁰⁸Pb) in addition to ²³Na, whereas QMS and SFMS detect only one to two isotopes (⁸⁵Rb and/or ¹³³Cs). As shown in Fig. 9, the analysis of a 5 µm fluid inclusion by QMS allows only the detection of the ²³Na signal, present as the major isotope. Minor isotopes such as ⁸⁵Rb, ⁸⁸Sr and ¹³³Cs cannot be detected by OMS, but were detected using the TOFMS. Detection of ³⁵Cl signal is improved with the TOFMS, which represents a major benefit for the quantification of fluid inclusions based on their chlorinity.²⁵ Considering signal to background ratios of different isotopes as function of 23 Na signal to background ratio for a 25 μ m fluid inclusion analysed by TOFMS (Fig. 10), it appears that all isotopes show a linear positive correlation with the ²³Na used as internal standard. The correlation is particularly strong for the first 1.3 s of the signal, which represents 95% of the total ²³Na intensity and corresponds to ca. 44 measurements cycles. About 90% of fluid inclusions total ²³Na intensity is contained in the first 0.7 s, which

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438 corresponds to ca. 24 measurements cycles (Fig. 10). Due to its quasi-simultaneous detection,
439 quantification of two-phase fluid inclusions with the TOFMS could be consequently realised
440 on one data point at the maximum peak intensity of the ²³Na signal, corresponding to the first
441 30 ms of the signal.

3.2.3. Limits of detection

LODs calculated for fluid inclusions from means of individual acquisitions (n=24 to 40) for the QMS, SFMS and TOFMS are given in Table 3. As shown in Fig. 11, the LODs are inversely correlated to the inclusion diameter with a parabolic decrease, regardless of the element considered. LODs calculated for isotopes analysed by QMS, SFMS and TOFMS and variable diameters of fluid inclusions (< 10 μ m, 10-25 μ m and > 25 μ m) are shown in Fig. 12. For fluid inclusions $> 25 \mu m$, LODs for QMS and TOFMS are within the same order of magnitude, varying typically within 10^1 to $10^4 \ \mu g \ g^{-1}$ for light isotopes (m/Q \leq 57) and within 10^{-1} to $10^{1} \ \mu g \ g^{-1}$ for heavy isotopes (m/Q \ge 85), whereas SFMS shows the lowest LODs, generally within one to two orders of magnitude below QMS and TOFMS. For fluid inclusions between 10 and 25 µm in diameter, LODs for SFMS and TOFMS are within the same order of magnitude, varying between 10^2 to $10^5 \ \mu g \ g^{-1}$ for light isotopes (m/Q ≤ 57) and between 1 to $10^3 \ \mu g \ g^{-1}$ for heavier isotopes. LODs for QMS tend to be higher by ca. one order of magnitude compared to TOFMS and SFMS. For fluid inclusions < 10 µm, the lowest LODs are achieved by TOFMS, varying within 10^2 to $10^5 \ \mu g \ g^{-1}$ for m/Q < 85 and within 10^1 to $10^2 \ \mu g \ g^{-1}$ for m/Q > 85, for which they are lower by ca. one order of magnitude compared to those of OMS and SFMS. Thus, the size of fluid inclusions strongly constrains the achievable LODs of each instrument and the results show particularly that TOFMS provide the lowest LODs for fluid inclusions with diameter $\leq 10 \ \mu m$.

- 3.3. Multi-phase fluid inclusions
- 3.3.1. Signal structure

468 Typical transient signals from QMS and TOFMS acquisition of 15 μ m multi-phase (liquid + 469 vapour + solids) fluid inclusions from sample 7703-25 (Kabompo domes, Zambia) are shown 470 in Fig. 13. The signal durations (based on ²³Na) obtained for such fluid inclusions are longer

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 than those obtained for fluid inclusions of similar size from the Alps (sample BP-66-210) due to their higher salinities and last for ca. 60 s for QMS and ca. 20 s for TOFMS. With a cycle time of 195 ms for QMS and 30 ms for TOFMS (Table 1), this corresponds to ca. 307 and 667 acquisitions cycles respectively. Peak signal/background ratios for ²³Na are ca. 10³ for QMS and 2×10^2 for TOFMS. The QMS allows the detection of 13 isotopes (²³Na, ²⁵Mg, ³⁹K, ⁴⁴Ca, ⁴⁷Ti, ⁵⁷Fe, ⁶⁵Cu, ⁸⁵Rb, ⁸⁸Sr, ⁹⁵Mo, ¹³⁷Ba, ²⁰⁸Pb and ²³⁸U) on the 15 measured, whereas TOFMS detects 38 isotopes (²³Na, ²⁴Mg, ²⁵Mg, ²⁶Mg, ²⁷Al, ³⁵Cl, ³⁹K, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁴Zn, ⁶⁵Cu, ⁶⁶Zn, ⁶⁷Zn, ⁶⁸Zn, ⁸⁵Rb, ⁸⁶Sr, ⁸⁸Sr, ⁹⁵Mo, ⁹⁶Mo, ⁹⁷Mo, ⁹⁸Mo, ¹³⁰Te, ¹³³Cs, ¹³⁵Ba, ¹³⁶Ba, ¹³⁷Ba, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴³Nd, ²⁰⁵Tl, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²⁰⁹Bi and ²³⁸U) on the whole analysed mass range.

The signals obtained for QMS for all detected isotopes have all the same shape and are correlated in time, as observed in Fig. 13 by constant ratios normalized to ²³Na. The different solids (halite, calcite, hydrates, hematite) observed in the fluid inclusions by optical microscopy and determined by Raman spectroscopy are consequently not individualized with OMS.⁵⁴ For a similar 15 µm multi-phase fluid inclusion, the liquid and solid phases are properly discriminated during TOFMS measurement, with the signals of the majority of the detected isotopes displaying specific shapes during acquisition. This confirms that elements or groups of elements are present in different physical phases within the fluid inclusions, as previously observed by microscopy and Raman spectroscopy. The observed elemental discrimination, shown here for the first time using TOFMS, is possible only due to the fast washout of the ablation cell used in combination with the quasi-simultaneous detection of the TOF mass analyser. The different phases present within the fluid inclusion are thus not dispersed significantly within the ablation cell and are transported separately during laser ablation to the MS. As a result, the signals of Rb-Sr-Cu-Al-Pb-Ba-Cs, Na-Mg-K-Cl and Fe-Mn-Ti could be interpreted respectively as those of the aqueous phase, hydroxides and hematite crystals, as previously identified by Raman spectroscopy.⁵⁴ However, some signals are mixed and could indicate a partitioning of the elements between different phases. The 23 Na signal is not completely correlated to the signal of 35 Cl, which is probably due to quasi-simultaneous ablation of NaCl solid and liquid phase in which Na and Cl are major solutes but present in different proportions to NaCl. The same observation is made with the Ba isotopes, which show a common signal shape compared to those of Rb and Sr isotopes, but with minor differences, suggesting that Ba could be present both in the aqueous phase and in a solid phase (e.g. barite, BaSO₄) not identified previously by Raman spectroscopy. The signal of ⁶⁵Cu is partially correlated with those of ⁶⁴Zn, ⁶⁶Zn, ⁶⁷Zn and ⁶⁸Zn, suggesting that

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these elements are likely associated within a single phase. Finally, the signal of U shows a peak clearly distinct from the other signals, and correlated with the one of Mo (not shown), indicating that these two elements are present in an independent phase and not as a solute in the aqueous phase. However, the presence of a U-bearing mineral is not common in these fluid inclusions, since its signal has not been detected systematically here.

Discrimination between elements in fluid phase and daughter minerals has been previously observed by LA-ICPMS (Günther et al.³ for the first occurrence), but this was obtained for large-size (> 40 μ m in diameter) and high-salinity fluid inclusions^{3,4,38}, and could not be reached for the tested small fluid inclusions, as demonstrated by the QMS results (Fig. 13). These previous observations suggest that the aerosol dispersion in the large volume ablation cells does not allow distinguishing the different phases at such extent. This preliminary result requires an extensive investigation, in particular, by testing the capabilities and the limits on synthetic fluid inclusions in comparison with natural multi-phase fluid inclusions from different geological contexts. Nevertheless, this result opens interesting perspectives, for instance to allow: (i) identification of solids difficult to analyse by Raman spectroscopy (small size and/or transparent solids) and (ii) detailed analysis of minor to trace elements concentrations within solids.

3.3.2. Concentrations, standard deviations, precisions and limits of detection

The calculated mean concentrations, standard deviations (1σ) and precisions (RSD) for multi-phase fluid inclusions from sample 7703-25 for QMS and TOFMS are presented in Table 4. The major input of TOFMS is the detection of 38 isotopes on the whole mass range, with particularly the discrimination of several isotopes of a same element, such as Mg, Zn, Mo, Ba and Pb isotopes (Table 4), with a good reproducibility. Concentrations are variable among the analysed fluid inclusions, in particular for isotopes such as ³⁹K, ⁶⁵Cu or ⁵⁷Fe for instance, resulting in relatively high RSD. For isotopes detected both by QMS and TOFMS, the calculated RSD are lower on average for TOFMS, as already shown for two-phase fluid inclusions, and range within 39 to 154% and 6 to 100% for QMS and TOFMS, respectively. Considering that these fluid inclusions have approximately the same dimension (10 to 25 μ m), these variations are likely related to a heterogeneous trapping of the fluid during the quartz crystallization. The calculated LODs for QMS and TOFMS show the same results as for the two-phase fluid inclusions, that is similar LODs for QMS and TOFMS for m/Q < 57and lower LODs for TOFMS for heavy isotopes (m/Q > 95).

540 4. Summary and conclusions

542 Three different configurations of LA-ICPMS, namely a quadrupole (QMS), a sector-field 543 (SFMS) and an orthogonal time-of-flight (TOFMS), were tested in this study in order to 544 address their respective capabilities for sequential (QMS, SFMS) and quasi-simultaneous 545 (TOFMS) multi-element analysis of small quantities of liquids (pl to nl) contained in silica 546 capillaries and in natural fluid inclusions.

The two sets of objects studied, namely multi-element solutions in silica capillaries and natural fluid inclusions, allowed to evaluate the capabilities of SFMS and TOFMS and to compare them to QMS, which is currently the traditionally used and state-of-the-art instrument for the measurements of fluid inclusions by LA-ICPMS. The main results obtained in this study are: (i) QMS, SFMS and TOFMS have similar signal to background ratios for 23 Na within the same order of magnitude of ca. 10^3 to 10^4 , those of OMS being slightly higher to the other ones; (ii) Signals durations are similar (20-30 s) for silica capillaries and two-phase fluid inclusions using a standard cylindrical ablation cell with QMS and SFMS, but are 2 to 30 times shorter (1-15 s) using the fast washout tube cell in combination with the TOFMS. In the case of high-salinity and multi-phase fluid inclusions, the signals durations are longer and last for ca. 60 s and 20 s for QMS and TOFMS, respectively; (iii) Cycle times for covering the range of measured masses with QMS and SFMS are ca. 10 to 30 longer compared to those of TOFMS, where cycle time is only 30 ms for quasi-simultaneous measurement of the entire mass range, resulting in a number of cycles of ca. 2 to 5 times higher compared to QMS and SFMS and compensating for the multiplicative noise in the ICPMS; (iv) RSD calculated are on average lower for TOFMS compared to QMS and SFMS, for all measured isotopes, indicating better precision achievable by TOFMS; (v) LODs for silica capillaries are approximately 10 times lower for SFMS compared to QMS and TOFMS for isotopes with m/O < 137 (except ¹¹B) and almost equivalent for SFMS and TOFMS for heavier isotopes and ca. 3 times lower than for QMS. For fluid inclusions, LODs are inversely correlated to the inclusion diameter with a parabolic decrease. SFMS presents lower LODs of ca. one order of magnitude compared to QMS and TOFMS for diameter $> 25 \mu m$, whereas TOFMS achieve the lower LODs for inclusions $< 10 \,\mu$ m, with one order of magnitude below SFMS and QMS for isotopes with m/Q > 85.

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571 Consequently, the present study demonstrates that SFMS and TOFMS provide improvements,

- 572 particularly in terms of precision and LODs, compared to the QMS instrumentation tested, 573 and leads to the following conclusions:
- (1) QMS is a very efficient instrument for the multi-element analysis of fluid inclusions,
 with good reproducibility, precisions and accuracies, but is limited by relatively high
 LODs compared to SFMS and TOFMS, in particular for heavy isotopes, and by a
 limited set of measureable elements (generally less than 20) due to a compromise
 between signal duration and cycle time.
- 579 (2) SFMS has the great advantage to reduce LODs within one order of magnitude
 580 compared to QMS and TOFMS, especially for light isotopes, but has longer
 581 acquisition times, due to the necessary magnet jumps, which limits the number of
 582 measureable elements and the attainable precision. It is consequently a well-adapted
 583 instrument for the precise measurement of a few isotopes (< 5) present at low
 584 concentrations in fluid inclusions.
- (3) TOFMS presents both advantages to have rapid, quasi-simultaneous data acquisition for all isotopes from ⁶Li to ²³⁸U in a cycle time of 30 us. The precisions were found to be better than for QMS and SFMS and LODs are slightly higher or even similar than SFMS for heavy isotopes and lower for small fluid inclusions. Using TOFMS coupled to the fast washout ablation cell, which improves considerably the signal to noise ratio by decreasing the aerosol dispersion, allows detection of small-size (< 10 μ m) and low-salinity fluid inclusions. Its application to complex multi-phase and high-salinity fluid inclusions allows discrimination of signals of the different phases (liquid and solids), as well as the detection of a higher number of isotopes, even for a same element. Moreover, detection of ³⁵Cl is improved with the TOFMS, which could represent a major benefit for the quantification of fluid inclusions based on their chlorinity.
 - In conclusion, the orthogonal TOFMS reveals to be a highly promising instrument for the multi-element analysis of fluid inclusions, particularly since it provides fast and relatively complete information on fluid inclusions composition. Its use is consequently of high interest for the study of geological fluids, which are characterized by an extremely wide variety of chemical elements, potentially from Li to U, with a very variable range of concentrations, from a few parts per billions (ppb) to tens of percents. Future applications could be considered in particular for the analysis of melt inclusions by TOFMS (e.g. Pettke et al.⁵⁷), but also for the measurement of isotopic ratios in fluid inclusions (e.g. Pettke et al.³³). By

extension, these results demonstrate the analytical potential of the TOFMS for the
determination of minor and trace elements in small volumes of liquids (pl to nl) trapped in
various solid matrices.

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720	Tables captions
721	
722	Table 1: Operating conditions and acquisition parameters used for this study.
723	
724	Table 2: Nominal and measured compositions of silica capillaries with internal diameter of 20
725	μm containing multi-element solutions at concentration of ca. 0.1, 1, 10 and 50 $\mu g~g^{-1}$
726	analysed by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS. The analytical conditions are
727	given in Table 1. SD: standard deviation; LOD: limit of detection; n.m.: not measured; n:
728	number of analyses.
729	
730	Table 3: Chemical compositions of two-phase fluid inclusions from sample BP-66-210 (Mont
731	Blanc Massif, French Alps) analysed by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS.
732	See Table 1 for the analytical conditions. The limits of detections (LOD) are reported as a
733	function of the fluid inclusions diameter (< 10 μ m, 10-25 μ m and > 25 μ m respectively). FI:
734	fluid inclusion; n: number of fluid inclusions analysed; SD: standard deviation; RSD: relative
735	standard deviation; n.m.: not measured.

Table 4: Chemical compositions of multi-phase fluid inclusions from sample 7703-25
(Kabompo domes, Zambia) analysed by LA-ICPQMS and LA-ICPTOFMS. See Table 1 for
the analytical conditions. SD: standard deviation; LOD: limit of detection; n: number of
analyses.

742 Figures captions

Fig. 1: Microphotographs in transmitted light of fluid inclusions observed at room temperature from selected quartz (Qtz) samples. (a) Two-phase fluid inclusions (sample BP-66-210, Mont Blanc Massif, Pointe des Amethystes, French Alps) containing a dominant aqueous phase with dissolved salts (L_{aq}) and a vapour phase (V). This sample contains numerous 5 to 100 μ m fluid inclusions of this type with high compositional homogeneity. (b) Multi-phase fluid inclusion (sample 7703-25, Kabompo domes, Lolwa occurence, Zambia) containing a dominant aqueous phase with dissolved salts (Lag), a vapour phase (V) and various solids: calcium chloride hydrates (Hyd), halite (Hl), hematite (Hem) and calcite (Cal).

Fig. 2: Typical transient signals for silica capillaries with internal diameter of 20 µm containing multi-element solutions at concentration of 10 μ g g⁻¹ (except Na with 1000 μ g g⁻¹) analysed by LA-ICPQMS (a), LA-ICPSFMS (b) and LA-ICPTOFMS (c). Seven representative isotopes (⁷Li, ²³Na, ²⁹Si, ⁶⁵Cu, ⁸⁸Sr, ¹³⁹La, ²⁰⁹Bi) are shown here, but the dataset for all isotopes is given in Table 2. For QMS and SFMS, 35 isotopes were measured, whereas all isotopes are measured with the TOFMS (see Table 1). Signal duration (based on ²³Na), number of cycles and cycle times for each setup are indicated. Analytical conditions for the three setups are given in Table 1.

Fig. 3: Standard deviation versus mean concentration (n=4 to 7) for five selected isotopes (⁷Li, ⁶⁵Cu, ⁸⁸Sr, ¹³⁹La, ²⁰⁹Bi) from silica capillaries with internal diameter of 20 μ m containing four different multi-element solutions at concentration of 0.1, 1, 10 and 50 μ g g⁻¹ (except for ²³Na with 1000 μ g g⁻¹) analysed by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS. The precision is represented by the RSD (relative standard deviation). Dataset for all measured isotopes is given in Table 2. Elements with concentration below limit of detection are not represented. Analytical conditions for the three setups are given in Table 1.

Fig. 4: Mean and standard deviation (1σ) of concentrations measured by LA-ICPMS (LA-ICPOMS, LA-ICPSFMS and LA-ICPTOFMS) versus nominal concentration in standard solution for five selected isotopes (7Li, 65Cu, 88Sr, 139La, 209Bi) from silica capillaries with internal diameter of 20 µm containing multi-element solutions. The accuracy is a function of the length of the orthogonal projection of the data points on the 1:1 slope. Circles and error bars stand for mean (n=4 to 7) and standard deviation (1σ) values respectively (see Table 2). Dataset for all measured isotopes is given in Table 2. Analytical conditions for the three setups are given in Table 1.

Fig. 5: Mean value for limits of detection (LOD) calculated for silica capillaries with internal diameter of 20 μ m containing multi-element solutions at concentration of 10 μ g g⁻¹, and analysed by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS. Analytical conditions for the three setups are given in Table 1.

Fig. 6: Typical transient signals for 25 μm two-phase fluid inclusions (sample BP-66-210, Alps) analysed by LA-ICPQMS (a), LA-ICPSFMS (b) and LA-ICPTOFMS (c). Corresponding signal/background ratios of analysed isotopes normalised to ²³Na (internal standard) are presented for LA-ICPQMS (d), LA-ICPSFMS (e) and LA-ICPTOFMS (f). Nine selected isotopes (⁷Li, ¹¹B, ²³Na, ²⁹Si, ³⁵Cl, ⁸⁵Rb, ⁸⁸Sr, ¹²¹Sb, ¹³³Cs) are shown here, but the dataset for all isotopes is given in Table 2.Analytical conditions for the three setups are given in Table 1.

Fig. 7: Total signal duration (a) and number of acquisition cycles (b) as function of fluid inclusion diameter for individual two-phase fluid inclusions measurement (sample BP-66-210, Alps) analysed by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS. The number of acquisition cycles is function of the cycle time for each configuration of LA-ICPMS (273 ms for QMS, 560 ms for SFMS and 30 ms for TOFMS). Analytical conditions for the three setups are given in Table 1. n: number of fluid inclusions analysed.

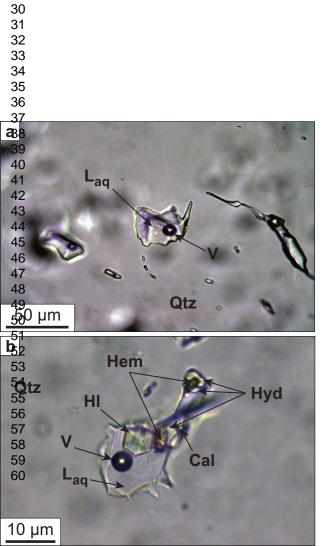
Fig. 8: Composition of two-phase fluid inclusions (sample BP-66-210, Alps) with different diameters (< 10 μ m, 10-25 μ m, > 25 μ m) analysed by LA-ICPQMS (a), LA-ICPSFMS (b) and LA-ICPTOFMS (c). Dataset for all fluid inclusions is given in Table 3. Analytical conditions for the three setups are given in Table 1. n= number of fluid inclusions analysed.

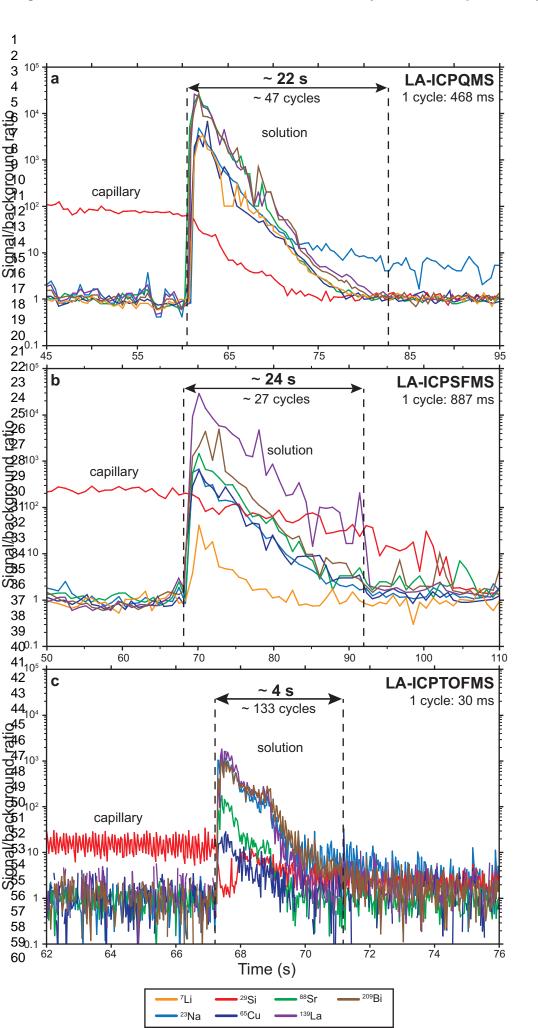
2 3	803	
4 5	804	Fig. 9: Typical transient signals for 5 µm two-phase fluid inclusions (sample BP-66-210,
6	805	Alps) analysed by LA-ICPQMS (a) and LA-ICPTOFMS (b).
7 8	806	
9 10	807	Fig. 10: Representation of different integration windows for a transient LA-ICPTOFMS
11	808	signal from a 25 µm fluid inclusion (sample BP-66-210, Alps). (a) Na signal/background ratio
12 13	809	as a function of time for 90, 95 and 100% of the total fluid inclusion Na signal. (b)
14 15	810	Signal/background ratios for different isotopes as a function of Na signal/background ratio.
16	811	
17 18	812	Fig. 11: Limits of detection (LODs) for LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS as
19 20	813	a function of two-phase fluid inclusion diameter (sample BP-66-210, Alps) for ¹¹ B (a), ⁸⁵ Rb
21 22	814	(b), ¹³³ Cs (c) and ²⁰⁸ Pb (d). The values are reported in Table 3. Analytical conditions for the
23	815	three setups are given in Table 1. n= number of fluid inclusions analysed.
24 25	816	
26 27	817	Fig. 12: Mean limits of detection (LODs) calculated for a series of individual fluid inclusions
28	818	(sample BP-66-210, Alps) of diameter < 10 μm (a), 10-25 μm (b) and > 25 μm (c), analysed
29 30	819	by LA-ICPQMS, LA-ICPSFMS and LA-ICPTOFMS. The values are reported in Table 3.
31 32	820	Analytical conditions for the three setups are given in Table 1.
33	821	
34 35	822	Fig. 13: Typical transient signals for 15 μ m multi-phase fluid inclusions (sample 7703-25,
36 37	823	Zambia) analysed by LA-ICPQMS and LA-ICPTOFMS. The signals for detected elements
38	824	obtained by QMS with the standard ablation cell have all the same shape and are correlated in
39 40	825	time (top left to middle left), as observed by constant ratios normalised to Na (bottom left).
41 42	826	The signals obtained by TOFMS with the fast washout cell differ from one group of isotopes
43	827	to another, as shown by variable ratios normalised to Na (bottom right), allowing to
44 45	828	distinguish the signals of the aqueous phase, halite (Hl) and magnesium hydroxides (Hyd)
46 47	829	(top right), and hematite (Hem) and uraninite crystals (Urn) (middle right). Analytical
48 49 50	830	conditions for the three setups are given in Table 1.

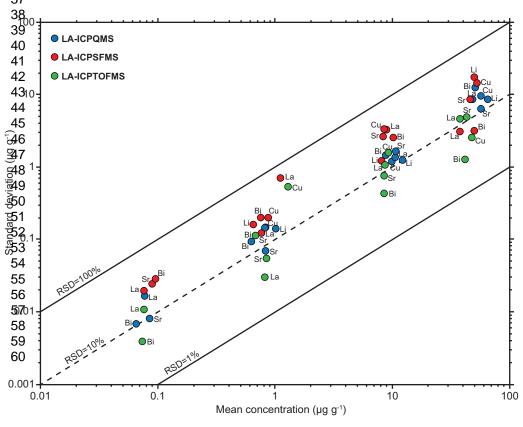


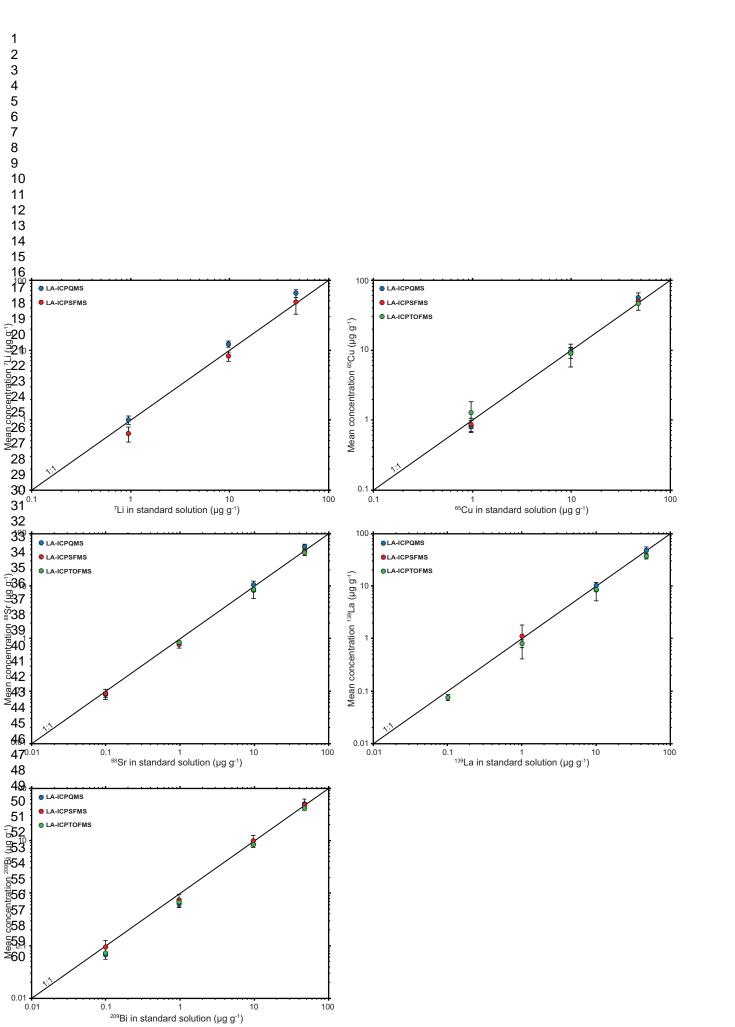


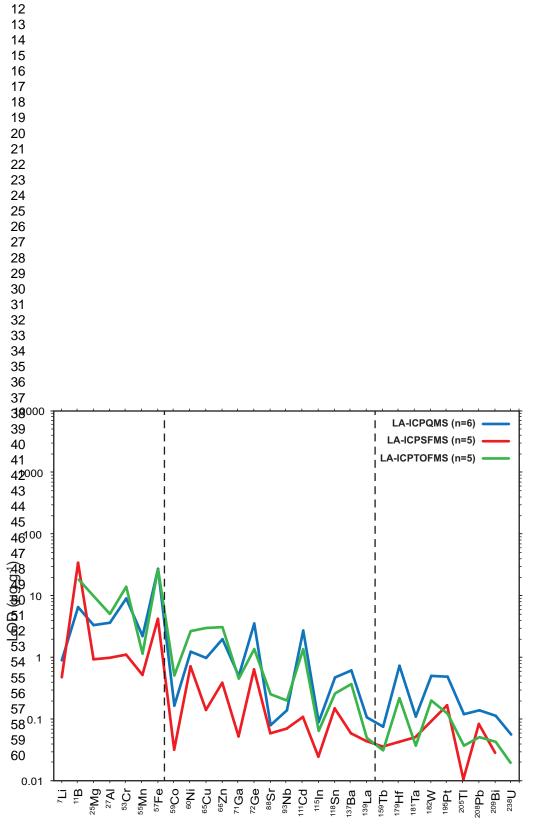


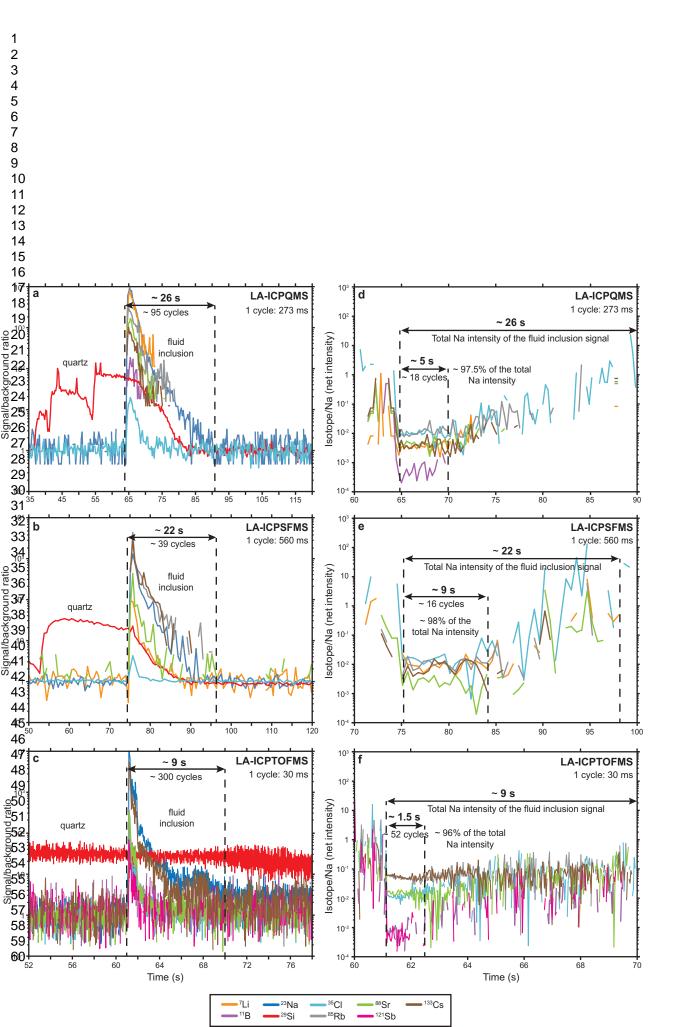


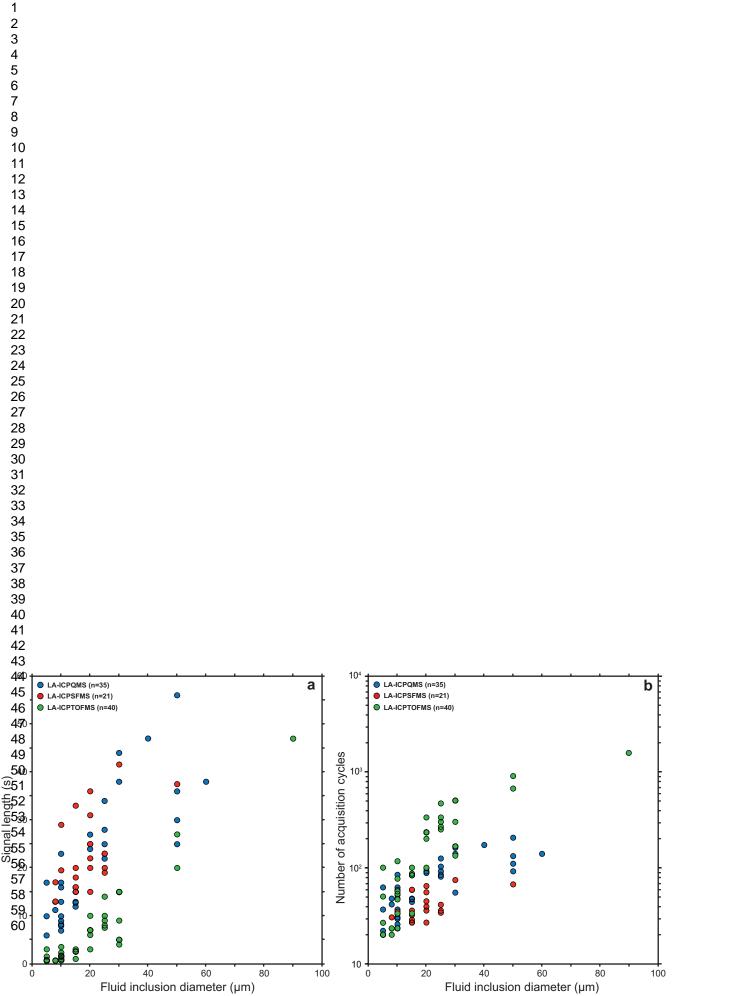


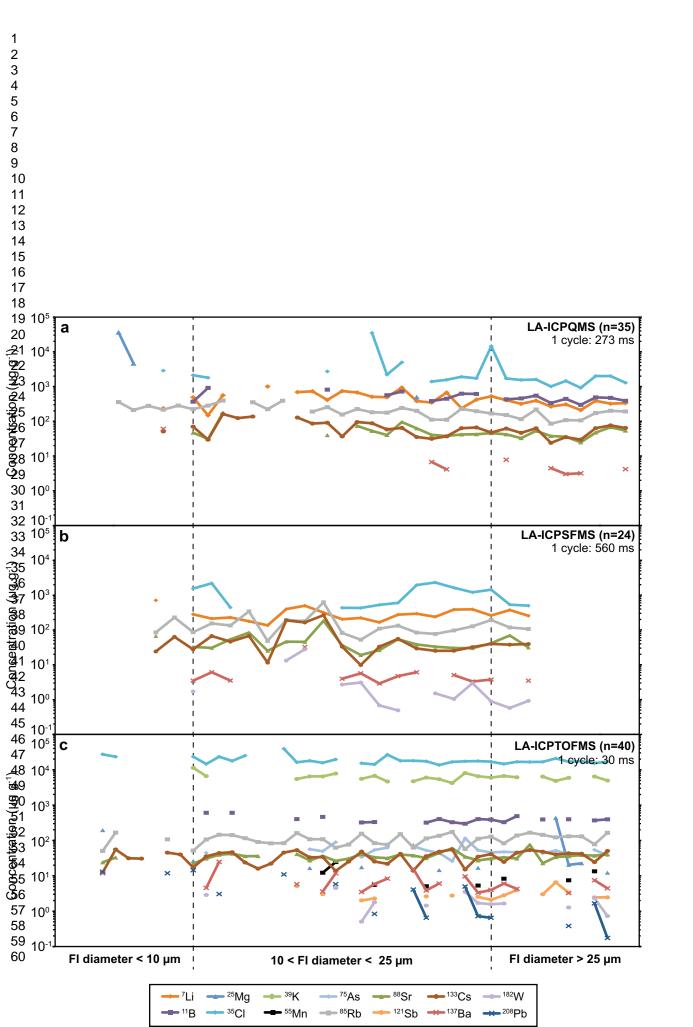


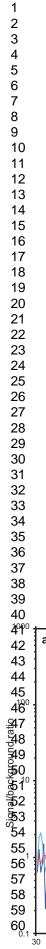


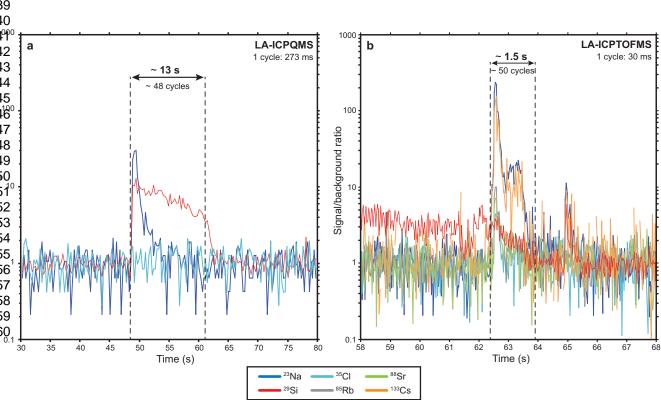


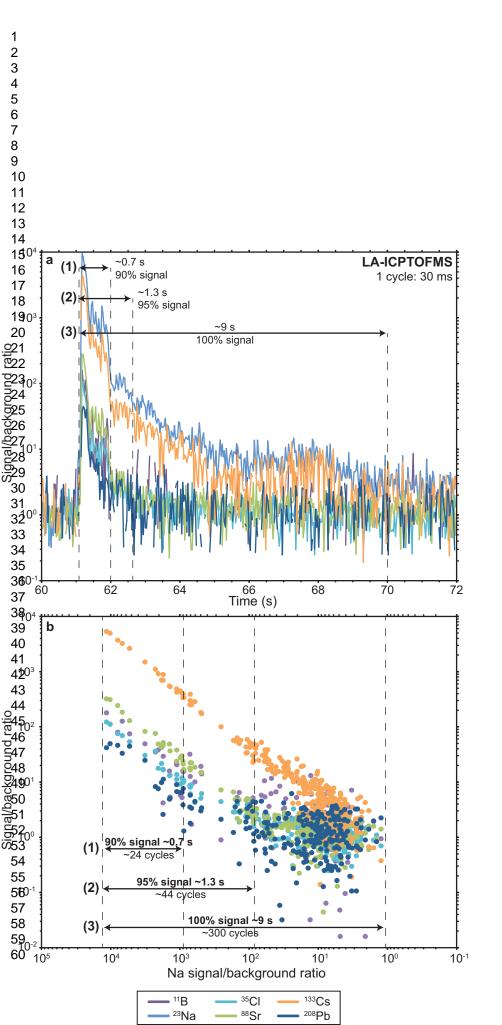












	LA-ICPQMS	LA-ICPSFMS	LA-ICPTOFMS
Model	Elan DRC Plus	Element 2	Prototype
	(PerkinElmer Inc.)	· · · · · · · · · · · · · · · · · · ·	
Laser		ArF Excimer 193 nm	
Ablation cell	Standard cy	lindrical cell	Fast washout tube ce
ICP-MS	1380 W	1280 W	1300 W
Plasma RF power		1280 W 16 L min ⁻¹	16.5 L min^{-1}
Cooling gas (Ar)			
Carrier gas (He)		$1.1 \mathrm{Lmin^{-1}}$	$0.6 \mathrm{Lmin^{-1}}$
Nebulizer gas (Ar)		0.84 Lmin^{-1}	1.2 Lmin^{-1}
50 ()	$0.8 \mathrm{L} \mathrm{min}^{-1}$	$0.66 L min^{-1}$	1.2 L min ⁻¹
· - ·	NIST SRM 610 for		· · ·
²³ Na	1.6×10^{7}	1.2×10^{8}	5.3×10^{5}
¹⁴⁰ Ce	1.5×10^{5}	1.7×10^{6}	$4.7 imes 10^4$
²⁰⁹ Bi	1.0×10^5	$1.7 imes 10^6$	$7.0 imes 10^4$
Acquisition param	eters for multi-elem	ent solutions in silic:	a capillaries
Cycle time	468 ms ⁷ Li, ¹¹ B, ²² Ne, ²³ Na, ²	887 ms	30 ms
	¹²¹ Sb, ¹³³ Cs, ¹³⁷ Ba, ¹⁷⁹ Hf, ¹⁸¹ Ta, ¹⁸² W, ¹⁹⁵	b, ¹¹¹ Cd, ¹¹⁵ In, ¹¹⁸ Sn, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁵⁹ Tb, ⁹ Pt, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi ured with SFMS)	⁶ Li to ²³⁸ U
Acquisition param		,	ple BP-66-210, Alps)
Cycle time	273 ms	560 ms	30 ms
Isotopes measured			
-		²⁵ Mg, ²⁹ Si, ³⁵ Cl, ⁴⁴ Ca, Zn, ⁷⁹ Br, ⁸⁵ Rb, ⁸⁸ Sr, , ¹⁸² W, ¹⁹⁷ Au, ²⁰⁸ Pb	⁶ Li to ²³⁸ U
Acquisition param	eters for multi-phas	e fluid inclusions (sa	mple 7703-25, Zambi
Cycle time	195 ms		30 ms
	²³ Na, ²⁵ Mg, ²⁹ Si, ³⁴ S,		
	³⁹ K, ⁴⁴ Ca, ⁴⁷ Ti, ⁵⁷ Fe,		
	⁶⁵ Cu, ⁸⁵ Rb, ⁸⁸ Sr,		⁶ Li to ²³⁸ U
	⁹⁵ Mo, ¹³⁷ Ba, ²⁰⁸ Pb,		
	²³⁸ U		

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	Solution	LA-ICPQ	MS				Concentra LA-ICPSF y Mean (n=6	MS	ca. 50 j	45°		LA-ICPT	OFMS			
Isotopes	Concentratio HE E	n Mcan (n=5 H8 8 ⁻¹) SD F8.8	LOD FE E	Precision %	Accuracy %	y Mean (n=6 µg g ¹ 49.5 ≺ LOD) SD H8.8 17.2	LOD FE E	Precision %	Accuracy %	Mean (n=7 HE B ⁻¹) SD F8.8	LOD F8.8	Precisio %	n Accura %
Ъ.	H88 ⁻¹ 46.9 47.7 47.5 46.7	με ε ¹ 64.7 59.1	P8.8 8.6 23.1	P8.8 0.6 4 1 2	13	38 24 1	49.5	17.2	PE 8'	35	6	µg g ⁴ n.m. 41.8 31.9 46.5	n.m. 4.0 2.8			
	47.7	59.1	23.1	4	39 7	24	< LOD 40.8	7.7	130	19	-14	41.8	4.0	2	9	-12 -33 -0.5
"AI	46.7	48.1 47.2	4.1	2	9	÷.	40.8 53.6	14.9	2	28	15	46.5	6.8	0.4	15	-0.5
"Li "B "Mg "Al "Cr "Ma	47.3	51.9	3.6 4.1 5.7 7.5 15.3 3.8 9.4 10.5 9.1 9.2 6.4 5.8	5		10	48.8	13.1	3	27		44.0	1.6	1		-7
"Ma	47.3 47.5 47.1 46.8	51.9 53.5 58.6 58.0	7.5	5 1 16 0.2	11 14 26 7	13 24 24	48.8 47.0 49.7 42.4	13.1 7.6 12.2 5.4 11.7 14.4 11.4 7.4 12.3	3 1 9 0.1	27 16 24 13	3 -1 5 -9	44.0 47.3 54.1 45.8	1.6 2.4 10.1 1.3	1 0.1 2.5 0.05	4 5 19 3	-7 -0.4 15 -2
"Fe	47.1	58.6	15.3	16	26	24	49.7	12.2	9	24	5	54.1	10.1	2.5	19	15
"NI	47.4	58.8	8.8	0.9	15	24	49.2	11.7	2	24	4	47.2	2.0	0.3	4	-0.5
"Cu	47.4 47.0 47.1 47.4 47.4	58.8 57.0 51.1 51.2 49.9	9.4	0.9 0.7 1.2 0.4 2	15 17 21 18 18	20 9 9	49.2 52.0 47.0 43.3 47.5	14.4	2 0.3 1 0.2 2	28 24 17 26 18	4 10	47.2 47.4 40.5 41.3 41.0	2.5 2.3 2.3 2.5	0.3 0.3 0.04 0.3	5	-0.5 0 -14 -12 -13 -9 -13
"Za	47.0	51.1	10.5	1.2	21	9	47.0	11.4	1	24	0.1 -8 0.1	40.5	2.3	0.3	6	-14
"Ga	47.1	51.2	9.1	0.4	18	5	43.3	7.4	0.2	17	-8	41.3	2.3	0.04	6	-12
"Sr	47.4	56.9	6.4	0.04	11	20	47.5	8.5	0.1	18	-2	43.1	4.9	0.03	11	-13
¹⁰ Nb	47.5	50.1 48.5	5.8	0.06	12	6 3	46.3 42.2	8.5 8.3 7.1 5.6 8.6 13.7	0.1	20 14	-11	41.5 41.5	4.9 5.1	0.02	12	-13
-Cd	47.3	48.5	13.0 15.3 8.8 11.3	1.5	27	3	49.2 46.8 42.7 92.2	7.1	0.3	14	-11 4 -1 -10 95	41.5	2.6	0.15	6	-12 -6 -11 84 -21 -17 -17 -12 -20 -58
The second	47.5 47.5 47.2	54.2 49.3 109.6 47.9 53.0 51.7 21.2 51.9 55.0	15.3	0.05 0.2 0.4	28 18 10	14 4 132	46.8	5.6	0.06 0.3 0.1	12 20 15	-1	41.7 42.2	1.4 1.7 10.2	0.01 0.03 0.04	3 4 12	-6
	47.5	49.3	8.8	0.2	18	4	42.7	8.6	0.3	20	-10	42.2	1.7	0.03	4	-11
"La	47.8	47.9	8.5	0.07	18	0	37.9	3.1	0.04	8	-21	37.5	4.6	0.004	12	-21
ть	47.2	53.0	8.5 5.1 7.1 4.2 7.6 22.9	0.07 0.05 0.3 0.05 0.4 0.5	18 10 14 20 15	0 12 10 -55 9 16	37.9 38.2 43.3 19.2 48.7 48.6 37.0 52.2	3.1 4.2 10.0 2.8 11.5 14.1 12.9 7.4 3.1	0.04 0.05 0.09 0.05	8 11 23 15 24 29 35 14	-21 -19 -8 -89 3 2	37.5 39.0 38.9 13.5 37.9	4.7	0.004 0.003 0.02 0.004 0.02 0.01	12	-17
.""Hf	47.2	51.7	7.1	0.3	14	10	43.3	10.0	0.09	23	-8	38.9	5.6	0.02	14	-17
Ta	47.3	21.2	42	0.05	20	-55	19.2	2.8	0.05	15	-59	13.5	4.0	0.004	30	-72
-"n	47.5	55.0	22.9	0.5	42	16	48.6	14.1	0.4	29	2	20.0	4.8	0.02	24	-20
^{an} n	47.4	48.6	32.6	0.07	67 32	2	37.0	12.9	0.09 0.4 0.01 0.2	35	-22	19.6	3.4	0.005	17	-59 -5
=rs	47.6	57.5	18.4	0.1	32	21	52.2	7.4	0.2	14	10	45.2	1.1	0.01	3	-5
"" Fr "Co " " Go " " " " " " " " " " " " " " " "	47.8 47.2 47.2 47.3 47.5 47.5 47.5 47.4 47.6 47.3 46.6	48.6 57.5 50.6 52.6	32.6 18.4 12.4 6.3	0.07 0.1 0.06 0.03	25 12	7 13	49.4	3.1	0.05	6	4	19.6 45.2 41.7 46.8	4.6 4.7 5.6 4.0 5.7 4.8 3.4 1.1 1.3 1.8	0.005 0.01 0.01 0.003	12 14 30 15 24 17 3 4	-12 0.4
U	40.6	52.6	6.3	0.03	12	13	n.m.	n.m.				46.8	1.8	0.003	4	0.4
	Solution	LA-ICPQ	MS				Concentra LA-ICPSF y Mean (n=5	tion at MS) SD +8.8 ⁻¹ 1.2	ca. 10 j	45°		LA-ICPT	DFMS			
Isotopes	Concentratio µg g ⁻¹	n Mean (n=t µg g ⁻¹ 12.2 13.9) SD P88 12 43 1.7 2.6 10.4 1.2	LOD 198.8 0.9 7 3 4 9 2	Precision %	Accuracy %	y Mean (n=5 µg g ¹ 8.1 ≺ LOD) SD #8.8	LOD FE E	Precision %	Accuracy %	Mean (n=3 µg g ² n.m. < LOD	0FMS) SD PE 8 n.m.	FEE	Precisio %	n Accura %
'n	με ε ¹ 9.7 9.9 9.9 9.7 9.8 9.9	12.2	1.2	0.9	% 10	% 26 40	8.1	1.2	P8.8 ⁻¹ 0.5 35	% 15	% -16	n.m.	n.m.			
"B ≈M	9.9	13.9	-43	7	31	40	< LOD		35	49		< LOD		19		-11
2 AI	9.9	10.4	1.7	3	16	6	11.0	5.3	0.9	49	11	8.7	1.0 2.1	10	11 17	-11 33
"Cr	9.8	10.4 9.2 17.1 10.2	10.4	9	16 29 61 11	6 -5 74 4	11.0 10.2 9.8 9.0	5.3 2.3 3.1 2.3	0.9 1.0 1 0.5	31	11 5 -0.5 -8 77 -7	8.7 12.9 < LOD 9.1		10 5 14 1		
"Ma	9.9	10.2	1.2	2	11	4	9.0	2.3	0.5	25	-8	9.1	0.8	1	8	-8
"Fe	9.8	26.5 9.9	9.4 1.4	27	35	170		8.3	4	48	77		0.4	27 0.5		
"NI	9.7	9.9	1.4		15	2 16	9.0	2.5	0.03	28	-7	8.7	0.4		5	-11
"Ca	9.8 9.7 9.9 9.8 9.8 9.8 9.9 9.9	11.4 9.9 5.7 9.8	2.6 1.2 1.7 2.0 2.4	1 1 2	15 23 12 30 21	0.2	12.5 9.0 8.2 8.1 8.6 8.4	8.3 2.5 6.2 3.2 1.8 2.1 1.9 2.6 3.5 2.0	0.7 0.1 0.4 0.05	36	27 -9 -16 -17 -13	8.7 10.2 9.3 6.7 8.3	1.4 1.6 0.3 0.5 1.8 0.8	3 3 3	14 17 5 6 18	-11 4 -6 -31
"Za	9.8	5.7	1.7	2	30	0.2 -42 0 3 9 7 -41 -7	8.2	1.8	0.4	22	-16	6.7	0.3	3	5	-31
Ga	9.8	9.8	2.0	0.5 4 0.1	21	0	8.1	2.1	0.05	26	-17	8.3	0.5	0.5	6	-16 4 -14
Ge	9.9	10.2	2.4	4	23 15	3	8.6	1.9	0.6	22	-13 -15	10.2	1.8	1	18	4
"Nb	9.9	10.2 10.8 10.5 5.8 9.2	2.0	0.1	19	7	8.7	3.5	0.07	40	-12	8.5 8.6 8.0 8.9	1.1	0.2		-13
=ca	9.9 9.8 9.9	5.8	2.0 1.4 1.7	0.1 3 0.1	19 24 18	-41	10.1	2.6	0.07 0.11 0.02	26	-12 2 -16	8.0	1.1 0.5 0.3	0.2 1 0.1	13 7 3	-18
-"te	9.9	9.2	1.7	0.1	18	-7	8.3	2.0	0.02	24	-16	8.9	0.3	0.1		-10
"Sn	10.1	9.2	1.5	0.5	16	-9	7.3	1.6	0.15	21	-28	8.4	0.5	0.3	6 8	-17
	10.2	10.5	1.9	0.1	13	3	8.5	3.3	0.04	39	-16	8.6	1.1	0.05	8 12	-11
^m n	9.7	10.5 10.5 9.5 10.0	1.5 1.9 1.4 1.0 1.0 0.7 1.7 1.1	0.5 0.6 0.1 0.1 0.7 0.1	18 13 11 10	6 3 -2 2	8.1	2.1	0.04 0.04 0.04	23 11 23 48 28 29 21 26 21 21 28 26 26 76 26 26 26 26 26 26 26 26 26 26 26 26 26	-28 -1 -16 -17 -14 -14 -14 -24	8.0	1.1	0.3 0.4 0.05 0.03 0.2	12 13 11	-13 -18 -10 -17 -15 -18 -11 -46 -10
¹⁷⁹ Hf	9.8	10.0	1.0	0.7	10	2	8.4	2.0	0.04	24	-14	8.7	0.9	0.2		-11
Ta	9.8	6.6	0.7	0.1	10	-33	5.5	1.6	0.05	30	-44	5.3	0.8	0.04	16	-46
-w	10.1	10.5	1.7	0.5	16	4 -28	7.7	2.4	0.09	31 19		9.1	0.7	0.2	8	-55
	9.9	3.6	1.2	0.1	34	-63	24		0.01	42	-36 -74 -1	2.9	0.4	0.04	13	-70
-n																
=10	9.9	9.9	1.6	0.1	16	0.4	9.8	3.4	0.08	35	-1	9.1	0.3	0.05	3	-8
n ≃ns ≈ns	10.2 9.7 9.8 9.8 10.1 10.1 9.9 9.9 9.8 10.0	6.6 10.5 7.3 3.6 9.9 8.8 10.7	1.2 1.6 1.4 0.5	0.1 0.1 0.1	16 15 34 16 16 5	-63 0.4 -11 7	8.7 10.1 8.3 7.3 9.8 8.5 8.1 8.4 8.5 7.7 6.5 2.5 9.8 10.1 0.0	1.6 6.4 3.3 2.1 2.0 1.6 2.4 1.2 1.1 3.4 2.6 mm	0.17 0.01 0.08 0.03	30 31 19 42 35 25	-1 3	8.8 8.6 8.7 5.3 9.1 4.5 2.9 9.1 8.4 8.8	0.7 1.1 1.9 0.8 0.7 0.6 0.4 0.3 0.4 0.6	0.04 0.2 0.1 0.04 0.05 0.04 0.02	16 8 13 13 3 5 7	-70 -8 -14 -12
	9.9 9.8 10.0	10.7	0.5	0.1 0.1 0.1	16 16 5	0.4 -11 7	n.m.	3.4 2.6 n.m.			-1 3	9.1 8.4 8.8	0.3 0.4 0.6	0.05 0.04 0.02	3 5 7	-8 -14 -12
, LI = 8 MAL COM RECT 4 NO 10 10 10 10 10 10 10 10 10 10 10 10 10	9.9 9.8 10.0 Solution	10.7	0.5	0.1 0.1 0.1	16 16 5	0.4 -11 7	n.m. Concentr LA-ICPSF	n.m. ation at	ca. 1 µ		-1 3	8.8 LA-ICPT	0.6	0.05 0.04 0.02	3 5 7	-8 -14 -12
Isotopes	10.0 Solution Concentratio	10.7	0.5	0.1 LOD	5 Precision	7 Accuracy	n.m. Concentr LA-ICPSF y Mean (n=5	n.m. ation at MS) SD	ea. 1 p	E E ⁴ Precision %	3 Accuracy %	8.8 LA-ICPT	0.6 9FMS) SD 18.5	0.05 0.04 0.02 LOD H8.8	3 5 7 Precisio %	-8 -14 -12 n Accura %
Isotopes	10.0 Solution Concentratio	10.7 LA-ICPQ n Mean (n=5 µ8 8 ⁻¹ 1.01	0.5	0.1 LOD P8.8	16 16 5 Precision % 14	0.4 -11 7 Accuracy % 6	n.m. Concentr LA-ICPSF y Mean (n=5 µg g ² 0.64	n.m. ation at	ca. 1 µ LOD P8.8 ⁻¹ 0.5		-1 3 1 Accuracy % -33	8.8 LA-ICPTI Mean (n=0 µ8.8 ^d n.m.	0.6 DFMS () SD	0.02 LOD	7 Precisio	-12 n Accura
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Mean (n=5 µ8 8 ⁻¹ 1.01	0.5 MS) SD P8.8 0.1	0.1 LOD H8.8 0.3 2	5 Precision % 14	7 Accuracy % 6	n.m. Concentr LA-ICPSF y Mean (n=5 µg g ² 0.64	n.m. ation at MS) SD	ca. 1 p LOD PE 8 ¹ 0.5 52	E E ⁴ Precision %	3 1 Accuracy 54 -33	8.8 LA-ICPTI Mean (n=0 µ8.8 ^d n.m.	0.6 9FMS) SD 18.5	0.02 LOD	7 Precisio	-12 n Accura
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Mean (n=5 µ8 8 ⁻¹ 1.01	0.5	0.1 LOD H8.8 0.3 2	5 Precision	7 Accuracy	n.m. Concentr LA-ICPSF y Mean (n=5 µg g ² 0.64	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ca. 1 p LOD PE 8 ¹ 0.5 52	EE ¹ Precision % 25	3 1 Accuracy 54 -33	8.8 LA-ICPTI Mean (n=0 µ8.8 ^d n.m.	0.6 9FMS) SD 18.5	0.02 LOD P8.8 ⁻¹ 7 3	7 Precisio	-12 n Accura
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD 98.8 0.1 0.2	0.1 LOD P8.8 0.3 2 1 0.8 2	5 Precision % 14 18	7 Accuracy % 6 -11	n.m. Cancentr LA-ICPSF y Mean (n=5 µg g ² 0.64 < LOD < LOD 1.15 1.78	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ca. 1 p LOD P8.8 ⁻¹ 0.5 52 2 0.9 1	EE ¹ Precision 25 26 29	3 Accuracy % -33 20 84	8.8 Mean (s=0 µg g ² nm. < LOD < LOD < LOD < LOD	0.6 XFMS) SD P8.8 	0.02 LOD H8.8 ⁻¹ 7 3 2 5	7 Precisio %	-12 n Accura %
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD P8.8 0.1	0.1 LOD H8.8 ⁻¹ 0.3 2 1 0.8 2 0.5	5 Precision % 14	7 Accuracy % 6	n.m. Concentr LA-ICPSF Mean (n=5 µg g ¹ 0.64 < LOD < LOD 1.15 1.78 0.88	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ca. 1 p LOD P8.8 ⁻¹ 0.5 52 2 0.9 1	8 8 ⁴ Precision 25 26 29 20	3 1 Accuracy 54 -33	8.8 Man (n=0 P8 8 ² n.m. < LOD < LOD < LOD < LOD	0.6 9FMS) SD 18.5	0.02 LOD H8.8 ⁻¹ 7 3 2 5	7 Precisio	-12 n Accura
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD 98.8 0.1 0.2 0.1	0.1 LOD H8.8 ⁻¹ 0.3 2 1 0.8 2 0.5	5 Precision % 14 18 15	7 1 Accuracy % 6 -11 -15	n.m. Concentr LA-ICPSF Mean (n=5 µg g ¹ 0.64 < LOD < LOD 1.15 1.78 0.88	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ca. 1 p LOD P8.8 ⁻¹ 0.5 52 2 0.9 1	8 8 ⁴ Precision 25 26 29 20	3 Accuracy % -33 20 84 -10	8.8 Man (n=0 P8 8 ² n.m. < LOD < LOD < LOD < LOD	0.6 9 MS 9 SD 988 0.3	0.02 LOD H8.8 ⁻¹ 7 3 2 5	7 Precisio %	-12 n Accura %
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD 98.8 0.1 0.2 0.1	0.1 LOD H8.8 ⁻¹ 0.3 2 1 0.8 2 0.5	5 Precision % 14 18 15	7 1 Accuracy % 6 -11 -15	n.m. Concentr LA-ICPSF Mean (n=5 µg g ¹ 0.64 < LOD < LOD 1.15 1.78 0.88	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ca. 1 p LOD P8.8 ⁻¹ 0.5 52 2 0.9 1	8 8 ⁴ Precision 25 26 29 20	3 Accuracy % -33 20 84 -10	8.8 Man (n=0 P8 8 ² n.m. < LOD < LOD < LOD < LOD	0.6 9 MS 9 SD 988 0.3	0.02 LOD H8.8 ⁻¹ 7 3 2 5	7 Precisio % 26 8	-12 n Accura %
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD 98.8 0.1 0.2 0.1	0.1 LOD P8.8 0.3 2 1 0.8 2 0.5 6 0.05 0.3 0.2	5 Precision 35 14 18 15 13 16 18	7 1 Accuracy % 6 -11 -15	n.m. Concentr LA-ICPSF y Mean (n=5 9 8g s ² 0.64 < LOD 1.15 1.78 0.88 9.68 0.89 2.06 0.87	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	LOD F8.8 ⁻¹ 0.5 52 2 0.9 1 0.5 4 0.03 0.7 0.1	55 ¹ Precision 25 25 20 50 13 79 23	3 Accuracy % -33 20 84 -10	8.8 Man (n=0 P8 8 ² n.m. < LOD < LOD < LOD < LOD	0.6 9 MS 9 SD 988 0.3	0.02 LOD H8.8 ⁻¹ 7 3 2 5	7 Precisie % 26 8 41 41	-12 m Accura % 9 -12 87 33
Isotopes	10.0 Solution Concentratio µg g ² 0.96 0.98	10.7 LA-ICPQ n Man (s ⁻² µg g ² 1.01 < LOD 0.87 < LOD < LOD	0.5 MS) SD 98.8 0.1 0.2 0.1	0.1 LOD P8.8 0.3 2 1 0.8 2 0.5 6 0.05 0.3 0.2	5 Precision % 14 18 15 15 16 18 60	7 1 Accuracy % 6 -11 -15	n.m. Concentr LA-ICPSE y Mann (n=5 9 0.64 < LOD 1.15 1.78 0.88 9.68 0.69 2.06 0.87 0.75	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	LOD F8.8 ⁻¹ 0.5 52 2 0.9 1 0.5 4 0.03 0.7 0.1	55 ¹ Precision 25 25 20 50 13 79 23	3 Accuracy 5 -33 20 84 -10 -29 113 -10 -19	8.8 LA-ICPT (man (n=6 pg g ² n.m. < LOD < LOD < LOD 1.07 < LOD 0.54 1.27 	0.6 97MS 9 SD 988 0.3 0.3 0.1 0.7 0.5 0.5	0.02 H8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1	7 Precisie % 26 8 41 41 39	-12 n Accura 5 9 -12 87 33 31
Isotopes	10.0 Solution Concentration 10.96 0.96 0.96 0.96 0.97 0.96 0.97 0.97 0.97 0.97 0.97	10.7 LA-ICPQ n Mean (n=5 P8 g ² 1.01 < LOD 0.87 < LOD 0.87 < LOD 0.87 < LOD 0.81 0.98 0.83 0.59 0.79	0.5 MS 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	0.1 H0 8 1 1 0.8 2 0.5 6 0.06 0.3 0.2 0.5 0.1 0.5 0.1	5 Precision % 14 18 15 15 13 16 18 60 11	7 14 Accuracy 56 6 -11 -15 -16 1 -14 -14 -39 -28	n.m. Concentr: LA-ICPSF 9 Mam (n=5 9 0.64 < LOD 1.15 1.78 0.68 0.69 2.06 0.67 0.77 0.78	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	68.1 p LOD 1885 ⁷ 0.5 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.1	55 ¹ Precision 25 26 29 20 50 13 79 23 40 18	3 Accuracy 54 -33 20 84 -10 -29 113 -10 -19 -36	8.8 Man (s=6 P8 g ² n.m. < LOD < LOD < LOD 1.07 < LOD 0.84 1.81 1.29 1.27 0.73	0.6 97MS 9 SD 988 0.3 0.3 0.1 0.7 0.5 0.5 0.03	0.02 H8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1	7 Pracisic % 26 8 41 41 39 5	-12 n Accura 5 9 -12 87 33 31
Isotopes	10.0 Solution PES ² 0.96 0.98 0.98 0.98 0.98 0.97 0.97 0.97 0.97 0.97 0.97 0.97	10.7 LA-ECPQ pg g ² 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.84 0.98 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.84 0.99 0.79 0.79 0.75 0.99 0.75 0.99 0.75 0.99 0.75 0.99 0.75 0.99 0.75 0.99 0.75 0.99 0.75 0.99 0.94 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.99 0.97 0.99 0.99 0.99 0.99 0.99 0.97 0.99 0.99 0.99 0.99 0.97 0.99 0.99 0.99 0.99 0.97 0.99 0.99 0.99 0.97 0.99 0.99 0.97 0.99 0.99 0.97 0.99 0.99 0.97 0.99 0.97 0.99 0.99 0.97 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.99 0.97 0.97 0.99 0.97 0.99 0.97 0.	0.5 MS 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	0.1 HER 1.00D 1.00D 1.00D 1.00D 1.00D 0.5 0.05 0.05 0.05 0.05 0.1 0.5 0.05	5 Precision % 14 18 15 13 16 18 60 11 23	7 56 6 -11 -15 -16 1 -14 -39 -20	n.m. Concentr LA-ECPSF y Mean (u=5 pg gd 0.64 <lod <lod <lod 1.15 1.78 0.88 9.68 0.69 2.06 0.87 0.78 0.63 1.11</lod </lod </lod 	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	68.1 p LOD 1885 ⁷ 0.5 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.1	8.8 ⁴ Precision 25 26 29 20 50 13 79 23 40 18 31	3 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14	8.8 LA-ICPT Mass (s=6 P8.8 ^d nm. <lod <lod <lod <lod <lod 0.84 1.81 1.29 1.27 0.73 0.89</lod </lod </lod </lod </lod 	0.6 97MS 9 SD 988 0.3 0.3 0.1 0.7 0.5 0.5 0.03	0.02 H8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1	7 Pracisic % 26 8 41 41 39 5 10	-12 n Accara % 9 -12 87 33 31 -24 -9
Isotopes	10.0 Solution PES ² 0.96 0.98 0.98 0.98 0.98 0.97 0.97 0.97 0.97 0.97 0.97 0.97	10.7 LA-ECPQ pg g ² 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.84 0.98 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.84 0.99 0.79 0.79 0.79 0.70 0.84 0.99 0.79 0.	0.5 MS 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	0.1 HER 1.00D 1.00D 1.00D 1.00D 1.00D 0.5 0.05 0.05 0.05 0.05 0.1 0.5 0.05	5 Precision % 14 18 15 13 16 18 60 11 23	7 56 6 -11 -15 -16 1 -14 -39 -20	n.m. Concentr LA-ECPSF y Mean (u=5 pg gd 0.64 <lod <lod <lod 1.15 1.78 0.88 9.68 0.69 2.06 0.87 0.78 0.63 1.11</lod </lod </lod 	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	68.1 p LOD 1885 ⁷ 0.5 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.1	8.8 ⁴ Precision 25 26 29 20 50 13 79 23 40 18 31	3 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14	8.8 LA-ICPT Mass (s=6 P8.8 ^d nm. <lod <lod <lod <lod <lod 0.84 1.81 1.29 1.27 0.73 0.89</lod </lod </lod </lod </lod 	0.6 97MS 9 SD 988 0.3 0.3 0.1 0.7 0.5 0.5 0.03	0.02 H8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1	7 Pracisic % 26 8 41 41 39 5 10	-12 n Accara % 9 -12 87 33 31 -24 -9
Isotopes	10.0 Solution PES ² 0.96 0.98 0.98 0.98 0.98 0.97 0.97 0.97 0.97 0.97 0.97 0.97	10.7 LA-ECPQ pg g ² 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.84 0.98 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.87 0.99 0.70 0.84 0.99 0.79 0.79 0.79 0.70 0.84 0.99 0.79 0.	0.5 MS 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2 0.2	0.1 HER 1.00D 1.00D 1.00D 1.00D 1.00D 0.5 0.05 0.05 0.05 0.05 0.1 0.5 0.05	5 Precision % 14 18 15 13 16 18 60 11 23	7 56 6 -11 -15 -16 1 -14 -39 -20	n.m. Concentr LA-ECPSF y Mean (u=5 pg gd 0.64 <lod <lod <lod 1.15 1.78 0.88 9.68 0.69 2.06 0.87 0.78 0.63 1.11</lod </lod </lod 	n.m. ation at MS) SD P8.8 ⁻¹ 0.2	ea. 1 p LOD 198 8 ⁻¹ 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.1 0.6 0.03 0.02 0.05	8.8 ⁴ Precision 25 26 29 20 50 13 79 23 40 18 31	3 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14	8.8 LA-ICPT Mass (s=6 P8.8 ^d nm. <lod <lod <lod <lod <lod 0.84 1.81 1.29 1.27 0.73 0.89</lod </lod </lod </lod </lod 	0.6 97MS 9 SD 988 0.3 0.3 0.1 0.7 0.5 0.5 0.03	0.02 H8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1	7 Pracisic % 26 8 41 41 39 5 10	-12 n Accara % 9 -12 87 33 31 -24 -9
Isotopes	10.0 Solution Concentratio PAR g ⁻¹ 0.96 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 0.97 0	10.7 LA-ICPQ pgg ⁴ 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.83 0.98 0.83 0.99 0.70 0.82 0.82 0.35 0.52 0.35 0.5	0.5 MS P88 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD H88 ⁰ 0.3 2 1 0.5 6 0.06 0.3 0.2 0.5 0.1 0.8 0.02 0.03 0.4 0.02	5 Precision % 14 18 15 13 16 11 23 8 15 60 11 23 8 15 60 16	7 5 6 -11 -15 -16 1 -14 -39 -28 -40 -15 -41 -25	n.m. Concentr LA-CCPSU y Mean (u=5 16,64 < LOD 1.15 1.78 0.68 0.69 2.06 0.87 0.78 0.63 1.11 0.77 0.51 0.77 0.51 0.92 0.68	nm attion at MS) SD PEE 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.1 0.3 0.2 0.3 0.1 0.3 0.1 0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	ea. 1 µ LOD 1885 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.02 0.06 0.01	88 ⁴ Precision 55 23 20 20 20 20 20 20 20 20 20 20 20 20 20	3 1 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14 -21 -48 -6 -30	8.8 LA-RCPTH PR 8 ^d n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.43 0.71 0.75	0.6 39 MS) SD P68 ² nm 0.3 0.3 0.3 0.1 0.5 0.5 0.03 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.02 LOD #8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.5 0.08 0.07 0.5 0.02	7 Precisio % 26 8 41 41 39 5 10 6 15 14 8	-12 m Accura 5 9 -12 87 33 31 -14 -9 -14 -56 -27 -23
Isotopes	10.0 Solution Concentratio PAR g ⁻¹ 0.96 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 0.97 0	10.7 LA-ICPQ pgg ⁴ 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.83 0.98 0.83 0.99 0.70 0.82 0.82 0.35 0.52 0.35 0.5	0.5 MS P88 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD H88 ⁰ 0.3 2 1 0.5 6 0.06 0.3 0.2 0.5 0.1 0.8 0.02 0.03 0.4 0.02	5 Precision % 14 18 15 13 16 11 23 8 15 60 11 23 8 15 60 16	7 5 6 -11 -15 -16 1 -14 -39 -28 -40 -15 -41 -25	n.m. Concentr LA-CCPSU y Mean (u=5 16,64 < LOD 1.15 1.78 0.68 0.69 2.06 0.87 0.78 0.63 1.11 0.77 0.51 0.77 0.51 0.92 0.68	nm attion at MS) SD PEE 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.1 0.3 0.2 0.3 0.1 0.3 0.1 0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	ea. 1 µ LOD 1885 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.02 0.06 0.01	88 ⁴ Precision 55 23 20 20 20 20 20 20 20 20 20 20 20 20 20	3 1 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14 -21 -48 -6 -30	8.8 LA-RCPTH PR 8 ^d n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.43 0.71 0.75	0.6 39 MS) SD P68 ² nm 0.3 0.3 0.3 0.1 0.5 0.5 0.03 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.02 LOD #8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.5 0.08 0.07 0.5 0.02	7 Precisio % 26 8 41 41 39 5 10 6 15 14 8	-12 m Accura 5 9 -12 87 33 31 -14 -9 -14 -56 -27 -23
Isotopes	10.0 Solution Concentratio PAR g ⁻¹ 0.96 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 0.97 0	10.7 LA-ICPQ pgg ⁴ 1.01 < LOD 0.87 < LOD 0.84 < LOD 0.84 < LOD 0.83 0.98 0.83 0.99 0.70 0.82 0.82 0.35 0.52 0.35 0.5	0.5 MS P88 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.5 0.1 0.5 0.1 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	0.1 LOD H88 ⁰ 0.3 2 1 0.5 6 0.06 0.3 0.2 0.5 0.1 0.8 0.02 0.03 0.4 0.02	5 Precision % 14 18 15 13 16 11 23 8 15 60 11 23 8 15 60 16	7 5 6 -11 -15 -16 1 -14 -39 -28 -40 -15 -41 -25	n.m. Concentr LA-CCPSU y Mean (u=5 16,64 < LOD 1.15 1.78 0.68 0.69 2.06 0.87 0.78 0.63 1.11 0.77 0.51 0.77 0.51 0.92 0.68	nm attion at MS) SD PEE 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.1 0.3 0.2 0.3 0.1 0.3 0.1 0.3 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	ea. 1 µ LOD 1885 52 2 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.02 0.06 0.01	88 ⁴ Precision 55 23 20 20 20 20 20 20 20 20 20 20 20 20 20	3 1 Accuracy 5 -33 20 84 -10 -29 113 -10 -19 -36 14 -21 -48 -6 -30	8.8 LA-RCPTH PR 8 ^d n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.43 0.71 0.75	0.6 39 MS) SD P68 ² nm 0.3 0.3 0.3 0.1 0.5 0.5 0.03 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.02 LOD #8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.5 0.08 0.07 0.5 0.02	7 Precisio % 26 8 41 41 39 5 10 6 15 14 8	-12 m Accura 5 9 -12 87 33 31 -14 -9 -14 -56 -27 -23
Isotopes	10.0 Solution P&g ² 0.96 0.98 0.98 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.95 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97 0.95 0.95 0.95 0.95 0.95 0.97 0.97 0.95	10.7 LA-ICPQ PR 8 1.01 <lod 0.87 <lod 0.84 <lod 0.84 <lod 0.84 <lod 0.84 <lod 0.84 0.98 0.99 0.70 0.87 0.82 0.82 0.82 0.82 0.33 0.42 0.82 0.82 0.82 0.82 0.85 0.82 0.82 0.85 0.82 0.85 0.82 0.85 0.82 0.85 0.8</lod </lod </lod </lod </lod </lod 	0.5 MS 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD 165.5 0.3 2 0.5 6 0.06 0.3 0.2 0.5 0.1 0.8 0.02 0.3 0.1 0.8 0.02 0.3 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.02 0.	5 Precision 55 14 15 15 13 16 18 60 11 23 8 15 23 8 15 16 16 16 17 10 18 14	7 8 Accuracy % 6 -11 -15 -16 1 -14 -14 -15 -28 -0 -28 -41 -6 -5 -5 -6 -11 -15 -15 -15 -15 -15 -15 -15	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	ca. 1 µ LOD 165 52 0.9 1 0.5 4 0.0 1 0.3 0.7 0.1 0.3 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 Accuracy % -33 20 84 -10 -29 113 -10 -29 113 -10 -48 -6 -46 -42 -12 11 11 -14	8.8 LA-RCPTH PR 8 ^d n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.43 0.71 0.75	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD HE 8 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.09 1 1 0.2 0.00 0.00 0.00 0.00 0.01 0.01 0.02 0.01 0.00 0.0	7 Precisio 26 8 41 41 41 9 5 10 6 15 4 8 10 17 4 5	-12 9 9 -12 87 33 31 -24 -46 -56 -27 -23 39 -99 -19 -19 -23
Isotopes	10.0 Solution Concentration 0.96 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.96 0.97 0.9	10.7 IA-SCPQ # Mean (m=5 # R g ² 1.01 < LOD 0.57 < LOD 0.81 0.95 0.35 0.57 0.	0.5 MS P8.8 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 H88 100 H88 2 1 0.5 6 0.06 0.3 0.2 0.5 6 0.06 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.4 0.3 0.2 0.3 0.4 0.3 0.2 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.1 0.5 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	5 Precision 14 15 15 15 15 16 60 16 17 10 18 14 14 27	7 54 Accuracy 54 6 -11 -15 -16 1 -14 -39 9 -41 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -16 -10 -15 -10 -15 -16 -10 -15 -16 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -10 -15 -15 -10 -15 -15 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -17 -16 -15 -16 -17 -19 -19 -19 -19 -19 -19 -19 -19	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	CR. 1 P LOD PEE 0.5 2 0.9 1 0.5 4 0.03 0.1 0.03 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.05	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 54 54 -03 20 84 -10 -10 -10 -10 -10 -10 -10 -10 -10 -10	8.8 LA-ICPT0 / Mam (n=6 pg g ² n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.84 0.84 0.43 0.74 0.74	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD H8.8 ⁻¹ 7 3 2 0.4 9 0.2 0.9 1 0.2 0.9 1 0.2 0.5 0.08 0.07 0.1 0.1 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05	7 95 26 8 41 41 39 5 10 6 15 14 8 10 17 4 5 9	-12 9 9 -12 87 33 31 -24 -46 -56 -27 -23 39 -99 -19 -19 -23
Isotopes	10.0 Solution P8.87 0.96 0.98 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 1.00 1.96 1.97 0.97 0.98 1.96 1.96 0.97 0.97 0.98 1.96 0.97 0.97 0.97 0.98 1.97 0.97 0.97 0.98 1.97 0.97 0.97 0.97 0.98 1.97 0.98 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97	10.7 IA-SCPQ # Mean (m=5 # R g ² 1.01 < LOD 0.57 < LOD 0.81 0.95 0.35 0.57 0.	0.5 MS PEE 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ILOD 165.8 0.3 2 1 0.8 0.06 0.3 0.2 0.5 0.03 0.4 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.03	5 Precision % 14 15 15 15 15 16 10 11 23 8 15 60 16 16 16 17 10 18 14 27 33	7 5 6 -11 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -15 -16 -19 -28 -29 -29 -29 -29 -29 -29 -29 -29	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	ca. 1 pp HGB HG 8 ⁻¹ 2 0.9 1 0.5 4 0.03 0.1 0.1 0.03 0.02 0.06 0.01 0.02 0.05 0.55 0.55 0.55 0.55	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 4 Accuracy 5 -33 20 84 -10 -29 -36 -48 -6 -12 -48 -6 -12 -14 -14 -8 -8 -8 -8 -14 -8 -8 -8 -8 -8 -8 -8 -8 -8 -8	8.8 LA-ICPT0 / Mam (n=6 pg g ² n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.84 0.84 0.43 0.74 0.74	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD H8.8 ⁻¹ 7 3 2 0.4 9 0.2 0.9 1 0.2 0.9 1 0.2 0.5 0.08 0.07 0.1 0.1 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05	7 Precisio 35 26 8 41 41 39 5 10 6 5 14 8 10 6 15 14 8 10 77 4 5 9 77	-12 9 9 -12 87 33 31 31 -34 -66 -27 -39 -14 -36 -23 -39 -19 -23 -24 -24 -25 -25 -25 -25 -25 -25 -25 -25
Isotopes	10.0 Solution P8.87 0.96 0.98 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 1.00 1.96 1.97 0.97 0.98 1.96 1.96 0.97 0.97 0.98 1.96 0.97 0.97 0.97 0.98 1.97 0.97 0.97 0.98 1.97 0.97 0.97 0.97 0.98 1.97 0.98 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97	10.7 IA-SCPQ # Mean (m=5 # R g ² 1.01 < LOD 0.57 < LOD 0.81 0.95 0.35 0.57 0.	0.5 MS PEE 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ILOD 165.8 0.3 2 1 0.8 0.06 0.3 0.2 0.5 0.03 0.4 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.03	5 Precision % 14 15 15 15 15 16 10 11 23 8 15 60 16 16 16 17 10 18 14 27 33	7 5 6 -11 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -15 -16 -19 -28 -29 -29 -29 -29 -29 -29 -29 -29	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	ca. 1 pp HGB HG 8 ⁻¹ 2 0.9 1 0.5 4 0.03 0.1 0.1 0.03 0.02 0.06 0.01 0.02 0.05 0.55 0.55 0.55 0.55	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 4 Accuracy 5 -33 20 84 -10 -29 -36 -48 -6 -12 -48 -6 -12 -14 -14 -8 -8 -8 -8 -14 -8 -8 -8 -8 -8 -8 -8 -8 -8 -8	8.8 LA-ICPTI #R87, n87, n87, n87, n87, 187, 200, 200, 200, 200, 200, 200, 200, 20	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD H8.8 ⁻¹ 7 3 2 0.9 0.2 0.9 0.2 0.9 1 0.2 0.5 0.08 0.07 0.1 0.1 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.05 0.05 0.05 0.02 0.05	7 Precisio 35 26 8 41 41 39 5 10 6 5 14 8 10 6 15 14 8 10 77 4 5 9 77	-12 9 9 -12 87 33 31 31 -34 -66 -27 -39 -14 -36 -23 -39 -19 -23 -24 -24 -25 -25 -25 -25 -25 -25 -25 -25
Isotopes	10.0 Solution P8.87 0.96 0.98 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 1.00 1.96 1.97 0.97 0.98 1.96 1.96 0.97 0.97 0.98 1.96 0.97 0.97 0.97 0.98 1.97 0.97 0.97 0.98 1.97 0.97 0.97 0.97 0.98 1.97 0.98 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.97 0.96 0.97 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.96 0.97	10.7 IA-SCPQ # Mean (m=5 # R g ² 1.01 < LOD 0.57 < LOD 0.81 0.95 0.35 0.57 0.	0.5 MS PEE 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ILOD 165.8 0.3 2 1 0.8 0.06 0.3 0.2 0.5 0.03 0.4 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.03	5 Precision % 14 15 15 15 15 16 10 11 23 8 15 60 16 16 16 17 10 18 14 27 33	7 5 6 -11 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -15 -16 -19 -28 -29 -29 -29 -29 -29 -29 -29 -29	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.1 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	ca. 1 pp HGB HG 8 ⁻¹ 2 0.9 1 0.5 4 0.03 0.1 0.1 0.03 0.02 0.06 0.01 0.02 0.05 0.55 0.55 0.55 0.55	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 4 Accuracy 5 -33 20 84 -10 -29 -36 -48 -6 -12 -48 -6 -12 -14 -14 -8 -8 -8 -8 -14 -8 -8 -8 -8 -8 -8 -8 -8 -8 -8	8.8 LA-ICPTI #R87, n87, n87, n87, n87, 187, 200, 200, 200, 200, 200, 200, 200, 20	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD H8.8 ⁻¹ 7 3 2 0.9 0.2 0.9 0.2 0.9 1 0.2 0.5 0.08 0.07 0.1 0.1 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.05 0.05 0.05 0.02 0.05	7 Precisio 35 26 8 41 41 39 5 10 6 5 14 8 10 6 15 14 8 10 77 4 5 9 77	-12 9 9 -12 87 33 31 31 -34 -66 -27 -39 -14 -36 -23 -39 -19 -23 -24 -24 -25 -25 -25 -25 -25 -25 -25 -25
Isotopes	10.0 Solution P8.87 0.96 0.98 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 1.09 1.96 0.97 0.97 0.98 1.96 0.97 0.97 0.98 1.96 0.97 0.97 0.97 0.98 1.97 0.97 0.97 0.98 1.97 0.97 0.97 0.97 0.98 1.97 0.98 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.98 0.97 0.97 0.97 0.98 0.97 0.98 0.97 0.98 0.97 0.97 0.98 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.97 0.98 0.96 0.97 0.96 0.97 0.96 0.97 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.97 0.96 0.97 0.96 0.97 0.97 0.96 0.97 0.97 0.96 0.97	10.7 IA-SCPQ # Mean (m=5 # R g ² 1.01 < LOD 0.57 < LOD 0.81 0.95 0.35 0.57 0.	0.5 MS PEE 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ILOD 165.8 0.3 2 1 0.8 0.06 0.3 0.2 0.5 0.03 0.4 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.02 0.03	5 Precision % 14 15 15 15 15 16 10 11 23 8 15 60 16 16 16 17 10 18 14 27 33	7 54 Accuracy 56 6 -11 -15 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -16 -15 -15 -16 -15 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cancountr LL-ICCPSB y Mazn (n=5 0.64 < LOD 1.15 1.78 0.88 0.69 2.06 0.87 0.78 0.88 0.69 2.06 0.87 0.78 0.53 1.11 0.77 0.51 0.52 0.64 0.86 1.13	am. ation at a MS MS 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.1 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	ca. 1 µ HE 8 ⁻¹ 52 2 0.5 52 2 0.5 4 0.5 0.7 0.1 0.3 0.1 0.3 0.02 0.06 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.03 0.02 0.01 0.03 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.03 0.02 0.03 0.03 0.03 0.02 0.03 0.03 0.02 0.03 0.	88 ⁴ Precision 25 25 26 20 50 13 77 23 40 18 11 16 12 23 13 20 50 13 77 23 40 18 11 16 12 23 25 25 25 25 25 25 25 25 25 25 25 25 25	3 5 5 3 3 20 84 84 -10 -29 113 -10 -29 -36 8 4 -46 -42 -25 11 -14 -48 -45 -25 -25 -25 -20 -20 -20 -20 -20 -20 -20 -20 -20 -20	8.8 LA-ICPTI #R87, n87, n87, n87, n87, 187, 200, 200, 200, 200, 200, 200, 200, 20	0.6 WMS 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD H8.8 ⁻¹ 7 3 2 0.9 0.2 0.9 0.2 0.9 1 0.2 0.5 0.08 0.07 0.1 0.1 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.05 0.05 0.05 0.02 0.05	7 Precisio 35 26 8 41 41 39 5 10 6 5 14 8 10 6 15 14 8 10 77 4 5 9 77	-12 n Accura % % % ~ % ~ % ~ % % % % % % % % % % %
Isotopes	10.0 Solution Concentration 0.96 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.96 0.97 0.96 0.97 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.96 0.97 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.96 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.97 0.96 0.97 0.9	10.7 LA-ICPQ PR 8 1.01 <lod 0.87 <lod 0.84 <lod 0.84 <lod 0.84 <lod 0.84 <lod 0.84 0.98 0.99 0.70 0.87 0.82 0.82 0.82 0.82 0.33 0.42 0.82 0.82 0.82 0.82 0.85 0.82 0.82 0.85 0.82 0.85 0.82 0.85 0.82 0.85 0.8</lod </lod </lod </lod </lod </lod 	0.5 MS PEE 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 H88 100 H88 2 1 0.5 6 0.06 0.3 0.2 0.5 6 0.06 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.2 0.3 0.4 0.3 0.2 0.3 0.4 0.3 0.2 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.5 0.1 0.1 0.1 0.5 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	5 Precision 14 15 15 15 15 16 60 16 17 10 18 14 14 27	7 5 6 -11 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -1 -15 -16 -15 -16 -19 -28 -29 -29 -29 -29 -29 -29 -29 -29	n.m. Concentry UMane (mod-2) Ref. # 2 4.000 1.15 4.000 1.15 4.000 2.060 2.060 0.87 0.33 0.33 0.43 0.43 0.45 0.45 0.45 0.45 0.45 0.45 0.45 0.45	am. ation at MS 02 03 05 02 03 05 02 03 05 02 03 05 02 03 03 03 03 03 03 03 03 03 03	ca. 1 pp HGB HGB 105 2 0.9 1 0.5 2 0.9 1 0.3 0.1 0.3 0.01 0.03 0.02 0.05 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.02 0.05 0.55 0.55 0.55 0.55 0.55 0.55 0.55	55 ⁴ 52 26 29 20 50 30 30 30 30 30 30 30 31 31 31 31 31 31 31 32 32 32 30 50 31 31 31 31 31 31 31 32 32 32 32 32 32 32 32 32 32 32 32 32	3 4 Accuracy 5 -33 20 84 -10 -29 -36 -48 -6 -12 -48 -6 -12 -14 -8 -8 -8 -14 -8 -8 -8 -8 -8 -8 -14 -14 -14 -14 -14 -14 -14 -14	8.8 LA-ICPT0 / Mam (n=6 pg g ² n.m. < LOD < LOD < LOD 0.84 1.81 1.27 0.73 0.84 0.84 0.84 0.43 0.74 0.74	0.6 39 MS) SD P68 ² nm 0.3 0.3 0.3 0.1 0.5 0.5 0.03 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	LOD HE 8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.08 0.07 0.5 0.02 0.1 0.1 0.12 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.05 0.02 0.01 0.02 0.02 0.05 0.02 0.05 0.02 0.05 0	7 95 26 8 41 41 39 5 10 6 15 14 8 10 17 4 5 9	-12 9 9 -12 87 33 31 31 -34 -66 -27 -39 -14 -36 -23 -39 -19 -23 -24 -24 -25 -25 -25 -25 -25 -25 -25 -25
The second secon	10.0 Solution Fig.5 ² 0.96 0.98 0.98 0.97	10.7 1.4-KCPQ 1.6 Man (see) 1.6 Man (see)	0.5 MS P6.6 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ILOD 108 5 0.3 2 1 0.8 2 0.5 6 0.06 0.3 0.2 0.3 0.3 0.2 0.3 0.3 0.3 0.3 0.3 0.4 0.02 0.	5 Precision 14 15 15 13 16 10 11 23 8 15 16 16 17 10 18 14 27 20 20 16 10 15	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	nm. Concentry UMane (mod-2) R4A(759) R44 Concentry Conce	a.m. ation at MS 0.5 0.2 0.3 0.5 0.2 0.2 0.3 0.5 0.2 0.2 0.3 0.1 0.3 0.1 0.3 0.3 0.1 0.3 0.3 0.1 0.3 0.3 0.5 0.2 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	ra. 1 µ LOD 148 8 ⁻¹ 0.5 52 0.9 1 0.5 4 0.03 0.1 0.1 0.1 0.03 0.02 0.06 0.02 0.05 0.01 0.01 0.01 0.01 0.01 0.01 0.01	EE ⁴ Precision 25 26 20 20 20 20 20 20 20 20 20 20 20 20 20	3 5 5 3 3 20 84 84 -10 -29 113 -10 -29 -36 8 4 -46 -42 -25 11 -14 -48 -45 -25 -25 -20 -20 -21 -21 -21 -21 -21 -21 -21 -21 -21 -21	8.8 LA-LCTI Mana (se ⁻¹ max, se ⁻¹ LLD LLD LLD LLD LLD LLD LLD LL	0.6 39 MS 196 8 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	0.02 FE 5 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.5 0.05 0.02 0.1 0.02 0.01 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.01 0.02 0.0	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Isotopes	10.0 Salarias Concentration 0.56 0.56 0.57 0.55 0.57	10.7 14.4CP(0) 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.5 MS PEE 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD PERF 0.3 2 1 0.8 0.0 0.3 0.2 0.5 0.3 0.2 0.3 0.3 0.2 0.3 0.3 0.2 0.3 0.3 0.3 0.2 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	5 Precision 14 15 15 13 16 10 11 23 8 15 16 16 17 10 18 14 27 20 20 16 10 15	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cascentre LA-KCPSP Mana (new) LA-KCPSP 0.64 0.64 0.64 0.64 0.65 0.65 0.65 0.65 0.65 0.65 0.65 0.65	a.m. atten at MS 0.5 0.2 0.3 0.5 0.2 0.2 0.3 0.5 0.2 0.2 0.3 0.1 0.1 0.2 0.3 0.1 0.3 0.1 0.3 0.3 0.2 0.2 0.3 0.3 0.5 0.2 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	ra. 1 µ LOD H8 8 ⁻¹ 0.5 52 0.9 1 0.5 4 0.03 0.7 0.1 0.3 0.01 0.	88 ⁴ Precision 25 25 26 20 50 13 77 23 40 18 11 16 12 23 13 20 50 13 77 23 40 18 11 16 12 23 25 25 25 25 25 25 25 25 25 25 25 25 25	3 5 5 3 3 20 84 84 -10 -29 113 -10 -29 -36 8 4 -46 -42 -25 11 -14 -48 -45 -25 -25 -20 -20 -21 -21 -21 -21 -21 -21 -21 -21 -21 -21	83 LA-ICPTI Mana (10 ⁻¹⁰) R	0.6 39350 PEE 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD #8.8 ⁻¹ 7 3 2 5 0.4 9 0.2 0.4 9 0.2 0.5 0.05 0.02 0.1 0.02 0.01 0.02 0.01 0.02 0.01	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Salarias Concentration 0.56 0.56 0.57 0.55 0.57	10.7 14.4CP(0) 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.5 MS PEE 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD HEE 2 1 0.5 6 0.05 6 0.05 0.1 0.8 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.4 0.02 0.03 0.02 0.03 0.03 0.02 0.03 0.03 0.02 0.03 0.02 0.03 0.03 0.02 0.03	5 Precision 14 15 15 13 16 10 11 23 8 15 16 16 17 10 18 14 27 20 20 16 10 15	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cascentre LA-KCPSP Mana (new) LA-KCPSP 0.64 0.64 0.64 0.64 0.65 0.65 0.65 0.65 0.65 0.65 0.65 0.65	a.m. ation at MS 0.5 0.2 0.3 0.5 0.2 0.2 0.3 0.5 0.2 0.2 0.3 0.1 0.1 0.3 0.1 0.3 0.1 0.3 0.3 0.1 0.3 0.3 0.5 0.2 0.2 0.3 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.2 0.3 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	ca. 1 µ LOD HEE ³ 0.5 52 2 0.9 1 0.5 4 0.03 0.01	EE ⁴ Precision 25 26 20 20 20 20 20 20 20 20 20 20 20 20 20	3 5 5 3 3 20 84 84 -10 -29 113 -10 -29 -36 8 4 -46 -42 -25 11 -14 -48 -45 -25 -25 -20 -20 -21 -21 -21 -21 -21 -21 -21 -21 -21 -21	83 LA-ICPTI Mana (10 ⁻¹⁰) R	0.6 9FMS P68 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	0.02 FE 5 7 3 2 5 0.4 9 0.2 0.9 1 1 0.2 0.5 0.05 0.02 0.1 0.02 0.01 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.04 0.02 0.01 0.02 0.04 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05 0.02 0.05 0.5 0.	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Salarias Concentration 0.56 0.56 0.57 0.55 0.57	10.7 14.4CP(0) 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.5 MS PEE 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD HEE 0.3 2 1 0.5 6 0.05 0.2 0.5 6 0.05 0	5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cascentre LA-KCPSH Minn (10-52) (1-12)	a.m. ition at MS 0 SD 0 SD 0 SD 0 2 0 3 0 3 0 3 0 2 0 3 0 3 0 3 0 3 0 3 0 3 0 3 0 3	ca. 1 µ LOD HEE ² 0.5 52 2 0.9 1 0.5 4 0.03 0.1 0.3 0.1 0.3 0.02 0.06 0.01 0.02 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.05 0.01 0.05 0.05 0.05 0.01 0.05 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.	EE ⁴ Precision 25 26 29 20 20 20 20 20 20 20 20 20 20	3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48	83 LA-ICPTI Mana (10 ⁻¹⁰) R	0.6 39350 P8 8 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD HEES 7 3 2 3 0.4 9 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 0.1 0.00 0.01 0.01 0.00 0.01 0.01 0.02 0.01	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Salarias Concentration 0.56 0.56 0.57 0.55 0.57	10.7 14.4CP(0) 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.5 MS PEE 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD HEE 0.3 2 1 0.5 6 0.05 0.2 0.5 6 0.05 0	5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cascentre LA-KCPSH Minn (10-52) (1-12)	a.m. ition at MS 0 SD 0 SD 0 SD 0 2 0 3 0 3 0 3 0 2 0 3 0 3 0 3 0 3 0 3 0 3 0 3 0 3	ca. 1 µ LOD HEE ² 0.5 52 2 0.9 1 0.5 4 0.03 0.1 0.3 0.1 0.3 0.02 0.06 0.01 0.02 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.01 0.05 0.05 0.01 0.05 0.05 0.05 0.01 0.05 0.55 0.55 0.55 0.55 0.55 0.55 0.55 0.	EE ⁴ Precision 25 26 29 20 20 20 20 20 20 20 20 20 20	3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48	83 LA-ICPTI Mana (10 ⁻¹⁰) R	0.6 9FMS PEE 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD HEES 7 3 2 3 0.4 9 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 0.1 0.00 0.01 0.01 0.00 0.01 0.01 0.02 0.01	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Salarias Concentration 0.56 0.56 0.57 0.55 0.57	10.7 14.4CP(0) 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	0.5 MS PEE 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD HEE 0.3 2 1 0.5 6 0.05 0.2 0.5 6 0.05 0	5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.m. Cascentre LA-KCPSH Minn (10-52) (1-12)	a.m. rttion at 0 10 SD 10 S	Call I p ILOD 185 8 ⁻¹ 0.5 2 2 0.9 1 0.5 4 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.01	εε ⁴ Precision 22 25 25 25 25 25 25 25 25 25	3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48	83 LA-ICPTI Mana (10 ⁻¹⁰) R	0.6 9FMS PEE 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	LOD HEES 7 3 2 3 0.4 9 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.09 1 0.2 0.5 0.00 0.00 0.01 0.0	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Sabits PEF PEF 2000 200	10.7 LLLCQU 10.7 10.0	0.5 MS PEE 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 ICOD IFE 8 0.2 1 0.8 0.03 0.2 0.5 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.03 0.02 0.03 0.03 0.03 0.02 0.03 0.03 0.02 0.03 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.03 0.02 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.03 0.02 0.02 0.02 0.02 0.02 0.02 0.03 0.02 0.02 0.02 0.03 0.02 0.	5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.n. Cascentre Hanet (Cascentre) (Cascentr	nm. Hinn and S. SD. 9 KB 5 0 2 0 3 0 3 0 3 0 3 0 3 0 3 0 3 0 3	cs. 1 p LOD HE 5 ⁻¹ 0.5 2 2 0.9 1 0.3 0.7 0.1 0.3 0.3 0.1 0.3 0.02 0.05 0.01	EE ⁴ Precision 22 20 20 20 20 20 20 20 20 20 20 20 20	3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48	s3 LA-BCPTH Mane (s=c ⁴) nm < LOD	0.6 9FMS PEE 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	0.02 FE 5 7 3 2 5 0.4 9 0.2 0.5 0.07 0.5 0.07 0.1 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.01 0.02 0.	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
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Later provide the second secon	10.0 Sabitas Pags ²	LA-KCPQ μα μετά μα μετά μα μετά <td>0.5 MIS PEEF 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1</td> <td>0.1 LOD 198.8 0.3 2 1 0.5 6 0.3 2 1 0.5 6 0.3 0.2 0.5 0.1 0.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0</td> <td>5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17</td> <td>7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15</td> <td>n.n. LAACENP (Comparison of the comparison of t</td> <td>a.m. ettion at 4 MS 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5</td> <td>Ca. 1 p IGDD 165 85 52 2 0.9 1 0.1 0.1 0.1 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.05 0</td> <td>εε⁴ Precisient 22 23 20 90 13 79 23 20 90 13 16 12 23 30 15 23 30 15 23 30 15 25 20 90 13 16 21 25 20 90 13 13 25 25 20 90 13 13 25 25 20 90 13 13 25 25 20 90 13 13 25 25 25 20 90 13 15 25 25 25 25 25 25 25 25 25 2</td> <td>3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48</td> <td>53 LALGTM Mune (see* 100 107 107 107 107 107 107 107</td> <td>0.6 9FMS P68 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3</td> <td>0.02 FE 5 7 3 2 5 0.4 9 0.2 0.5 0.07 0.5 0.07 0.1 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.01 0.02 0.</td> <td>7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5</td> <td>-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24</td>	0.5 MIS PEEF 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD 198.8 0.3 2 1 0.5 6 0.3 2 1 0.5 6 0.3 0.2 0.5 0.1 0.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0	5 Precision % 14 15 15 15 16 18 15 16 18 16 18 16 18 15 16 10 11 12 35 16 16 17 12 13 14 14 15 16 16 17 16 16 17 16 17 17 16 16 17 17 17 17 17 17 17 17 17 17	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.n. LAACENP (Comparison of the comparison of t	a.m. ettion at 4 MS 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	Ca. 1 p IGDD 165 85 52 2 0.9 1 0.1 0.1 0.1 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.05 0	εε ⁴ Precisient 22 23 20 90 13 79 23 20 90 13 16 12 23 30 15 23 30 15 23 30 15 25 20 90 13 16 21 25 20 90 13 13 25 25 20 90 13 13 25 25 20 90 13 13 25 25 20 90 13 13 25 25 25 20 90 13 15 25 25 25 25 25 25 25 25 25 2	3 Accuracy 5: -33 20 84 -10 -29 84 -10 -29 113 -10 -29 133 -10 -29 14 -29 -30 -46 -48 -48 -48 -48 -48 -48 -48 -48	53 LALGTM Mune (see* 100 107 107 107 107 107 107 107	0.6 9FMS P68 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	0.02 FE 5 7 3 2 5 0.4 9 0.2 0.5 0.07 0.5 0.07 0.1 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.01 0.02 0.	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
Later provide the second secon	10.0 Sabitas Pags ²	10.7 LA-KTOY & Mann (e ⁺) ⁻ 10.7 10.7 10.0	0.5 MS PEE 0.1 0.1 0.2 0.1 0.1 0.1 0.1 0.1 0.1 0.1 0.1	0.1 LOD 1668 10.3 2 1 0.5 6 0.0 0.2 0.2 0.2 0.2 0.2 0.2 0.2	5 Precession 14 15 15 15 16 10 16 17 10 16 16 17 10 16 16 17 14 27 20 16 16 17 14 27 20 5 5	7 54 6 -11 -15 -15 -15 -15 -15 -15 -15 -15 -15	n.n. Cascrete LAACENP Nease	a.m. ettion at 4 MS 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	Ca. 1 p IGDD 165 85 52 2 0.9 1 0.1 0.1 0.1 0.02 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.05 0	g g ^d Procession 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	3 5 5 30 30 30 30 30 30 30 30 30 30	8.8 LALCTT β(β) β(β) β(β) δ(β) β(β) δ(β) × LOD δ(β) × LOD <t>δ(β) δ(β) × LOD δ(β) δ(β) × LOD δ(β) δ(β) × LOD δ(β) δ(β) × LOD × LOD × LOD × LOD × LOD × LOD × LOD</t>	0.6 9FMS P68 0.3 0.1 0.3 0.1 0.3 0.3 0.3 0.3 0.3 0.3 0.3 0.3	0.02 FE 5 7 3 2 5 0.4 9 0.2 0.5 0.07 0.5 0.07 0.1 0.01 0.01 0.01 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.01 0.02 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.01 0.02 0.02 0.02 0.02 0.02 0.01 0.02 0.	7 Precisis 5 26 8 41 41 39 5 10 6 5 14 8 10 6 5 14 8 10 7 7 8 5 16 15 7 5	-12 n Accura % 9 -12 87 75 87 75 87 73 31 -24 4 -36 6 -27 -23 -24 -24 -24 -24 -24 -24 -24 -24
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particip perform		All FI n=35			FI diamete n=5				diameter < 25	μm	FI diamete n=9	r > 25 μm			
me g ² <th>Isotopes</th> <th></th> <th>SD</th> <th>RSD</th> <th></th> <th>Range</th> <th></th> <th></th> <th>Range</th> <th>RSD</th> <th></th> <th>Range</th> <th>1</th>	Isotopes		SD	RSD		Range			Range	RSD		Range	1		
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************************************	¹⁹⁷ Au						118	22		165	0.9				
Part of the part o	²⁰⁸ Pb		0.2	10											
								10 μm < FI	diameter < 25	μm		r > 25 µm			
	Isotopes	Mean concentration			Mean LOD		RSD	Mean LOD			Mean LOD		1		
	⁷ Li	μg g ΄ n.m.		%	μg g ΄	μg g ΄	%	μg g ΄	μg g ΄	%	μg g '	μg g ΄			
	¹¹ B			23	3010	485 - 6040	68	443	38 - 1455	92	290	43 - 700			
	²⁵ Mg	78	130	167	1935	43 - 4130	81	180	3 - 1000	163	24	3 - 58			
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	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁵ Cu	< LOD < LOD < LOD < LOD	10												
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Cn ⁷⁵ As	< LOD < LOD < LOD < LOD 53													
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Zn ⁷⁵ As ⁸⁵ Rb	<lod <lod <lod <s3 113</s3 </lod </lod </lod 	37	33	155		75		0.4 - 41	1.50	5				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Zn ⁷⁵ As ⁸⁵ Rb ⁸⁸ Sr	<lod <lod <lod 53 113 36</lod </lod </lod 	37 10	33 28	155 81	6 - 162			0.1 21	120	2	0.4 9			
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Zn ⁷⁵ As ⁸⁵ Rb ⁸⁸ Sr ¹²¹ Sb	< LOD < LOD < LOD 53 113 36 3.1	37 10 1.2	33 28 39	155 81 68	6 - 162 5 - 135	76	8			-				
M2 2 1 60 56 4 - 115 78 6 0.3 - 28 125 2.2 0.3 - 5 M3 < LOD	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Zn ⁷⁵ As ⁸⁵ Rb ⁸⁵ Sr ¹²¹ Sb ¹³³ Cs ¹³⁷ Po	< LOD < LOD < LOD 53 113 36 3.1 35	37 10 1.2 13	33 28 39 37	155 81 68 12	6 - 162 5 - 135 1 - 24	76 77	8 1.3	0.1 - 5	120	0.5	0.1 - 1.3			
¹⁹⁷ Au <lod 0.2-17="" 0.2-3.5<="" 1.4="" 117="" 2.5-70="" 34="" 4.3="" 77="" td=""><td>55 Mn 57 Fe 57 Co 46 Cu 46 Zn 46 Zn 47 As 88 Rb 88 Sr 121 Sb 123 Cs 137 Ba 140 Co</td><td>< LOD < LOD < LOD 53 113 36 3.1 35 7.4</td><td>37 10 1.2 13</td><td>33 28 39 37</td><td>155 81 68 12 109</td><td>6 - 162 5 - 135 1 - 24 10</td><td>76 77 73</td><td>8 1.3 12</td><td>0.1 - 5 0.6 - 55</td><td>120 123</td><td>0.5 5</td><td>0.1 - 1.3 0.7 - 11</td><td></td></lod>	55 Mn 57 Fe 57 Co 46 Cu 46 Zn 46 Zn 47 As 88 Rb 88 Sr 121 Sb 123 Cs 137 Ba 140 Co	< LOD < LOD < LOD 53 113 36 3.1 35 7.4	37 10 1.2 13	33 28 39 37	155 81 68 12 109	6 - 162 5 - 135 1 - 24 10	76 77 73	8 1.3 12	0.1 - 5 0.6 - 55	120 123	0.5 5	0.1 - 1.3 0.7 - 11			
²⁰⁸ Pb 4.9 5 104 18 1.2-38 78 2.0 0.1-9 127 0.7 01-18	55 Mn 57 Fe 59 Co 46 Cu 46 Zn 75 As 88 Rb 88 Sr 121 Sb 123 Cs 137 Ba 140 Ce 182 W	< LOD < LOD < LOD 53 113 36 3.1 35 7.4 < LOD	37 10 1.2 13 5	33 28 39 37 72	155 81 68 12 109 14	6 - 162 5 - 135 1 - 24 10 1 - 26	76 77 73 71	8 1.3 12 1.6	0.1 - 5 0.6 - 55 0.1 - 6	120 123 117	0.5 5 0.6	0.1 - 1.3 0.7 - 11 0.1 - 1.5			
	⁵⁵ Mn ⁵⁷ Fe ⁵⁹ Co ⁶⁶ Cu ⁶⁶ Zn ⁷⁵ As ⁸⁸ Rb ⁸⁸ Sr ¹²¹ Sb ¹³³ Cs ¹³³ Ba ¹⁴⁰ Ce ¹⁸² W ¹⁹⁷ Au	< LOD < LOD < LOD 53 113 36 3.1 35 7.4 < LOD 2	37 10 1.2 13 5	33 28 39 37 72	155 81 68 12 109 14 56	6 - 162 5 - 135 1 - 24 10 1 - 26 4 - 115	76 77 73 71 78	8 1.3 12 1.6 6	0.1 - 5 0.6 - 55 0.1 - 6 0.3 - 28	120 123 117 125	0.5 5 0.6 2.2	0.1 - 1.3 0.7 - 11 0.1 - 1.5 0.3 - 5			

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1 2 3 4 5 6		
7 8 9	Isotopes	N µ
$\begin{array}{c} 10\\ 11\\ 12\\ 13\\ 14\\ 15\\ 16\\ 17\\ 18\\ 19\\ 20\\ 21\\ 22\\ 23\\ 24\\ 25\\ 26\\ 27\\ 28\\ 29\\ 30\\ 31\\ 32\\ 33\\ 34\\ 35\\ 36\\ 37\\ 38\\ 39\\ 40\\ 41\\ 42\\ 43\\ 44\\ 546\\ 47\\ 48\\ \end{array}$	⁷ Li ¹¹ B ²⁵ Mg ³⁵ Cl ⁴⁴ Ca ⁵⁷ Fe ⁵⁹ Co ⁶⁵ Cu ⁶⁶ Zn ⁷⁹ Br ⁸⁵ Rb ⁸⁸ Sr ¹³³ Cs ¹³⁷ Ba ¹⁴⁰ Ce ¹⁸² W ¹⁹⁷ Au ²⁰⁸ Pb	
10		

					LA-Q-ICP-I	MS (n=35)			
sotopes	Mean	SD	Precision			LOD (µថ	g g⁻¹)		
3010003	µg g⁻¹	µg g⁻¹	%	< '	15 µm	15 -	30 µm	> 30) µm
				Mean (n=14)	Range	Mean (n=15)	Range	Mean (n=6)	Range
Li	470	210	45	750	35 - 1550	90	5 - 360	5	2 - 11
¹ B	520	170	33	9000	207 - 19000	1115	0 - 4900	26	14 - 38
⁵ Mg	13900	19600	141	2700	140 - 6600	400	23 - 2100	15	4 - 33
⁵ Cl	4110	7640	186	84200	740 - 163000	8240	120 - 45700	92	30 - 190
⁴Ca	< LOD			300000	18300 - 533000	46560	3050 - 257000	2085	1180 - 4000
⁷ Fe	< LOD			24600	1000 - 49300	2850	185 - 12400	125	42 - 260
⁹ Co	< LOD			222	9 - 430	29	2 - 165	1	0.5 - 3
⁵Cu	< LOD			905	55 - 1600	101	6 - 480	4	2 - 6
⁶ Zn	< LOD			1900	50 - 4000	221	8 - 1300	9	3 - 20
⁹ Br	< LOD			46400	1300 - 81500	5350	220 - 26000	163	53 - 300
⁵Rb	210	80	38	128	4 - 270	14	0.7 - 63	0.7	0.2 - 1.5
⁸ Sr	55	30	55	106	0 - 260	10	0.7 - 37	0.3	0 - 0.6
³³ Cs	70	35	50	85	2 - 180	9	0.3 - 38	0.3	0.1 - 0.6
³⁷ Ba	10	20	200	1420	24 - 2670	147	3 - 635	4	0.7 - 7
⁴⁰ Ce	< LOD			88	3 - 217	10	0 - 59	0.3	0.1 - 0.6
⁸² W	< LOD			460	13 - 1050	71	4 - 333	2	1 - 4
⁹⁷ Au	< LOD			516	0 - 1050	62	3 - 362	2	0.8 - 4
⁰⁸ Pb	< LOD			187	5 - 375	19	0 - 112	0.8	0.3 - 1.5
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LA-SF-ICP-MS (n=24)

lsotopes	Mean	SD	Precision		I	LOD (µg g⁻¹)		
13010663	µg g⁻¹	µg g⁻¹	%	< 1	15 µm	15 - 3	30 µm	> 30 µm
				Mean (n=7)	Range	Mean (n=16)	Range	Mean (n=1)
⁷ Li	300	130	43	4370	15 - 18000	63	3 - 254	0.4
¹¹ B	< LOD			744000	2160 - 3000000	10350	337 - 42600	62
²⁵ Mg	< LOD			13000	29 - 56000	173	6 - 700	1
³⁵ CI	1100	710	65	1500000	330 - 6000000	16250	32 - 79000	4
⁴⁴ Ca	1430	610	43	427000	1555 - 1600000	6615	163 - 29000	38
⁵⁷ Fe	< LOD			75500	134 - 300000	955	23 - 4200	4.5
⁵⁹ Co	< LOD			680	1.3 - 2750	6	0.2 - 37	0.1
⁶⁵ Cu	< LOD			2450	6 - 9750	33	1 - 171	0.2
⁶⁶ Zn	< LOD			5500	15 - 23000	70	2 - 315	0.3
⁷⁹ Br	< LOD			72000	238 - 295000	1027	43 - 4915	4
⁸⁵ Rb	155	127	82	342	0.6 - 1170	6	0.1 - 34	0.1
⁸⁸ Sr	49	36	73	680	2 - 2160	10	0.3 - 36	0.1
¹³³ Cs	62	65	105	180	0.1 - 737	3	0.1 - 15	0.1
¹³⁷ Ba	6.5	8	123	1400	1 - 5000	10	0 - 40	0
¹⁴⁰ Ce	< LOD			97	0 - 387	2	0 - 8	0.3
¹⁸² W	4.4	8	182	224	0 - 1267	4	0 - 23	0.1
¹⁹⁷ Au	< LOD			1640	2 - 6000	23	0.5 - 109	0.1
²⁰⁸ Pb	2	0.2	10	387	2 - 1650	7	0.3 - 35	0.1

LA-TOF-ICP-MS (n=40)

LOD (µg g⁻¹)

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Precision

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เอบเบреอ	µg g⁻¹	µg g⁻¹	%	< '	15 µm	15 -	30 µm	> 30	μm
				Mean (n=15)	Range	Mean (n=22)	Range	Mean (n=3)	Range
′Li	< LOD			141500	15000 - 570000	14500	1800 - 44000	10800.02	030 - 27500
¹ B	400	90	23	1840	243 - 6040	270	38 - 694	233.0	43 - 600
⁵Mg	78	130	167	1150	22 - 4128	36	3 - 338	19.0	3 - 48
ĊI	19000	5140	27	41150	3564 - 136500	3520	490 - 11570	2700.0	490 - 7000
¹ Ca	< LOD			220000	30600 - 630000	52200	7400 - 136700	42050.0}	160 - 106000
⁷ Fe	< LOD			4930	319 - 17050	370	48 - 1450	270.0	48 - 690
°Co	< LOD			82	6 - 280	7	0.8 - 23	5.0	0.9 - 12
⁵Cu	< LOD			280	35 - 884	39	5 - 105	30.0	6 - 75
⁶ Zn	< LOD			466	40 - 1517	42	4 - 150	32.0	6 - 82
Br	< LOD			10450	1424 - 33000	640	50 - 3100	280.0	64 - 555
⁵Rb	113	37	33	93	7 - 311	7	0.9 - 27	5.0	1 - 12
⁸ Sr	36	10	28	48	3 - 162	3	0.4 - 15	2.3	0.5 - 6
³³ Cs	35	13	37	7	0.5 - 24	0.6	0.1 - 2	0.4	0.1 - 1
³⁷ Ba	7.4	5		65	5 - 213	5	0.7 - 20	3.8	0.7 - 10
⁴⁰ Ce	< LOD			8	0.6 - 25	0.7	0.1 - 2.5	0.5	0.1 - 1
⁸² W	2	1		34	2 - 115	2.5	0.3 - 10	1.8	0.4 - 5
⁹⁷ Au	< LOD			20	1.5 - 70	2	0.2 - 12	1.2	0.2 - 3
²⁰⁸ Pb	4.9	5	104	11	0.8 - 38	0.8	0.1 - 4	0.5	0.1 - 1.5

		LA-ICPQMS (n=10)					LA-ICPTOFM				
	Concent			LOD			Concentration		LOD		
Isotopes	Mean	SD		Mean	0	RSD	Mean	SD	RSD	Mean	
24	$\mu g g^{-1}$	μg g ⁻¹	%	μg g ⁻¹	$\mu g g^{-1}$	%	μg g ⁻¹	μg g ⁻¹	%	$\mu g g^{-1}$	
²⁴ Mg	n.m.	n.m.					384	168	44	39	
²⁵ Mg	600	628	105	142	14 - 710	140	470	126	27	238	
²⁶ Mg	n.m.	n.m.					625	35	6	325	
²⁷ Al	n.m.	n.m.					518	117	23	87	
³⁴ S	< LOD			11400	1325 - 51300	125	< LOD			14410	
³⁵ Cl	n.m.	n.m.					60350	18800	31	6000	
³⁹ K	6090	7135	117	360	40 - 1500	115	7700	3578	46	3350	
⁴⁴ Ca	19670	14502	74	12600	1400 - 55300	122	< LOD			176000	
⁴⁷ Ti	55	37	68	123	15 - 470	112	< LOD			930	
⁵⁵ Mn	n.m.	n.m.					3750	1870	50	30	
⁵⁷ Fe	15300	6040	39	1015	115 - 4250	117	15000	5065	34	850	
⁵⁹ Co	n.m.	n.m.					22	10	47	12	
⁶⁴ Zn	n.m.	n.m.					313	295	94	52	
⁶⁵ Cu	1800	1459	81	40	5 - 200	138	2100	362	17	96	
⁶⁶ Zn	n.m.	n.m.					346	271	78	77	
⁶⁷ Zn	n.m.	n.m.					457	395	86	410	
⁶⁸ Zn	n.m.	n.m.					475	461	97	310	
⁸⁵ Rb	61	80	133	6	0.6 - 27	122	52	45	86	11	
⁸⁶ Sr	n.m.	n.m.					639	346	54	81	
⁸⁸ Sr	818	1259	154	3	0.4 - 12	122	510	360	70	6	
⁹⁵ Mo	16	13	79	32	4.5 - 150	128	33	23	71	26	
⁹⁶ Mo	n.m.	n.m.					20	12	61	17	
⁹⁷ Mo	n.m.	n.m.					18			36	
⁹⁸ Mo	n.m.	n.m.					16	4	24	14	
¹³⁰ Te	n.m.	n.m.					23			22	
¹³³ Cs	n.m.	n.m.					14	14	95	1.1	
¹³⁵ Ba	n.m.	n.m.					1128	569	50	18	
¹³⁶ Ba	n.m.	n.m.					1123	553	49	39	
¹³⁷ Ba	1700	2217	130	45	7 - 180	111	1143	570	50	10	
¹³⁸ Ba	n.m.	n.m.					1119	565	51	1.4	
¹³⁹ La	n.m.	n.m.					2.1	0.8	40	1.2	
¹⁴⁰ Ce	n.m.	n.m.					1.5	0.7	46	1.1	
¹⁴¹ Pr	n.m.	n.m.					0.8	0.6	70	0.9	
¹⁴³ Nd	n.m.	n.m.					9		, 0	8.5	
1.44	11.111.						,			0.5	

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	²⁰⁵ Tl	n.m.	n.m.					1	1	77	1.5	
	²⁰⁶ Pb	n.m.	n.m.					387	380	98	4.2	
	²⁰⁷ Pb	n.m.	n.m.					328	326	99	5.0	
	²⁰⁸ Pb	390	512	131	6	0.8 - 21	103	321	322	100	2.0	
า	²⁰⁹ Bi	n.m.	n.m.					2.5	0.9	37	1.5	
1	²³⁸ U	4	2	39	1.7	0.1 - 7	107	3.3	1.6	48	0.8	

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Range	RSD
$\mu g g^{-1}$	%
10 - 76	75
54 - 510	83
74 - 660	78
20 - 170	78
3800 - 30000	76
1640 - 10650	71
900 - 6150	74
40200 - 350000	78
222 - 1900	80
7 - 60	76
220 - 1600	73
3 - 25	75
12 - 105	76
20 - 250	99
18 - 160	77
100 - 825	77
80 - 640	77
3 -21	71
22 - 150	71
2 -10	69
7 - 50	74
5 - 32	72
10 - 67	72
4 - 27	75
6 - 45	78
0.3 - 2	77
5 - 35	76
12 - 71	70
3 - 20	77
0.3 - 3	74
0.3 - 2	75
0.3 - 2	73
0.2 - 1.8	75
2 - 17	74

0.4 - 3 1.1 - 9 1.3 - 10 0.5 - 4 0.3 - 3 0.2 - 2	76 79 78 77 82 79