

1 **Recent developments in element concentration and**
2 **isotope ratio analysis of individual fluid inclusions by**
3 **laser ablation single and multiple collector ICP–MS**

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24 **Please cite as:**

25 **Pettke, T., Oberli, F., Audetat, A., Guillong, M., Simon, A. C., Hanley, J. J.,**
26 **and Klemm, L. M., 2012. Recent developments in element concentration**
27 **and isotope ratio analysis of individual fluid inclusions by laser ablation**
28 **single and multiple collector ICP-MS. Ore Geology Reviews 44, 10-38.**
29 **DOI: [10.1016/j.oregeorev.2011.11.001](https://doi.org/10.1016/j.oregeorev.2011.11.001)**

30 **Abstract**

31 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-
32 MS) has become a most powerful technique for the elemental analysis of
33 individual, polyphase inclusions completely enclosed in minerals, be they solid
34 or a solid-liquid-gas mixture at the time of measurement. Simultaneous,
35 accurate quantification of major to ultra-trace element concentrations from Li
36 to U by well-controlled ablation of the entire fluid or melt inclusion content and
37 successful use of largely matrix-independent external calibration protocols are
38 unique features of this method.

39 This contribution reviews fluid inclusion fundamentals relevant for their
40 bulk analysis by LA-ICP-MS and discusses key aspects of the analytical
41 protocol. Emphasis is on figures of merit (precision, accuracy) obtained from
42 the analysis of individual inclusions and fluid inclusion assemblages, and
43 procedures and technical developments to improving data quality are
44 elaborated. A new equation for the calculation of detection limits for LA-ICP-
45 MS analysis is presented, which closely follows IUPAC conventions.

46 Applications are reviewed with emphasis on the use of synthetic fluid
47 inclusions in constraining metal solubility and distribution between co-existing
48 phases. New data for natural bismuth "fluid" inclusions document the
49 seamless transition to melt inclusion analysis by LA-ICP-MS, thus highlighting
50 the fact that the procedures presented here are generally applicable to the
51 analysis of inclusions in complex host minerals.

52 Isotope ratio analysis of individual fluid inclusions by multicollector ICP-
53 MS (MC-ICP-MS) is a recent development that requires fast transient signals
54 to be accurately recorded by instrumentation designed for high-precision static
55 measurements of long-lasting stable ion beams. We address the general
56 principles based on Pb isotopes and review a first application to the Bingham
57 Canyon porphyry Cu-Au±Mo deposit. A pilot study using about 50 synthetic
58 fluid inclusions containing SRM 987 Sr and variable NaCl, Ca, and Rb
59 concentrations demonstrates that accurate $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios can be
60 obtained on an individual Rb-poor fluid inclusion, at absolute 2σ precisions of
61 0.0003 to 0.002. A residual trend in $^{87}\text{Sr}/^{86}\text{Sr}$ as a function of the Rb/Sr

62 abundance ratio in the fluid inclusions suggests that interference correction of
63 ^{87}Rb on mass 87 assuming identical mass bias coefficients for the two
64 elements may be inaccurate; however, the offset can be accurately corrected
65 for by regressing the data to zero ^{87}Rb .

66 The versatility and detection power of LA-ICP-MS makes this technique
67 the method of choice for solute abundance and isotope ratio analysis of
68 individual fluid inclusions. Significant future progress can be achieved by
69 improvements in ion production, transmission and data recording efficiency
70 and by further improving control on inclusion ablation by pulsed laser beams.
71 Data quantification strategies may also have to be further refined to keep pace
72 with instrumental progress and innovation.

73

74 **Keywords**

- 75 - Laser ablation ICP-MS
- 76 - Fluid inclusions
- 77 - Analytical protocols
- 78 - Detection limit
- 79 - Hydrothermal ore deposit

80

81 **INTRODUCTION**

82 Fluids play a fundamental role in mass and heat transport in the Earth. The term "fluid"
83 encompasses all phases that are not solid at the P–T–X (pressure-temperature-composition)
84 conditions of the process of interest, including aqueous or carbonic solutions, silicate,
85 sulphide or carbonate melts, and supercritical liquids. Minerals may incorporate tiny droplets
86 of such fluids while they crystallize; hence, such fluid inclusions represent direct, fossil
87 samples of the agents present during mineral growth. Thus, fluid inclusions hold a wealth of
88 information on the composition and phase state of such mobile phases participating in
89 geological processes. Fluid inclusions can be trapped in natural samples down to depths
90 exceeding 200 km and can be synthesized at controlled experimental conditions (e.g.,
91 Roedder, 1984). The solute composition of fluid inclusions can provide key constraints on

92 past processes of fluid-mediated chemical transfer in Earth systems, and solute isotope ratios
93 may place robust constraints on the source(s) of fluids.

94 In-situ analysis of solutes from individual fluid inclusions by laser ablation (LA) has
95 been explored for more than 30 years (Tsui and Holland 1979, Bennett and Grant 1980,
96 Deloule and Eloy 1982). In more recent times, laser ablation inductively coupled plasma mass
97 spectrometry (LA–ICP–MS) has become the method of choice for solute analysis of fluid
98 inclusions due to its excellent detection and fast data acquisition capabilities (e.g., Rankin et
99 al., 1992; Shepherd and Chenery, 1995; Moissette et al., 1996; Günther et al., 1998; Audétat
100 et al., 1998; Heinrich et al., 1999; Loucks and Mavrogenes, 1999; Kamenetsky et al., 1999;
101 Ulrich et al., 1999; Audétat et al., 2000a,b; Ulrich et al., 2002; Audétat and Pettke, 2003; Rusk
102 et al., 2004; Klemm et al., 2004; Stoffell et al., 2004; Landtwing et al., 2005; Allan et al., 2005;
103 Hanley et al., 2005a; Spandler et al., 2007; Klemm et al., 2007, 2008; Audétat et al., 2008;
104 Ulrich and Mavrogenes, 2008; Piqué et al., 2008; Wilkinson et al., 2009; Seo et al., 2009;
105 Richard et al., 2010; Audétat, 2010; Kouzmanov et al., 2010; Catchpole et al., 2011; Allan et
106 al., 2011; Appold and Wenz, 2011). All elements of the periodic table but the noble gases, F,
107 O, N and H can be analyzed in fluid inclusions by LA-ICP-MS, but the limits of detection
108 (LOD) vary largely between elements (e.g., Heinrich et al., 2003). Polyatomic species such as
109 CO₂ and SO₂ are currently not measured in fluid inclusions by LA-ICP-MS, except for one
110 pilot study reporting the analysis of alkanes and aromatic hydrocarbons from single petroleum
111 inclusions (Volk et al., 2010). The in-situ analysis of individual fluid inclusions overcomes
112 many of the problems inherent in bulk crush-leach techniques (e.g., Czamanske et al., 1963;
113 Bottrell et al., 1988; Banks et al., 1991; Pettke and Diamond, 1995), most importantly
114 because it avoids problems arising from the analysis of a priori unconstrained mixtures of fluid
115 inclusion assemblages. The basic principles of the LA–ICP–MS analytical approach to
116 element concentration determination of individual fluid or melt inclusions (Günther et al.,
117 1998; Halter et al., 2002b; Heinrich et al., 2003; Allan et al., 2005) have remained largely
118 unchanged; however, methods refinement has continuously improved the techniques and
119 diversified the applications.

120 Previous literature (Günther, 2001; Heinrich et al., 2003; Pettke, 2006, 2008; Mason et
121 al., 2008) has reviewed the history and the basics of LA-ICP-MS fluid/melt inclusion analytical
122 techniques. Here, we first focus on briefly reviewing the concepts and principles, emphasize
123 critical aspects of the technique, address recent analytical developments and illustrate
124 progress made on fluid inclusion element concentration analysis using selected applications.
125 We then introduce novel techniques for isotope ratio analysis of individual fluid inclusions.
126 This review will not address the current state of other microbeam techniques, notably the non-
127 destructive ones (e.g., RAMAN, PIXE, PIGE, SR-XRF or XANES), nor will it discuss other
128 destructive techniques such as LA-ICP- optical emission spectroscopy (LA-ICP-OES) or laser
129 induced breakdown spectroscopy (LIBS) that currently return inferior results for solute
130 analysis of individual fluid inclusions (Pettke et al., 2000b; Fabre et al., 2002). Note, however,
131 that LA-ICP-OES was the first method evaluated in detail for solute analysis of individual fluid

132 inclusions (Ramsey et al., 1992) and, as such, initiated this line of analytical development.
133 While the principles for fluid and melt inclusion analysis by LA-ICP-MS are fundamentally the
134 same, melt inclusions are, at least partially, solid at room temperature when they are
135 analyzed. Thus, measurements can be performed on glassy, exposed parts of homogeneous
136 melt inclusions, whereby a tiny fraction of the inclusion - considered to be representative of
137 the bulk inclusion - is analyzed in situ by various microbeam techniques (most importantly
138 electron probe microanalysis, EPMA; secondary ion mass spectrometry, SIMS). Because
139 melt inclusions will not be further addressed here, the reader is referred to the literature (e.g.,
140 Halter et al., 2002a; Danyushevsky et al., 2002; Pettke, 2006; Mason et al., 2008; or Audétat
141 and Lowenstern, submitted) for detailed discussion.

142 Experience has shown that accurate analysis of fluid inclusions for chemical and
143 isotopic compositions is largely limited by (a) the fluid inclusion ablation process and aerosol
144 transport to the ICP, (b) limitations resulting from incomplete ionization and signal recording,
145 and (c) by the internal standardization required for quantification of solute concentrations;
146 hence, these aspects will be emphasized in this paper. Topic (a) equally applies to element
147 concentration and isotope ratio analysis, while topics (b) and (c) are application-specific and
148 thus will be addressed in the respective sections.

149 This manuscript is structured as follows. The peculiar sample characteristics of
150 individual fluid inclusions and the concept of fluid inclusion assemblages are reviewed first,
151 followed by a brief description of how LA-ICP-MS fluid inclusion analyses are performed.
152 Then, various methods of producing fluid inclusion data, and sources of uncertainties, are
153 explained in detail. Based on this, optimization techniques for obtaining the best-possible
154 individual fluid inclusion measurements are outlined. This is followed by a section focusing on
155 element concentration determination on individual fluid inclusions which also contains a
156 discussion on detection limits (LOD) applicable to LA-ICP-MS in general and an assessment
157 of measures that can be taken to specifically lower the LOD in fluid inclusion analysis. The
158 section on selected applications then presents a previously unavailable review of applications
159 employing synthetic fluid inclusions, and a new application on fluid/melt transition based on Bi
160 inclusions. The following section is devoted to Pb isotope ratio analysis of individual fluid
161 inclusions, discussing both analytical aspects and a first application to constraining the metal
162 source(s) of porphyry-type ore deposits. We then present the results of our pilot study on Sr
163 isotope ratio analysis of fluid inclusions based on synthetic fluid inclusion standards. The
164 paper closes with a brief section on potential directions of future developments.

165 **Fluid inclusions: Peculiar sample characteristics**

166 Fluid inclusions are tiny droplets trapped as a single phase at elevated temperatures
167 and pressures. The exception to this involves heterogeneous entrapment in a two or more
168 phase stability volume (e.g., Roedder, 1984). Key to the applicability of fluid inclusion (and
169 melt inclusion) chemical data for the characterization of paleo-fluids is that, after entrapment,

170 the inclusions have behaved as a chemically closed systems, i.e., individual fluid inclusions
171 did not lose or gain chemical components (isoplethic behaviour).

172 In inclusion research, the concept of fluid inclusion assemblages (see Goldstein and
173 Reynolds, 1994, for an excellent review) is critical to inclusion analysis and interpretation. A
174 fluid or melt inclusion assemblage comprises a series of inclusions entrapped at the same
175 time in a host mineral. Petrographically, geometric criteria are employed to argue for coeval
176 entrapment of fluid inclusions, such as the entrapment of fluid inclusions along a host mineral
177 growth zone or a fracture plane. Consequently, a fluid inclusion assemblage contains a series
178 of individual fluid inclusions that are compositionally identical, i.e., each inclusion representing
179 an isolated sample of this homogeneous fluid (Fig. 1A). This does not apply, however, for the
180 case of heterogeneous entrapment addressed below. Compositional uniformity can be tested
181 for by performing non-destructive fluid inclusion microthermometry, which is also a
182 prerequisite for quantification of fluid inclusion LA-ICP-MS measurements (see below).

183 Figure 1A shows a homogeneously entrapped fluid inclusion assemblage viewed at
184 room temperature. At this temperature, individual fluid inclusions consist of several phases,
185 and the phase volume proportions are identical for all individual fluid inclusions, provided
186 equilibrium conditions prevailed during their formation. After entrapment as a single,
187 homogeneous fluid phase at some P and T, daughter minerals crystallize and other phases
188 (e.g., a vapour bubble) unmix while the fluid inclusions cool isochorically (i.e., at constant
189 volume and thus constant bulk density) to room temperature. It is this gas-liquid-crystal
190 polyphase mixture of confined volume that we wish to analyze in bulk in order to reconstitute
191 the one-phase chemical composition of the fluid inclusion at the time of entrapment. Even
192 apparently simple aqueous, aqueo-carbonic or vapour-like fluid inclusions may contain major
193 proportions of certain trace elements concentrated in tiny daughter minerals (Fig. 1B), which
194 often are too small for microscopic detection, in particular when hidden beneath a large
195 vapour bubble. It is therefore essential not to miss any fraction of the fluid inclusion content
196 (solids, liquids or gases) during fluid inclusion ablation in order to quantitatively analyze the
197 entire fluid inclusion. Best-possible control on the fluid inclusion ablation process is thus
198 mandatory. Incomplete ablation of a fluid inclusion, e.g., due to uncontrolled rupturing or
199 employing scanning laser ablation across the inclusion, will sample an unconstrained fraction
200 of the bulk inclusion content and thus compromise the analysis.

201 There are many exceptions to the ideal fluid inclusion assemblage, however. Fluid
202 inclusion assemblages can show variable phase proportions at room temperature and are
203 thus compositionally heterogeneous. This may be a result of either heterogeneous
204 entrapment (Fig. 1C), post-entrapment modification, or of accidental entrapment of solids
205 during fluid inclusion formation.

206 Heterogeneously entrapped fluid inclusion assemblages can provide important geologic
207 constraints, notably on element distribution between coexisting fluid phases or on metal
208 solubilities at known temperatures (as directly derived from microthermometry). The best-

209 known examples of heterogeneous entrapment are the so-called boiling assemblages (Fig.
210 1C; see also Diamond, 1990) for which relevant data have been obtained on both natural
211 (e.g., Heinrich et al., 1992; Audétat et al., 1998; Heinrich et al., 1999; Ulrich et al., 1999;
212 Klemm et al., 2004) and synthetic fluid inclusions (see below). Coexisting aqueous fluid
213 inclusions and hydrous melt inclusions are another example for immiscible fluid phases for
214 which compositional data may provide essential constraints (e.g., Audétat and Pettke, 2003;
215 Zajacz et al., 2008). In either case, the analysis of individual fluid inclusions belonging to the
216 endmember compositions of coexisting immiscible fluids (e.g., vapour and brine, aqueous and
217 carbonic fluids, aqueous fluids and silicate melt) can provide insight into element distribution
218 and transport during progressive fluid evolution.

219 Post-entrapment modification of fluid inclusion contents can affect bulk density and/or
220 composition (e.g., Sterner and Bodnar, 1989; Bakker and Jansen, 1991; Audétat and
221 Günther, 1999; Bodnar, 2003). This is a serious problem as it often passes unrecognized.
222 Evidence for post-entrapment modification of bulk composition may be obtained from diverse
223 sources. Brine inclusions of boiling assemblages that homogenize via salt dissolution rather
224 than via bubble disappearance have been argued to be the result of post-entrapment loss of
225 water, leading to an increase in their bulk salinity (e.g., Audétat and Günther, 1999; Klemm et
226 al., 2008; Rusk et al., 2008). Loss of hydrogen may increase f_{O_2} , promoting the crystallization
227 of hematite, sulphate and carbonate daughter crystals in brine inclusions and inhibiting re-
228 dissolution of chalcopyrite daughter crystals during heating (Mavrogenes and Bodnar, 1994;
229 Hanley et al., 2008). Diffusional exchange between fluid inclusions and later external fluids
230 may occur in both directions, resulting in loss or gain of elements (e.g., Sterner and Bodnar,
231 1989; Bakker and Jansen, 1991; Li et al., 2009; see also Kamenetsky and Danyushevsky,
232 2005; Portnyagin et al., 2008; Zajacz et al., 2009). A detailed discussion of post-entrapment
233 modifications in fluid inclusions is beyond the scope of this paper, and the reader is referred
234 to the abundant literature both from experimental and natural investigations. Because the
235 extent of post-entrapment modification of fluid inclusions is a priori unconstrained it is best
236 practice to avoid inclusions that show signs of modification such as irregular shapes,
237 decrepitation halos, or poorly reproducible microthermometric behaviour for homogeneously
238 entrapped assemblages (Audétat and Günther, 1999), unless such secondary processes are
239 to be investigated.

240 **Brief recapitulation of how to analyze fluid inclusions by LA-ICP-MS**

241 This short section addresses the basic principles of fluid inclusion analysis by LA-ICP-
242 MS reviewed in detail previously (Heinrich et al., 2003; Pettke, 2008). It shall serve as a basis
243 for the following sections, where relevant aspects will be addressed in more detail. Note that
244 procedures and instrument optimization strategies may differ for the various LA-ICP-MS
245 setups used. Fluid inclusion analysis by LA-ICP-MS involves the following steps. The content
246 of the inclusion is liberated by drilling it out of the host mineral, and the aerosol is transported

247 to the ICP-MS where analyte signals are recorded as specified in the analytical routine
248 (measurement method). For laser ablation of quartz-hosted fluid inclusions, a relatively high
249 energy density of between 10 and 25 J/cm² on the sample surface is required. Laser pulse
250 repetition rates are commonly between 7 and 10 Hz, and the laser beam has to be larger than
251 the largest diameter of the inclusion to ensure complete ablation. The aerosol is transported
252 out of the ablation chamber using He as carrier gas, then mixed with Ar gas and introduced to
253 the mass spectrometer. Aerosol particles are atomized and ionized in the inductively coupled
254 plasma, the ions are then extracted from the plasma and filtered according to their mass-to-
255 charge ratio and finally registered by the detector system of the mass spectrometer. This way,
256 a transient signal of 5 to 50 seconds duration is produced (Fig. 2).

257 Quadrupole and single-collector sector field mass spectrometers are typically employed
258 for element concentration analysis. The former allows for very fast mass jumping between
259 elements in a range from Li to U, a real advantage for the analysis of fast transient signals
260 produced from fluid inclusions, and returns LODs as low as 0.01 µg g⁻¹ for the best-detected
261 elements. Whereas between 5 and 20 elements are typically analyzed for average-size liquid
262 inclusions, this number reduces for smaller inclusions or vapour inclusions, because resulting
263 signals are shorter. For 20 elements at 10ms typical dwell time and 3 ms quadrupole settling
264 time, a total analysis time of 260 ms results for a single sweep with all elements measured
265 once. Signal duration of about 5 s would result in 20 measurements per element; longer
266 signals correspondingly return more data. If it is desirable to optimize recordings for specific
267 elements, e.g., ore metals in fluid inclusions, the dwell time can be increased, resulting in
268 lower LODs (see below). However, this will increase sweep duration; hence, a compromise
269 between fast scanning protocols (at 10 ms dwell time) and improved LODs for selected
270 elements has to be defined for each analytical session.

271 Quantification of the measurements requires the analysis of external standard materials
272 bracketing the fluid inclusion measurements in order to determine instrumental sensitivities for
273 the elements of interest and to correct for machine drift. In addition, an internal standard
274 element is required, whose concentration in the inclusion has to be independently known.
275 Using such an element, the relative sensitivity factor between inclusion and external standard
276 analysis is determined for each inclusion analysis, allowing for calculation of absolute element
277 concentrations in individual inclusions.

278 All elemental data reported in this paper were produced using a GeoLas (Lambda
279 Physik, Germany) pulsed 193 nm ArF excimer laser system coupled with an ELAN ICP
280 quadrupole mass spectrometer (DRCe or 6100 DRC, Perkin Elmer, Canada), at operating
281 conditions similar to those reported in Pettke (2008). As many different analytical setups have
282 been explored, each having its characteristic features, it will be the task of the operator to
283 determine which setup will most likely provide best overall analytical performance for a
284 particular application. The reader is referred here to the literature (largely addressed in
285 Pettke, 2008).

286 **Data and figures of merit**

287 Best practice in LA-ICP-MS analysis of fluid inclusions is to analyze a series of
288 individual inclusions belonging to an assemblage, thus allowing for repetitive analysis of
289 individual samples of a fluid of constant composition. This is identical to analyzing several
290 spots on a homogeneous solid. Consequently, the fluid composition of a fluid inclusion
291 assemblage is best characterized by the mean or median and external error (based on
292 reproducibility) of data obtained on individually analyzed fluid inclusions (Tables 1, 2). This
293 enables the most robust characterization of element compositions in the fluid at the time of
294 entrapment. Provided that careful fluid inclusion petrography was performed to establish the
295 relative age sequence of fluid inclusion assemblage entrapment, such data monitor fluid
296 evolution in the system of interest.

297 Data and figures of merit are only useful when the statistical and instrumental
298 parameters used are disclosed. Such parameters should include whether standard deviation
299 or standard error of the mean was used (as is often hidden behind the commonly used
300 symbol σ), LOD calculation criteria (see below), and laser beam size, pulse repetition rate and
301 energy density on sample surface employed during analysis. To arrive at accurate fluid
302 inclusion compositions we specifically advocate the practice of employing average data on
303 several fluid inclusions from the same assemblage because individual inclusion analyses are
304 prone to outliers such as those listed in Tables 1, 2, or observed for Au in inclusion 3 or 28 of
305 Fig. 3. If the number of analyses available for characterization of a fluid inclusion assemblage
306 is small, the median may offer a more robust estimate, as it is less prone to outliers. In any
307 case, outliers can only be identified through multiple analyses on inclusion assemblages (see
308 examples in Pettke et al., 2004). The detailed rationale has been published by Pettke (2008)
309 and will be used throughout this review.

310 It can be rather difficult to reliably estimate the uncertainty of an individual inclusion
311 analysis, because it is affected by the quality of fluid inclusion ablation, which is not easily
312 quantifiable, and potentially suffers from non-representative recording of the fast transient
313 signal. The signal quality from ablation of an individual fluid inclusion can vary enormously
314 because inclusions can be of very different size, shape and bulk salinity; hence, the amount
315 of analyte available from an individual inclusion varies over more than three orders of
316 magnitude in common applications (see below). For low count rate analytes near their
317 respective LODs, counting statistics are the dominant contribution to the total uncertainty and
318 thus provide a relatively robust minimum estimate (values given for Au in Table 2). For high
319 count rate analytes, more elaborate uncertainty estimates are required (e.g., Halter et al.,
320 2002b; Guillong et al., 2008b). These return minimum values, too, because the uncertainty
321 related to the process of fluid inclusion ablation cannot be quantified.

322 Therefore, we consider uncertainties based on external precision to be a much more
323 robust assessment of analytical error for both element concentration and isotope ratio
324 determinations in fluid inclusions, rather than estimates based on internal precision of

325 individual analyses. The external precision can be determined on a series of individually
326 measured, compositionally identical inclusions belonging to the same fluid inclusion
327 assemblage. In the absence of systematic analytical error, this represents, strictly speaking, a
328 maximum uncertainty estimate because it is based on the assumption that all averaged fluid
329 inclusions were compositionally identical. Counting-uncertainty weighted averaging is
330 preferred for low count rate analytes (see e.g., Pettke et al., 2004; Pettke, 2008; Table 2),
331 while simple averaging can be appropriate for high count rate analytes. The average/mean
332 plus standard deviation/error of a fluid inclusion assemblage (after statistical outlier rejection)
333 thus defines most reliably the composition and associated uncertainty of a fluid stage. The
334 data in Table 1 serve as an illustration for such an approach. Here, successively entrapped
335 fluid inclusion assemblages record the temporal evolution of fluid chemistry, e.g., Cu
336 precipitation recorded by 4 successively entrapped inclusion assemblages (Fig. 3).

337 Synthetic fluid inclusions were used to assess the accuracy of fluid inclusion LA-ICP-
338 MS analysis (see Günther et al., 1998; Heinrich et al., 2003; Allan et al. 2005; Seo et al.,
339 2011). Heinrich et al. (2003) have demonstrated that neither absolute nor volume-normalized
340 signal intensities have any direct relation to absolute element concentrations within individual
341 fluid inclusions. Consequently, attempts to derive element concentration data without the use
342 of internal standardization may not even provide the correct order of magnitude.

343 The accuracy of LA-ICP-MS element concentration data of chemically complex fluid
344 inclusions, to date, is mainly limited by the uncertainty associated with an independent
345 estimate of the concentration of an element appropriate for internal standardization. For Na-K-
346 Ca-Cl dominated fluid inclusions, the empirical algorithm proposed by Heinrich et al. (2003)
347 for correction of microthermometrically determined $\text{NaCl}_{\text{equiv}}$ values for the presence of other
348 cations is appropriate. Fluid inclusions dominated by other salts yield lower accuracy
349 (Heinrich et al., 2003), because experimental data for such systems are lacking at present.
350 Allan et al. (2005) suggested that data reduced using the approach of Heinrich et al. (2003)
351 tend to overestimate concentration and that procedures based on charge balance may be
352 beneficial for typical ionic solutions. This and the internal standardization based on
353 microthermometrically determined Cl concentrations require the correct measurement of Cl in
354 inclusions. Because Cl needs to be analyzed as Cl^+ , poor sensitivities result due to the high
355 first positive ionization energy of 12.97 eV. This translates to low signal-to-background ratios,
356 which confines the use of Cl as an internal standard to high salinity inclusions only. But even
357 with this technique, other problems are inherent to Cl-based fluid inclusion quantification that
358 may severely limit its general applicability (Guillong et al., 2011). Our experience with
359 synthetic and natural inclusions of (Na-K-Ca-Fe±Mg±Mn)Cl fluid compositions has shown that
360 use of corrected Na concentrations generally returns more accurate data compared to Cl-
361 based quantification approaches. Finally, the analytical data cannot be more accurate than
362 the element concentration data and homogeneity of the external standards used for
363 quantification. This fact is especially important when dealing with "uncommon" elements, such

364 as Te, Pd or Pt, for which accurate and widely applicable standard reference materials are
365 needed for external analyte calibration (Spandler et al., 2011; Jochum et al., 2011).

366 It is important to appreciate that with controlled ablation and correct analysis of
367 individual fluid inclusions external standardization alone returns accurate element
368 concentration ratios. Moreover, if it can be assumed that major element concentrations do not
369 significantly change across a series of successively entrapped fluid inclusion assemblages,
370 measured variations in trace or ore element concentration ratios are correct in sense and
371 magnitude, even without accurate internal standardization (Fig. 3B). This is often the case for
372 single stage porphyry-type ore fluids that precipitate metals at high T over an extended period
373 (for Cu-Au deposits: see Na, K, Fe, Mn in Table 1; also, Ulrich et al., 2002; Rusk et al., 2004;
374 Landtwing et al., 2005, 2010; Klemm et al., 2007; Kouzmanov et al., 2010; for Mo deposits:
375 Klemm et al., 2008). For cases where microthermometry cannot return $\text{NaCl}_{\text{equiv}}$ values for
376 internal standardization, this may be the only useful approach to follow, e.g., for vapour
377 inclusions (e.g., Landtwing et al., 2005) or for CO_2 bearing inclusions that have no liquid CO_2
378 stable at final clathrate dissolution (Diamond, 1992). The fundamental assumption behind this
379 is that element sensitivity ratios do not vary between the LA-ICP-MS analysis of external
380 standard and sample materials. This has been shown to be also true, at least within
381 uncertainty, for synthetic fluid inclusion analysis when appropriate analytical procedures
382 including robust plasma conditions (see below) were employed.

383 **Technical aspects of LA-ICP-MS fluid inclusion analysis**

384 The peculiar sample characteristics of fluid inclusions define the specific technical
385 demands on the LA-ICP-MS systems and the procedures to be used for analysis. Below we
386 address several reasons why LA-ICP-MS is currently the method of choice for fluid inclusion
387 solute chemical and isotopic analysis.

388 - Of foremost importance is the fact that LA-ICP-MS analyzes a volume rather than a surface;
389 hence, the entire fluid inclusion content is available for analysis. This way, inclusions
390 containing gas, liquid and crystals that separated after entrapment on cooling of the one-
391 phase fluid inclusion can be analyzed altogether to reconstitute its bulk composition (Fig. 1).
392 Other microbeam techniques requiring solid material for analysis (e.g., EPMA) cannot be
393 employed. SIMS does sputter away sample material, but the "drilling rate" is very slow. This
394 and the strong matrix dependence of signal quantification are probably the main reasons why
395 SIMS analysis of individual fluid inclusions so far has not exceeded the stage of
396 reconnaissance study (Nambu and Sato, 1981; Diamond et al., 1991).

397 - LA-ICP-MS has a key advantage, in that it allows independent optimization of two
398 fundamentally different processes, (i) sample liberation by laser ablation and (ii) ion
399 production, analyte filtering and signal recording in an ICP-MS. This is an enormous
400 advantage over most other in-situ analytical techniques (e.g., SIMS or LIBS) where ion
401 production or light emission is directly related to sample ablation. This dual optimization

402 potential opens the possibility of considerably reducing matrix effects on signal quantification
403 as further outlined below.

404 Note, however, that not only the analyte of interest, but also the complete sample
405 matrix is present during LA-ICP-MS analysis. Pre-extraction or concentration of the analyte as
406 employed for precise isotope ratio determination by solution nebulisation ICP-MS or thermal
407 ionization MS (TIMS) is not feasible. Consequently, issues such as element fractionation and
408 matrix-dependent signal bias (addressed below) or matrix-related polyatomic interference
409 problems (a fluid inclusion-specific discussion can be found in Pettke, 2008) need special
410 attention.

411 **Figure 2** illustrates the general principle of fluid inclusion laser ablation. The aim of
412 ablation is to liberate the entire fluid inclusion content (avoiding any loss during ablation) and
413 to produce a transient fluid inclusion signal that can be correctly recorded by the mass
414 spectrometer used. While this is simple in principle, it is often difficult to achieve in practice.
415 Importantly, the ablation quality of quartz varies significantly, sometimes even for a given
416 sample, and it has so far not been possible to link this diverse behaviour to specific analytical
417 parameters. Allan et al. (2005) also concluded that the errors in their fluid inclusion data most
418 likely relate to the laser ablation sampling process. The following points should thus all be
419 considered in order to obtain adequate results (**Fig. 4A**):

420 (i) The visible light optics of the system need to be as good as possible in transmitted light
421 mode, so that 10x10x5 μm fluid inclusions within the sample can be clearly seen on a TV
422 monitor. A petrographic microscope is optimal.

423 (ii) The absorbance of the laser beam by the host mineral and the fluid inclusion phases
424 depends on the laser wavelength and needs to be maximized to allow for well controlled
425 drilling through the host mineral and ablation of the fluid inclusion content. For quartz, this is
426 achieved by use of short-wave UV radiation (193-213 nm). When inclusions explode during
427 the ablation process (i.e., open in an uncontrolled manner), an unconstrained fraction of the
428 inclusion content is lost, rendering such an analysis useless (**Fig. 4B**). To date, commercially
429 available 193 nm ArF excimer laser systems providing constant, high energy density across
430 the entire ablation spot are achieving adequate control on the laser ablation process for
431 quartz-hosted fluid inclusion analysis (see Pettke, 2008, and below). Successful applications
432 of 213 nm Nd:YAG laser systems for fluid inclusion analysis are also reported in the literature,
433 notably for host minerals other than quartz (Scambelluri et al., 2001; Stoffell et al., 2004;
434 Stoffell et al., 2008; Wilkinson et al., 2009; Berry et al., 2009).

435 (iii) The laser beam size needs to be adjustable in small steps in order to select a beam size
436 that is slightly larger than the largest diameter of the inclusion. The final beam size needs to
437 be larger than the inclusion to ensure complete ablation of the inclusion, but at the same time
438 it should be kept as small as possible to maximize the contribution of the inclusion relative to
439 the host to the mixed fluid inclusion plus host signal section (**Fig. 2**), thus minimizing the LOD
440 for elements in the fluid inclusion (see below).

441 (iv) The ablation chamber has to accommodate the sample and reference material(s) and

442 should, together with the other parts of the aerosol transport system, be characterized by
443 short washout times (1-3 seconds) as is beneficial for all LA-ICP-MS applications.

444 Laser ablation of an individual fluid inclusion, even when carried out ideally, produces
445 transient signals of limited duration, that may vary unevenly over several orders of magnitude
446 during a signal duration of typically 5 - 40 seconds (Fig. 4A), or, for elements concentrated in
447 tiny daughter crystals, possibly even during much shorter intervals. Because the entire,
448 heterogeneous inclusion is ablated, the entire signal needs to be integrated for quantification.
449 Partial signal integration is not viable because it uses an unknown and thus non-
450 representative fraction of the entire polyphase sample (recall that we want to quantify the bulk
451 inclusion content that was a single fluid phase at the time of entrapment). The length of the
452 signal primarily depends on inclusion size and shape, on laser ablation conditions and on the
453 aerosol transport system used. Note that even for apparently well-controlled fluid inclusion
454 ablations (as visually judged on screen; e.g., analysis 26jic08 in Table 2), a large fraction of
455 some elements, Au in this case, may be lost, as is indicated by the measured Au
456 concentration of below $0.035 \mu\text{g g}^{-1}$, significantly lower than the average Au content of 0.080
457 $\pm 0.020 \mu\text{g g}^{-1}$ of this fluid inclusion assemblage.

458 Among the several techniques applied for fluid inclusion analysis, two merit more
459 detailed consideration, the step-wise opening technique (Günther et al., 1998; Allan et al.,
460 2005) and the straight ablation technique (Pettke, 2008). A step-wise increase of laser beam
461 diameter during fluid inclusion ablation considerably improves control on the ablation process
462 for quartz-hosted inclusions (Günther et al., 1998), thus minimizing inclusion loss due to
463 rupturing, but, unfortunately, has three serious drawbacks.

464 (i) Surface contamination, if present (and it often is, see illustrations in Pettke, 2008) cannot
465 be properly separated from the inclusion signal. Such contamination can often not be
466 removed even by most careful cleaning with organic solvents or inorganic acids prior to laser
467 ablation analysis, because the polishing process generates a thin film ($< 200 \text{ nm}$) of likely
468 amorphous material that consists of a mixture of sample material and contaminants (see also
469 Marschall and Ludwig, 2004). Gangue quartz interspersed with soft ore minerals (e.g., native
470 gold, chalcopyrite or molybdenite) is most susceptible to surface contamination. Pre-ablation
471 cleaning with the laser beam is also not a viable option as such pre-ablation at large beam
472 size may already induce fluid inclusion rupturing.

473 (ii) Every fluid inclusion has a confined mass that will be analyzed over a longer time interval
474 when using the step-wise opening procedure. This will return lower signal-to-background
475 intensity ratios that translate into elevated LODs when compared to straight ablation (see
476 below).

477 (iii) Very fast change of beam size is essential to maintaining high signal-to-background
478 ratios. A manually controlled crater size selection is thus optimal because commercially
479 available motorized aperture change systems are often too slow and/or have a rather limited
480 choice on beam diameters. An elegant, custom-made device for fluid inclusion ablation in
481 quartz minimizing breakout has been described by Guillong and Heinrich (2007b). They

482 designed an iris diaphragm, allowing for fast and continuous increase of beam size from ca. 8
483 μm to the final beam size required for fluid inclusion ablation, either prior to opening the
484 inclusion (resulting in straight ablation; see below) or during fluid inclusion ablation
485 (corresponding to the stepwise ablation technique). An alternative technique, the so-called
486 traverse opening method (Gagnon et al., 2003) enhances the influence of surface
487 contamination (as with all scanning protocols that operate without pre-ablation) and does not
488 provide for adequate control on the completeness of fluid inclusion ablation, resulting in
489 reduced accuracy.

490 Straight ablation of fluid inclusions uses a beam size larger than the largest diameter of
491 the inclusion for ablation, set prior to opening the inclusion (Fig. 4). This way, the potential for
492 surface contamination is minimized and the signal to background ratio for the inclusion signal
493 is maximized, thus returning lower LODs (Pettke, 2008). The benefits from stepwise opening
494 regarding optimal control on the ablation process can still be maintained, if the laser beam
495 can be enlarged in stepwise fashion to its final size before the fluid inclusion is hit (Fig. 4A);
496 this technique strongly reduces the likelihood of fluid inclusion explosion during ablation.
497 Here, it is even more important to have fastest possible beam size change (i.e., by manual
498 control). We contend that this is currently best practice for the analysis of individual fluid
499 inclusions.

500 Signal intensity versus time plots provide a reliable basis to judge the quality of laser
501 ablation of a fluid inclusion. Ideally, the fluid inclusion content is liberated "layer by layer" as
502 for solids. Because ideal fluid inclusions are isometric and given minimal signal "smearing" by
503 the aerosol transport system, the resulting signal would be Gaussian-like as illustrated in
504 Figure 4A. Importantly, the signal rise is slower than that observed at beam size change, and
505 the signal decay is fast but also slower than that observed when the laser is switched off (too
506 slow signal decay, i.e., pronounced signal "smearing", is to be avoided because it elevates
507 LODs). Fast transient signal spikes that (rise and) decay as fast as the signal of the host
508 mineral on beam shut-off are highly indicative of uncontrolled ablation (e.g., when the fluid
509 inclusion has exploded; Fig. 4B). Because it cannot be determined what fraction of inclusion
510 content may have been lost, such analyses may be seriously compromised.

511 Active focusing during fluid inclusion ablation when using the GeoLas ablation system
512 maximizes the transport of fluid inclusion content to the ICP-MS. Because of fairly conical
513 beam shape (see Fig. 2 in Heinrich et al., 2003, for a sketch), material loss to the crater walls
514 is minimized; hence, problems arising from incomplete fluid inclusion sampling are minimized.
515 Most likely, such an imaging system also minimizes depth-related element fractionation.

516 Aqueo-carbonic fluid inclusions (three-phase at room T) always show particularly short
517 transient signals upon opening (Fig. 5; note the log scale on the intensity axis); hence, more
518 than 90% of the solute content is liberated during the first signal burst. This characteristic
519 signal pattern results from the internal overpressure in such inclusions at room temperature.
520 Because quartz does not completely absorb even 193 nm laser light, some of it can penetrate

521 down to the fluid inclusion, be absorbed there, heat the inclusion and thus further increase
522 internal pressure to the bursting point at the time the inclusion is reached. Consequently,
523 three-phase aqueo-carbonic fluid inclusions can only be analyzed for a limited number of
524 elements (say, less than 10) to ensure representative recording of the initial fast transient
525 signal peak that dominates the bulk solute signal (e.g., Klemm et al., 2004; Pettke et al.,
526 2000b). How representatively these fast transient signals are actually recorded is again best
527 evaluated on the basis of the distribution of results from a series of fluid inclusions belonging
528 to a homogeneous assemblage.

529 Another important factor to consider is the suitability of fluid inclusions selected for LA-
530 ICP-MS analysis. The following guidelines may be helpful.

531 (i) Optimum inclusion size is between 10 and 40 μm . Larger inclusions are generally not
532 beneficial because it is often rather difficult to analyze them at controlled ablation conditions
533 due to more frequent quartz break out at larger beam sizes.

534 (ii) Inclusions need to be located at an optimum depth beneath the sample surface. The larger
535 the inclusion, the larger is its optimum depth for analysis. A 10 μm sized inclusion is ideally
536 located ca. 20 μm below surface, a 40 μm sized inclusion about 50 μm ; shallow inclusions
537 such as preferred for RAMAN or microthermometric analysis are not suitable. For deep-
538 seated inclusions, the potential for surface contamination is minimized because the inclusion
539 can be ablated using the straight ablation technique. Moreover, the likelihood for inclusion
540 explosion is reduced for deeper inclusions. In case the inclusions are buried too deeply,
541 however, signal tailing occurs, which increases LODs. Deep-seated inclusions also bear the
542 dangers of incomplete sampling of the fluid inclusion contents and of element fractionation
543 induced by deep laser drilling (see Guillong et al., 2011).

544 (iii) Inclusions need to be well isolated from each other, so that an individual inclusion can be
545 drilled out without connecting to neighbouring inclusions (see Pettke, 2008). While the best
546 currently available laser systems allow for excellent spatial resolution of the laser ablation
547 process, stray light may modify the gas speciation in adjacent inclusions (Lambrecht et al.,
548 2008), which may prevent their use for further petrological investigation.

549 (iv) Optimum fluid inclusions are spherical, given that cylindrical inclusions at optimal
550 orientation do not exist. Such inclusions provide the largest possible mass of material
551 available per unit time, i.e., maximized signal to background intensity ratios for inclusion
552 solutes, because these are least diluted by co-ablated host mineral material. This translates
553 to higher sensitivities and thus lower LODs, notably for inclusions hosted by minerals that
554 contain significant amounts of trace elements in common with the inclusion (compare Halter
555 et al., 2002b).

556 (v) The amounts of solutes available for analysis are of importance, as they do not
557 necessarily correlate with the size of the fluid inclusion. For example, a 30 μm vapour
558 inclusion (e.g., 0.1g/cm³ density) has one order of magnitude less solutes by mass than a
559 high density inclusion of the same size (1.0 g/cm³). Given that the ablation speed of a fluid
560 inclusion is largely controlled by the host mineral ablation rates, high density inclusions return

561 higher sensitivities and thus lower LODs, for this specific example up to one order of
562 magnitude. Less dense vapour inclusions correspondingly yield even higher LODs.
563 (vi) Minimum thickness of the sample section is about 100 μm , preferably thicker (transmitted
564 light inspection permitting). If inclusions are too close to the lower surface of the section, they
565 may simply rupture through the lower surface during ablation. Moreover, for quartz hosts, a
566 significant fraction of light, even when using 193 nm lasers, penetrates a 100 μm thick quartz
567 section and thus can interact with the glue beneath or even the section support glass
568 (because of the high energy density required for controlled ablation of some quartz types).
569 This may add unrelated material to the fluid inclusion signal, or melting of glue may obscure
570 real-time observations that are important for assessment of ablation quality.

571 We emphasize that selection of ideal fluid inclusion material likely accounts for >50% of
572 the success of a LA-ICP-MS fluid inclusion investigation. Petrographic inspection of a large
573 selection of fluid inclusion samples to choose the best material available for analysis is
574 therefore highly rewarding.

575 **Element concentration analysis by single-collector ICP-MS**

576 Multi-element analysis of an individual fluid inclusion aims at returning significant
577 concentration data for as many elements as possible from the short transient signal as
578 introduced above. Therefore, in principle, all the sample solutes reaching the ICP should be
579 completely converted to single-charged cations, and these ions should all be recorded by the
580 mass spectrometer. This cannot be achieved, however, since different masses have to be
581 measured sequentially and because of limitations in transmission of the instruments. It is
582 therefore a challenge for the analyst to optimize the ICP-MS instrumental part in such a
583 fashion that the cations recorded by the detector are representative for the bulk composition
584 of the fluid inclusion analyzed. This may sound simple, but is far from trivial.

585 The function of the ICP is to break down the aerosol particles resulting from laser
586 ablation to atoms and to ionize these. In practice, most recent research has demonstrated
587 that this is currently a weak point in LA-ICP-MS analysis in general (e.g., Günther and
588 Hattendorf, 2005). Most well known in LA-ICP-MS are problems collectively referred to as
589 elemental fractionation, i.e., variations in element-specific sensitivities resulting from variable
590 LA-ICP-MS analytical conditions (e.g., Fryer et al., 1995; and countless subsequent
591 publications). Elemental fractionation has historically been assigned to processes occurring at
592 the laser ablation site (e.g., Fryer et al., 1995; Mank and Mason, 1999). However, it has
593 become more and more apparent that plasma processes are equally relevant for elemental
594 fractionation (e.g., Guillong and Günther, 2002). This insight has encouraged Günther and
595 Hattendorf (2005) to establish optimization criteria for “robust plasma conditions”; i.e.,
596 conditions where ion production in the ICP is uniform and as complete as possible. At such
597 conditions, fractionation effects resulting from incomplete ionization are minimized. Pettke
598 (2006) has provided a detailed summary of criteria relevant to the analysis of polyphase

599 inclusions aimed at minimizing matrix-dependence related to external calibration. Following
600 such recommendations, use of well characterized external standard materials (SRM) for
601 quantification, such as the SRM 610 and 612 glasses from NIST, can return accurate fluid
602 inclusion element concentration data for most elements. It has become clear, however, that
603 the type of aerosol produced at the laser ablation site is also extremely important. An ideal
604 aerosol would be chemically uniform, of <10 nm grain size and of narrow size distribution
605 such that it can become quantitatively atomized and ionized in a plasma source. Aerosols of
606 very broad size distribution (up to 1 μm) with particles having size-dependent chemical
607 composition (most recently Glaus et al., 2010) are unlikely to be completely ionized even in a
608 perfectly optimized ICP, considerably reducing analytical accuracy.

609 Single collector mass spectrometers with quadrupole mass filters are currently
610 preferred for fluid inclusion multi-element analysis because they allow for the fastest high-
611 sensitivity measurement over a range from Li to U. The ion extraction systems of common
612 quadrupole mass spectrometers are designed to measure positive ions. However, single-
613 collector instruments suffer from one serious drawback, namely that during the recording of a
614 particular isotope, all other isotopes pass the system unrecorded. The more isotopes are to
615 be measured, the lower is thus the duty cycle for a given isotope, i.e., the fraction of the entire
616 signal time spent for measuring a given isotope. Representative recording of fast transient
617 signals is thus critical, and various aspects relevant to the design of appropriate data
618 recording protocols have been discussed in detail in Pettke (2008). This discussion also dealt
619 with the so-called jump routine, in which the isotope of an element such as Au that is
620 especially prone to form micro-nuggets in fluid inclusions, is measured every other integration
621 cycle in a sweep. However, tests have since revealed that Perkin Elmer Elan mass
622 spectrometers when operated in “jump routine” mode actually measure the isotopes specified
623 in the analytical method strictly in mass-ascending order, failing to properly implement the
624 jump routine. Worse still, the data readout then reports the data as defined in the analytical
625 method and not in the sequence actually recorded during measurement. Therefore, the jump
626 routine results as reported in Pettke (2008) actually correspond to data recorded by an
627 extended dwell time routine (see below). This specific example can be taken as a warning
628 that the analyst cannot be careful enough during procedure optimization and that instrument
629 functionality needs to be continuously evaluated, in particular, when non-disclosure of the
630 source code for instrument control prevents the user from properly verifying such functionality.

631 To our knowledge, there is only one comprehensive data reduction software for fluid
632 inclusion analysis available to date, named SILLS (Guillong et al., 2008b;
633 <http://www.geopetro.ethz.ch/research/orefluids/software>). This user-friendly package allows
634 the reduction of transient LA-ICP-MS data for inclusions and homogeneous solids alike,
635 based on procedures and equations taken from Longerich et al (1996), Halter et al. (2002b),
636 Heinrich et al. (2003) and Allan et al. (2005) that are fully exposed. Other software that is in
637 use for inclusion data reduction is AMS (Mutchler et al., 2008;

638 <http://www.geochem.geos.vt.edu/fluids/laicpms/ams.shtml>) and Exlam2000, available at no
639 cost (Zacharias and Wilkinson, 2007).

640 Data reduction follows a stepwise procedure that includes a correction for host mineral
641 contributions on background-corrected signal intensities, followed by calculation of apparent
642 element concentrations based on the external standard used. The intermediate results are
643 then converted to fluid inclusion element concentrations by using an internal standard, e.g.,
644 Na from microthermometrically determined $\text{NaCl}_{\text{equiv}}$ concentrations corrected for the
645 presence of other major salt cations. Finally, each calculated element concentration is
646 compared to its analysis-specific "LOD". This procedure is described in detail in Heinrich et al.
647 (2003; summarized in their Fig. 10) and is based on the relationship (Longerich et al., 1996)

$$\begin{aligned} 648 \quad C_i(\text{sam}) / C_{\text{IS}}(\text{sam}) &= C_i(\text{std}) / C_{\text{IS}}(\text{std}) * \\ 649 &\quad (I_i(\text{sam}) * I_{\text{IS}}(\text{std})) / (I_{\text{IS}}(\text{sam}) * I_i(\text{std})) / \\ 650 &\quad (S_i(\text{sam}) * S_{\text{IS}}(\text{std})) / (S_{\text{IS}}(\text{sam}) * S_i(\text{std})) \end{aligned} \quad (1)$$

651 where C is the concentration of the subscripted element i or internal standard element IS in
652 the materials referred to in brackets (sam is sample, std is external standard material), I refers
653 to the background-corrected intensities (count rate in counts per second, cps) and S denotes
654 sensitivity (in cps per μg analyte per gram of material). The sensitivity ratios $S_x(\text{sam})/S_x(\text{std})$
655 are taken to be identical for all elements including the IS element, given robust ICP-MS
656 optimization. Therefore, although $S_x(\text{sam})/S_x(\text{std})$ is unknown, the sensitivity terms cancel,
657 and the concentrations of all elements in the sample (C_i) can be calculated when $C_{\text{IS}}(\text{sam})$
658 and the concentrations of all elements in the external standard ($C_i(\text{std})$) are known. In other
659 words, the internal standard constraint is required to define the analysis-specific relative
660 sensitivity factor (one factor for all analytes per analysis) by which the sensitivities determined
661 on the external standard material are converted to those obtained during a given sample
662 analysis. In the general case, this can be achieved either through independent knowledge of
663 an element concentration in the sample (Na from microthermometry for fluid inclusions) or by
664 adjustment of the sum of all analyzed cations, e.g., for silicates or melt inclusions to 100 wt%
665 element oxide minus those not analyzed (Leach and Hieftje, 2000; Halter et al., 2002b).

666 Evaluation criteria regarding the detection limit of an element, i.e., its presence or
667 absence in a given analysis, have to be calculated for each element in every inclusion
668 individually. One needs to be aware of the fact, however, that many different (and
669 inconsistent) "definitions" for "detection limit" do exist in LA-ICP-MS. One often cited approach
670 in LA-ICP-MS is that of Longerich et al. (1996), who defined "LOD" as three times the
671 calculated (expected) standard deviation of baseline corrected readings in the absence of the
672 analyte of interest:

$$673 \quad \text{"LOD}_i \text{ (}\mu\text{g g}^{-1}\text{)} = 3 * \text{stdev } I_i(\text{bkg}) * (1/N(\text{bkg}) + 1 / N(\text{an}))^{0.5} / S_i \quad (2)$$

674 where $\text{stdev } I_i(\text{bkg})$ stands for the precisely known standard deviation of the background count
675 rate $I_i(\text{bkg})$ for element i (in cps), S_i denotes the sensitivity of element i (in cps per $\mu\text{g g}^{-1}$;

676 analysis-specific as derived from the external standard multiplied by the relative sensitivity
677 factor), and N refers to the number of measurements (i.e., sweeps) integrated for the
678 background and analyte (an) signal intervals, respectively. The above example returns the
679 element concentration threshold value above which measured element concentrations are
680 deemed to be resolved from background at the 99.9% confidence level as selected by the
681 factor 3 (note that this is a one-sided interval of the distribution function; Currie, 1995).
682 However, equation 2 returns an LOD value of zero for zero counts in the background interval,
683 which is not sensible.

684 In the case that 5% of wrong positive detections are accepted (i.e., having detected
685 something although nothing is present, corresponding to 95% confidence), the factor in
686 equation 2 would reduce from 3 to 1.645. It is important to note that such confidence levels as
687 specified here only apply for normally distributed background readings.

688 Following IUPAC terminology (Currie, 1995) “LOD” as defined above in equation 2,
689 however, would translate to “critical value” or “critical level” (L_C), representing the minimum
690 significant value of an estimated net concentration. The “detection limit” or “minimum
691 detectable value” (L_D) as defined by IUPAC (Currie, 1995) is the true background corrected
692 mean signal or concentration value of a sample required to yield measurement data, for which
693 the probability to fall below L_C equals a specified value, e.g., 5% (corresponding to the
694 probability of false negative detections, i.e., of having nothing detected although something is
695 present). Assuming that L_C and L_D are both based on the same probability level of wrong
696 detection or rejection and that the variance of normally distributed measurements between L
697 = 0 and $L = L_D$ is constant, $L_D = 2 * L_C$. For this case, L_C is calculated according to equation
698 (2), using a numerical factor appropriate for the desired probability level (from the one-sided
699 tail of the normal distribution function).

700 For very low count rates as obtained in modern ICP-MS instruments, Poisson rather
701 than normal distribution statistics should be applied for estimation of L_C and L_D . Useful
702 approximations for these parameters are given by Currie (1968, 1995; see also Tanner and
703 Günther, 2009; Tanner, 2010):

$$704 \quad L_C = 1.645 * \sigma_0, \text{ and } L_D = 3.29 * \sigma_0 + 2.71 (= 2 * L_C + 2.71) \quad (3)$$

705 where L_C and L_D are given in terms of the sums of background corrected counts
706 acquired over the interval of analyte signal measurement. σ_0 is the standard deviation of this
707 sum as expected for a measurement with zero analyte (see equation 4 below). Note that the
708 numerical coefficients 1.645 and $2.71 = 1.645^2$ relate to 5% probabilities of false positive (L_C)
709 and false negative (L_D) detections as derived from normal distribution statistics. In the current
710 context, they thus serve as an approximation only; a precise application of the equation would
711 require use of coefficients taken from the Poisson distribution function (see Currie, 1968,
712 Tanner, 2010).

713 σ_0 depends on the background count rate and the actual times spent on counting the
 714 background and analyte sections of the signal. If R_{bkg} is the (precisely known) mean
 715 background count rate given in cps, N_{bkg} and N_{an} are the number of sweeps for the
 716 background and analyte integration sections, and DT is the dwell time (measurement duration
 717 per sweep for a given isotope, in s) used for recording element i, then the variance of the
 718 baseline-corrected (net) signal counts expected for a sample with zero analyte is

$$719 \quad \sigma_0^2 \text{ (in counts)} = R_{\text{bkg}} * DT * N_{\text{an}} (1 + N_{\text{an}} / N_{\text{bkg}}) \quad (4)$$

720 The detection limit L_D as expressed by equation (3) can be converted to $\mu\text{g g}^{-1}$ as
 721 required for LA-ICP-MS:

$$722 \quad L_{D,i} (\mu\text{g g}^{-1}) = L_{D,i} \text{ (in counts)} / (N_{\text{an}} * DT_i * S_i) \quad (5)$$

723 Division by $N_{\text{an}} * DT_i$ is required to convert counts into mean cps for the length of
 724 integration of the net analyte signal. Division by S_i transposes L_D given in cps into L_D
 725 expressed in $\mu\text{g g}^{-1}$. The complete LOD equation for general LA-ICP-MS analysis of element i
 726 at 95% confidence then reads

$$727 \quad L_{D,i} (\mu\text{g g}^{-1}) = (3.29 * (R_{\text{bkg},i} * DT_i * N_{\text{an}} * (1 + N_{\text{an}} / N_{\text{bkg}}))^{0.5} + 2.71) / (N_{\text{an}} * DT_i * S_i) \quad (6)$$

728 A numerical comparison of results calculated for L_C (critical limit at 99.9% confidence,
 729 analogous to "LOD" in equation 2) and L_D (detection limit, 95% confidence, corresponding to
 730 equation 6) demonstrates that the former yields lower values for low count signals (Fig. 6), for
 731 short analyte signals by a factor of two or more (Fig. 7; keeping stdev(bkg), N(bkg), S and DT
 732 constant). For low count rates and longer signals, values based on L_C at 99.9% confidence
 733 are lower by 20% only, for higher count rate background signals, the results are similar. Note
 734 that different confidence levels are compared in Figs. 6 and 7, owing to the conventional use
 735 of 3σ in equation 2 to quantify the LOD in LA-ICP-MS analysis.

736 **Figure 8** illustrates the LODs for Au calculated for a series of natural brine inclusions
 737 (Table 2; Fig. 3). This example represents the combined effects of analyte dwell time,
 738 variation of the background signal, fluid inclusion size and shape, fluid inclusion signal
 739 duration and analyte sensitivity that grossly vary for a series of natural fluid inclusion
 740 analyses. Recall that all parameters except dwell time and the background measurement are
 741 mutually dependent on each other. Nevertheless, the general trend persists that "LODs"
 742 calculated using equation 2 are lower (because $L_D \geq 2 * L_C$ according to statistical
 743 expectation), more so for short fluid inclusion signals. This example illustrates that for fast
 744 transient signals, too, the "LOD" formulation by Longerich et al. (1996) returns lower values,
 745 as documented for constant background above (Fig. 7).

746 This evaluation further illustrates that different LOD criteria can be, and often are,
 747 employed (e.g., L_C or L_D , 84%, 98 % or 99.9 % confidence regions for σ multipliers of 1, 2 or
 748 3), returning "LOD" values that may vary over more than one order of magnitude for a given
 749 data set. Therefore, disclosure of how LODs were calculated is essential in each case.

750 The above considerations allow to identify parameters relevant in lowering LODs in
751 fluid inclusion analysis. Note that lowering LODs also significantly improves the precision of
752 low-abundance element concentration determinations. Recall that the LODs are strongly
753 element-dependent because the analyzed isotopes are variably abundant in nature and
754 because instrument sensitivities vary strongly for different elements.

755 Given that element intensities are expressed as count rates (i.e., cps) to accommodate
756 variable dwell times, and because short dwell times, commonly 10 ms, are preferred for
757 representative recording of short transient inclusion signals in multi-element mode (Pettke et
758 al., 2000b), analytical uncertainties for low-intensity signals are inevitably high. For constant
759 numbers of background and analyte signal sweeps, L_D approximately scales with the inverse
760 of the square root of DT (see equation 6). Consequently, increasing selectively the dwell
761 times for a given element will translate into a lower L_D . Such an extended dwell time routine
762 does not only improve on L_D , but also increases the likelihood of representative recording of
763 element signals that are prone to originate from micronuggets in the sample (e.g., Au in many
764 fluid inclusions; see also Fig. 1B). Also note that an optimal recording of the analyte signal to
765 be used for internal standardization is mandatory because inaccuracies of the measurement
766 of the internal standard element directly transfer to all other “unknown” element
767 concentrations.

768 The sensitivity term S_i is obviously such that increasing sensitivity and keeping all else
769 constant decreases LODs. The most important procedures to enhance sensitivity in LA-ICP-
770 MS are to increase the amount of ablated and transported material per unit time (namely by
771 increasing the laser beam diameter, the repetition rate and/or the laser energy). If this is not
772 possible, e.g., for the analysis of inclusions of an a priori limited sample volume, other
773 methods have been described, e.g., the use of He in the ablation chamber (e.g., Eggins et al.,
774 1998; Günther and Heinrich, 1999), the reduction of the interface pressure (Günther et al.,
775 1997, 1998) and/or the addition of specific gases to the aerosol carrier gas, e.g., H_2 when
776 using Elan ICP-MS instruments (Guillong and Heinrich, 2007a). Not only the analyte signals
777 but also the gas backgrounds are variably affected by the above modifications (compare the
778 background signal for ^{29}Si in Fig. 4 run with H_2 admixture and Fig. 5 without H_2). The sum of
779 these effects will determine whether an improvement in signal-to-noise ratio can be achieved
780 with a given LA-ICP-MS instrumental setup, potentially lowering the LODs significantly and
781 improving the external reproducibility of ultra-trace concentration measurements.

782 For a given fluid inclusion ablation, Fig. 9 illustrates the effect of the choice of the
783 length of signal intervals, each indicated by the black arrows, on the resulting LODs (Fig. 9A).
784 The resulting “LOD”s calculated by equation 2 (L_C , 99.9 % confidence) and equation 6 (L_D , 95
785 % confidence) are expressed as the ratios of L_C (equation 2)/ L_D (equation 6) for the different
786 signal durations (Fig. 9B). Note that different confidence levels are again compared in Fig. 9
787 on purpose, in tune with conventional use. Each of these sample signal intervals returns
788 different mass fractions of analyzed inclusion content relative to host quartz that translate to

789 different sample and internal standard sensitivities as determined from the combined inclusion
790 plus host signal ($S_i(\text{sam})$ and $S_{is}(\text{sam})$), resulting in different LODs. Because the analyte
791 concentration within an inclusion is constant, calculated sensitivities are thus proportional to
792 count rate, yielding LODs which are then inversely proportional to count rate. For high
793 background count rates (e.g., Na) the LOD is very similar between the two equations (ratios ~
794 1) independent of the signal duration. For low background count rates (Pb = 0.3 cps; Au =
795 0.006 cps; Ba = 0 cps), equation 6 always returns higher LODs. Moreover, when decreasing
796 the signal interval duration, the ratio of LODs decreases, indicating a similar behaviour as
797 found for constant signals (Fig. 7). Note that for Ba, the ratio of LOD values is always zero
798 because of the zero LOD value returned by equation 2.

799 Integrating only the high-intensity part of the entire transient fluid inclusion signal for
800 minimizing the LODs is extremely dangerous, because cutting at the low-intensity wings of
801 the transient Na signal (commonly used to defining the fluid inclusion signal interval) may
802 cause loss of large fractions of other analyte signals (notably from tiny daughter crystals; Fig.
803 1B) that may sit on the inclusion bottom and thus be ablated very late during fluid inclusion
804 ablation. Careful inspection of all the analyte signals is thus mandatory for proper signal
805 interval selection. These considerations illustrate why fluid inclusions returning a "Gaussian-
806 like" signal shape of limited dispersion and without significant signal tailing are considered
807 ideal, yielding minimized LODs.

808 Because the amount of solutes available for analysis is highly variable between
809 individual fluid inclusions from a given assemblage, tabulated element concentration data are
810 lower for some inclusions than the LODs of the same element for other inclusions. This
811 variation has significant consequences:

- 812 (i) For the analysis of low fluid metal contents, measurements on a limited number of
813 inclusions with a large amount of solutes at optimum size, shape and depth in the host
814 mineral are much more important for a reliable determination than measurements on
815 numerous small inclusions.
- 816 (ii) Because the quality of an individual fluid inclusion analysis strongly depends on inclusion
817 size, shape and depth in host mineral, element concentrations of a fluid inclusion assemblage
818 are best determined as uncertainty-weighted average data (Pettke, 2006). This way, element
819 concentration data from well analyzed, large fluid inclusions are more significant in
820 determining the average, the effect of which often is that uncertainty-weighted element
821 concentration averages tend to be lower when compared to simple averages (e.g., Pettke et
822 al., 2004).

823 There are cases where independent determination of an element concentration within
824 the fluid inclusion as required for internal standardization is not possible. Such cases are
825 encountered for example in microthermometry of CO₂ bearing fluid inclusions that do not
826 contain liquid CO₂ at final CO₂ clathrate hydrate dissolution (Diamond, 1992) or fluid
827 inclusions where ionic species do not predominate. In the latter case, mass balance

828 constraints have been employed to estimate an element concentration to be used for internal
829 standardization (e.g., Scambelluri et al., 2004; Spandler et al., 2007), or the results were
830 simply given as concentrations of the inclusion plus host mineral mixture (at unknown mixing
831 proportions that vary between different analyses), in an attempt to approximate fluid
832 compositions (Ferrando et al., 2009). Some applications, however, may only require element
833 abundance ratios to constrain the processes of interest, e.g., ore metal precipitation across a
834 sequence of successively entrapped fluid inclusion assemblages. Note that element
835 abundance ratios do not depend on internal standardization. Landtwing et al. (2005, 2010)
836 used Cu/Na abundance ratios for vapour inclusions (where the tiny film of liquid was
837 insufficient for reliable microthermometry) to demonstrate that a two orders of magnitude
838 concentration decrease of Cu in the brines during Cu ore deposition is also reflected by the
839 associated vapour inclusions. Klemm et al. (2008) used scatterplots of Cs/(Na+K+Mn+Fe) vs.
840 Mo/(Na+K+Mn+Fe) to define two Mo-bearing fluid stages with different Cs contents, indicative
841 of two isolated events of fluid expulsion from progressively fractionating source magma.
842 Rather than normalizing the metal content to Na only, the sum of major cations was used
843 because their concentration remained largely constant across ore mineral precipitation (see
844 also Fig. 3B). These examples emphasize the usefulness of element abundance ratios in fluid
845 inclusions that can be accurately determined for host mineral corrected data by use of
846 external standardization only.

847 Finally, we like to emphasize that accurate fluid inclusion data can only be obtained
848 when the mixed inclusion plus host mineral signal is accurately corrected for host mineral
849 contribution. While for quartz-hosted inclusions, such a correction may not be significant for
850 many elements, results for Li, Ti, Al, B, Ga and Sn will be in excess without correction for host
851 quartz contribution (e.g., Flem et al., 2002; Landtwing and Pettke, 2005; Allan et al., 2007;
852 Rusk et al., 2011). Obviously, other elements too require correction when inclusions are
853 hosted in other minerals, by techniques that are identical to those outlined in detail for melt
854 inclusions by Halter et al. (2002b). Attempts to quantify fluid element concentrations without
855 correction for host mineral contribution may not even provide a correct magnitude.

856 **Selected applications and recent developments**

857 The application-driven LA-ICP-MS fluid inclusion analytical developments have largely been
858 based on materials from magmatic-hydrothermal (porphyry-type) ore deposits, resulting in
859 more than 50 publications to date. These will not be comprehensively reviewed here, and the
860 reader is referred to the corresponding literature. More recently, applications have diverged
861 towards the quantification of specific elements (e.g., S; Guillong et al, 2008a; Seo et al., 2009,
862 2011) or other hydrothermal systems (e.g., Klemm et al., 2004; Beuchat et al., 2004; Kostova
863 et al., 2004; Luders et al., 2005; Piqué et al., 2008; Stoffell et al., 2008; Heijlen et al., 2008;
864 Bertelli et al., 2009; Su et al., 2009; Williams et al., 2010; Richard et al., 2010; Catchpole et
865 al., 2011; Appold and Wenz, 2011). Most recently, the analysis of sulphur, chlorine and

866 bromine in quartz-hosted fluid inclusions by LA-ICP-MS has been investigated in detail (Seo
867 et al., 2011; Guillong et al., 2008a). Halogens are difficult to measure and quantify by ICP-
868 MS. They need to be analyzed as positive ions, with comparatively large first ionization
869 potentials, thus returning elevated LODs due to low sensitivity, notably for Cl. Moreover, as
870 for S, the absence of a reliable silicate glass SRM, potential contamination from tubing and/or
871 the ablation cell at variable and occasionally high levels during background and ablation
872 intervals, and polyatomic interferences all may compromise accuracy (Guillong et al., 2008a).
873 A well characterized scapolite crystal ($\text{Na}_4\text{Al}_3\text{Si}_9\text{O}_{24}\text{Cl} - \text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{SO}_4$) can be used as a
874 reference material, and the ablation cell needs to be carefully cleaned before analysis (Seo et
875 al., 2011). Synthetic fluid inclusions were used to determine analytical figures of merit such as
876 precision (1SD; S: 15-44 %, Cl: 7-20 %, Br: 12-26 %), accuracy and LODs (in $\mu\text{g/g}$ employing
877 equation 2; S: 60, Cl: 250, Br: 15) of the method. In natural brine inclusion assemblages the
878 precision of Br/Cl ratios (4 - 9 % 1SD) was found to be adequate to determine the source of
879 salinity in different ore-forming fluids. All the above contributions dealt with fluid inclusions
880 hosted in various minerals transparent to visible light.

881 LA-ICP-MS can also be used to analyze fluid inclusions hosted in opaque minerals, with
882 Kouzmanov et al. (2010) reporting a first application. Near-infrared microscopy was used to
883 locate fluid inclusions in pyrite and enargite, and combined transmitted and reflected light was
884 then employed to map the fluid inclusions relative to the surface features observed in
885 reflected light mode. Inclusions were then ablated in reflected light mode by positioning the
886 ablation spot according to the mapped positions. Solutes in the fluid inclusion assemblages
887 successively entrapped in quartz and pyrite-enargite showed evolving concentrations,
888 interpreted to result from successive pulses of compositionally distinct fluid passing through
889 the ore body. Such an approach allows the analysis of metals in individual fluid inclusions
890 hosted in the ore minerals of interest and produces the data needed to assess the general
891 validity of the assumption (though often supported by robust petrographic evidence) that
892 quartz-hosted fluid inclusions do represent trapped ore-forming fluid. While the latter most
893 likely applies to porphyry-type ore deposits, evidence has been presented, for example for
894 orogenic Au deposits (Pettke and Frei, 1996) and MVT deposits (Stoffell et al., 2008;
895 Wilkinson et al., 2009), that mineralization may involve highly transient episodes of ore-metal
896 rich fluid ingress in the much longer-lived hydrothermal activity of an ore deposit. Clearly,
897 further investigations are required to clarify this important issue.

898 **Experimental investigations of fluids at high pressure and temperature**

899 Synthetic fluid inclusions are employed in experimental efforts to quantify element
900 mobility and speciation in magmatic-hydrothermal fluids as a function of pressure-
901 temperature-composition (PTX). Such studies were historically confined to the one-phase
902 fluid field (i.e., vapour, brine, or supercritical fluid) at temperatures and pressures of no more
903 than a few hundred MPa (e.g., Chou and Eugster, 1977; Candela and Holland, 1984; Whitney
904 et al., 1985; Wood et al., 1987; Hemley et al., 1992). In experiments with low-salinity fluids

905 (<~5 wt. % NaCl_{equiv}), the quenched fluid is extracted from the charge and analyzed at
906 ambient conditions, and it is either demonstrated or simply assumed that the solute load of
907 the quenched fluid is equivalent to the solute load at the experimental PTX conditions, i.e.,
908 that no solutes precipitated upon quench. Precipitation upon quench has been demonstrated
909 to occur at higher pressures, resulting in an underestimation of the solute's elemental
910 concentration (Green, 1973) unless the fluid can be extracted from the autoclave at run P and
911 T conditions (e.g., Bourcier and Barnes, 1987; Seyfried et al., 1987). To experimentally
912 determine the solute load of aqueous fluids at higher pressures or of fluids of higher salinity,
913 experiments have been performed in an aqueous fluid ± melt ± crystal(s) system, and the
914 solute composition of the single-phase aqueous fluid has been determined by mass
915 difference between initial and final crystal or melt (e.g., Anderson and Burnham, 1965;
916 Manning, 1994; Manning and Boetcher, 1994; Newton and Manning, 2000; Newton and
917 Manning, 2002). This method can yield accurate mineral solubilities owing to the ability to
918 quantify masses with 1σ reproducibility down to 0.002 mg (Newton and Manning, 2000).
919 However, quench-induced crystallization of the melt, in charges where only melt and aqueous
920 fluid co-existed, or dissolution-precipitation processes along thermal gradients within the
921 charges during run introduce uncertainty in quantifying melt chemistry and, thus, affect the
922 accuracy of mass balance calculations required to quantify fluid element solubilities. The
923 mass balance technique also precludes the ability to investigate element mobility in
924 assemblages that are saturated with immiscible C-O-H-S fluids, e.g., vapour and brine.

925 Over the past decades, experimentalists have increasingly turned to the method of
926 synthetic fluid inclusions to study fluids at pressures and temperatures relevant to the
927 evolution of magmatic-hydrothermal systems (e.g., Sterner and Bodnar, 1984; Bodnar and
928 Sterner, 1985, 1987; Bodnar et al., 1985; Diamond, 1992). Synthetic fluid inclusions can be
929 produced at run PT by (i) trapping fluid(s) in pre-fractured mineral host phases such as quartz
930 (e.g., Simon et al., 2004, 2005, 2006, 2007, 2008a,b, 2009; Hanley et al., 2005b; Hack and
931 Mavrogenes, 2006; Spandler et al., 2007; Simon and Pettke, 2009; Lerchbaumer and
932 Audétat, 2009; Frank et al., 2011), (ii) trapping fluid(s) in self-healing mineral hosts that are
933 fractured during the experiment after the charge reached steady-state conditions (Li and
934 Audétat, 2009; Zajacz et al., 2010, 2011), (iii) trapping fluid(s) along the etched or pre-drilled
935 surface of a mineral during the formation of overgrowths (Loucks and Mavrogenes, 1999;
936 Duc-Tin et al., 2007; Li and Audétat, 2009), and (iv) trapping fluid(s) in coexisting silicate melt
937 as the melt is quenched through the glass transition temperature (e.g., Frank et al., 2002;
938 Hanley et al., 2005b; Simon et al., 2007). **Table 3** provides details from experimental studies,
939 which have used synthetic fluid inclusions to sample fluid(s) at elevated PT conditions in order
940 to quantify solute compositions and element speciation in fluids at high P and T by LA-ICP-
941 MS or other microbeam techniques.

942 One of the most significant progresses in the use of synthetic fluid inclusions has been
943 the ability to constrain directly the partitioning of metals between immiscible fluid phases (e.g.,
944 liquid - vapour - melt) and the speciation of metals in aqueous fluid(s) at magmatic-

945 hydrothermal conditions. These experimental investigations have been stimulated by solute
946 data from natural magmatic-hydrothermal systems that indicate specific element distribution
947 patterns between coexisting phases, e.g., the partitioning of Cu and Au between vapour and
948 brine (e.g., Heinrich et al., 1992; Audétat et al., 1998; Heinrich et al., 1999; Ulrich et al., 1999)
949 or metal distribution between coexisting aqueous fluid and silicate melt (e.g., Audétat et al.,
950 2000a; Audétat and Pettke, 2003; Zajacz et al., 2008) or silicate and sulphide melts (e.g.
951 Halter et al., 2002a) or even halide melts (Hanley et al., 2005a, 2008). Data accumulated from
952 various ore deposits have improved constraints on element partitioning between coexisting
953 phases, for example for the Mole Granite (using PIXE, Heinrich et al., 1992; using LA-ICP-
954 MS, Audétat et al., 1998, 2000a,b), the porphyry deposits of Bajo de la Alumbrera, Argentina
955 (Ulrich et al., 1999, 2002; Halter et al., 2002a), the Bingham Canyon, Utah (Redmond et al.,
956 2004; Landtwing et al., 2005, 2010), or Butte, Montana (Rusk et al., 2004, 2008), and the
957 Bismarck skarn deposit, Mexico (using PIXE; Baker et al., 2004).

958 An understanding of the relative abilities of vapour and brine to scavenge and transport
959 ore metals in various environments is required to accurately model the evolution of
960 hydrothermal ore formation. The studies described in **Table 3** document the significant
961 progress made based on synthetic fluid inclusions in the past decade. The results have lent
962 support for a much stronger role of magmatic vapour for scavenging and transporting ore
963 metals than was assumed before. Other studies have been performed to elucidate the relative
964 roles of chlorine and sulphur on metal complexation and partitioning. Importantly, these data
965 validate the hypothesis, formulated from the analysis of boiling assemblages in natural
966 systems (e.g., Heinrich et al., 1999; Seo et al., 2009), that sulphur is an important metal
967 ligand in high-temperature magmatic-hydrothermal fluid. Several studies have employed
968 synthetic fluid inclusions in order to investigate metal speciation in one-phase fluid, and the
969 role of varying PTX on metal-sulphur complexes. Direct information about metal speciation
970 has been obtained by using synchrotron based techniques to study bonding coordination
971 between metals and ligands (e.g., Berry et al., 2006), whereas indirect information has been
972 obtained by using LA-ICP-MS to measure changes in the concentration of a particular metal
973 (e.g., Au) as the metal-complexing ligand (e.g., S) is systematically varied. The results from
974 these speciation studies have advanced our knowledge on metal complexation considerably.
975 The general picture now emerges that both sulphur and chlorine are essential during the
976 evolution of magmatic-hydrothermal systems.

977 **An uncommon application: Bismuth melt inclusions**

978 A rather uncommon example of "fluid inclusions" is represented by droplets of bismuth
979 melt, trapped in hydrothermal vein minerals. Occurrences of native bismuth have been
980 reported from various magmatic-hydrothermal environments ranging from massive sulphide
981 deposits to epithermal vein-type deposits. They are of great interest to economic geologists
982 because bismuth grades typically correlate strongly with Au grades. Since bismuth remains
983 molten down to a temperature of ~270 °C and can take up large amounts of Au (up to 20 wt%

984 at 300 °C; e.g., Nathans and Leidner, 1962) it has been proposed that bismuth melts may act
985 as efficient scavenger of Au from hydrothermal fluids or pre-existing sulphide minerals
986 (Douglas et al., 2000). This model is supported by petrographic studies on natural samples
987 (e.g., Ciobanu et al., 2006; Oberthür and Weiser, 2008), and has proven to be
988 thermodynamically feasible by Tooth et al. (2008). However, quantitative determination of the
989 Au-contents of naturally occurring bismuth melts has always been hampered by the fact that
990 these melts unmix into various phases upon cooling to room temperature, such that bulk
991 compositions are difficult to estimate. The accurate quantification of sulphide melt
992 compositions, both from experiment and from exposed sulphide melt inclusions of natural
993 samples suffers from the same problem. Laser-ablation ICP-MS analysis of entire inclusions
994 provides the ideal solution.

995 The following example of bismuth melt inclusions analyzed from the Sn-W (-Cu, Pb, Zn,
996 Bi, Au, Ag)-mineralized Mole Granite, Australia, serves to illustrate the large potential of this
997 method. In the Mole Granite area (see Audétat et al., 2000a,b, for details), inclusions of
998 bismuth melt were found in fluorite of a hydrothermal vein in the surrounding sediments
999 (sample Taro20), in a large topaz crystal within quartz-topaz greisen (Bism3.3), and in a
1000 quartz crystal from a diffuse vein within quartz-topaz greisen (Gold4). The latter sample is
1001 particularly interesting because it was collected from a former Au-Bi mine. According to old
1002 reports the ore of this mine contained up to 3 wt% Bi and 30-120 g/t Au.

1003 From each occurrence, five to nine bismuth inclusions completely enclosed in the host
1004 mineral were analyzed. A typical signal of an inclusion analyzed from sample Bism3.3 is
1005 shown in Fig. 10. The LA-ICP-MS analyses were quantified by normalizing the sum of all
1006 major and minor elements (Bi, Te, As) to 100 wt%. An overview of the results is given in
1007 Table 4. The fact that the calculated element concentrations within a given sample are well
1008 reproducible (Table 4) strongly suggests that the Bi-melt was homogeneous at the time of
1009 entrapment. On the other hand, some minor and trace element contents vary strongly from
1010 locality to locality. By far the highest Au contents are observed in the sample from the former
1011 gold mine (Gold4), and the Au/Bi-ratio in the analyzed inclusions (2×10^{-3}) matches the Au/Bi-
1012 ratio of the ore ($1 - 4 \times 10^{-3}$). The Au content of bismuth melt inclusions may thus serve as an
1013 indicator of nearby gold ore.

1014 This application also illustrates the smooth transition between fluid inclusion and melt
1015 inclusion LA-ICP-MS analysis. The principles and procedures addressed in this review are
1016 equally valid and useful for bulk melt inclusion analysis in cases where reliable inclusion
1017 homogenization cannot be achieved, a prerequisite for the analysis of exposed parts of melt
1018 inclusions by microbeam techniques. Such examples include sulphide melt inclusions that
1019 always produce multiple quench phases, and crystallized silicate inclusions from water-
1020 saturated igneous systems that often have lost water or H by diffusion since entrapment;
1021 hence, homogenization at entrapment P and T in the lab cannot be achieved. A quick
1022 overheating of such melt inclusions for homogenization may also not be an option because an
1023 uncontrolled amount of host mineral will be remelted into the melt inclusion, potentially

1024 falsifying its bulk composition (see Pettke et al., 2004, for an example). Successful examples
1025 of combined fluid and melt inclusion applications are reported in the literature (e.g., Audétat et
1026 al., 2000a; Audétat and Pettke, 2003; Zajacz et al., 2008; Audétat et al., 2008), thus
1027 illustrating the unique capabilities of LA-ICP-MS for inclusion chemical analysis.

1028 **Isotope ratio analysis by MC-ICP-MS**

1029 Constraints on the sources of fluids help identify provenance of components, thus
1030 constraining processes of chemical and heat transfer in the Earth. Radiogenic isotopes are a
1031 prime tool for this, notably because different sources often possess distinct signatures. For
1032 heavier isotopes in particular, mass dependent fractionation during geological processes
1033 (e.g., fluid boiling of crystallization from fluid) does not modify the isotopic signatures much
1034 (unlike for light to middle mass stable isotopes, e.g., H, C, O, Li, B, Cl, Cr, Ni, Cu). Moreover,
1035 radiogenic isotope ratios may provide constraints on the age of the source (see below).

1036 To obtain precise isotope ratio measurements by laser ablation, multiple collector ICP-
1037 MS instruments are preferred over sequentially recording single collector instruments where
1038 noise in the ion signal from laser ablation and plasma flicker limits isotope ratio analytical
1039 precision to > 0.1 % uncertainty (e.g., Appelblad et al., 2001, and references therein).
1040 Moreover, simultaneous signal detection drastically improves the duty cycle, a key advantage
1041 for the analysis of an individual fluid inclusion with a priori limited sample amount and thus
1042 limited signal duration. This section summarizes current procedures to accurately analyze
1043 individual inclusions for Pb and Sr isotope ratios by LA-MC-ICP-MS. The detailed techniques
1044 for Pb isotope ratio analysis have been published elsewhere (Pettke et al., 2011), while
1045 specific procedures for Sr isotope ratio analysis of fluid inclusions of a pilot study are
1046 presented below. All data were acquired using a 193 nm ArF excimer laser system (GeoLas
1047 200Q, Lambda Physik, Germany) with computer-controlled sample stage connected to either
1048 a Nu Plasma or a Nu Plasma 1700 MC-ICP-MS instrument (Nu Instruments Ltd, Wrexham,
1049 UK).

1050 **Lead isotope ratio analysis of individual fluid inclusions**

1051 The challenge of analyzing an individual fluid inclusion for isotope ratios lies in the fact
1052 that it contains a strictly limited mass of analyte, of the order of 0.1 ng of Pb for magmatic-
1053 hydrothermal fluid inclusions 40x40x30 μm in size and containing a few 1000 $\mu\text{g g}^{-1}$ Pb. This
1054 tiny amount is to be measured as a highly transient signal varying in intensity over some 3
1055 orders of magnitude during a 10 - 30 s time interval (Fig. 11). This is opposite to common
1056 solution-based MC-ICP-MS analysis where stable ion beams are recorded over 10 - 20
1057 minutes. Note that commercial instruments have been developed to accurately record such
1058 constant signals as produced from solution nebulisation and, hence, the fast transient signals
1059 generated from laser ablation of an individual fluid inclusion need special measures. The

1060 requirements for controlled ablation of an individual fluid inclusion outlined above remain
1061 valid, of course.

1062 The results of extensive methods development have been reported in Pettke et al.
1063 (2011). They used synthetic fluid inclusions of known Pb isotopic composition, ca. 5400 µg
1064 SRM 981 Pb per g of 17 wt-% Na-K-Cl solution, Pb concentrations typically encountered for
1065 magmatic-hydrothermal fluids (e.g., Landtwing et al., 2005; Klemm et al., 2007, Audétat et al.,
1066 2008). The inclusion analyses were performed in static time-resolved mode using modified
1067 instrument control and data reduction software, collecting ^{200}Hg - ^{202}Hg - ^{203}Tl - $^{204}(\text{Hg,Pb})$ - ^{205}Tl -
1068 ^{206}Pb - ^{207}Pb - ^{208}Pb in 0.2 s readings simultaneously in 8 Faraday cups calibrated daily for their
1069 preamplifier gains. Only the signal on mass 204 required interference correction of ^{204}Hg .
1070 Polyatomic interferences were not significant, even when analyzing SRM 610 from NIST, a
1071 glass doped with nominally 500 µg g⁻¹ of all trace elements. This suggests that, for chemically
1072 complex natural fluid inclusions, polyatomic ion interferences may also not be significant in
1073 this mass range, at least not at the precision so far achieved. In any case, however, testing is
1074 required for specific applications in order to verify this assumption.

1075 Methods development identified several sources of isotope ratio bias, such as mass
1076 fractionation and delayed amplifier response. Instrumental mass bias in Pb isotope ratio
1077 analysis is successfully accounted for by within-run correction based on measured $^{205}\text{Tl}/^{203}\text{Tl}$
1078 from desolvated aerosol admixed to the laser ablation aerosol prior to ionization in the ICP
1079 (Fig. 11). Recording the data on Faraday detectors has revealed strong isotope ratio bias
1080 originating from differences in response among the amplifiers used for recording the individual
1081 ion beams (e.g., Hirata et al., 2003). Our investigations show that numerical correction
1082 schemes can compensate for most of the bias except for extremely fast changes in signal
1083 intensities such as generated from explosion of fluid inclusions or upon beam size increase
1084 during stepwise opening of the fluid inclusion. The latter signal types are thus better avoided.
1085 Data obtained from controlled, smooth ablations reveal isotope ratios that evolve from light to
1086 heavy across the transient signal when corrected for Faraday amplifier response by
1087 algorithms described in Pettke et al. (2011). This effect is ascribed to laser ablation-induced
1088 Pb isotope fractionation of the order of 0.5 % per a.m.u.

1089 To obtain accurate isotope ratios, the entire transient inclusion signals need to be
1090 integrated and processed. The best way to integrate the data for a given fluid inclusion
1091 ablation is bulk signal integration (e.g., Evans et al., 2001), i.e., to sum up all the individual
1092 readings and then take the isotope ratios and process these. This procedure has several
1093 benefits over the individual reading integration method as applied for solution nebulisation
1094 analysis, namely (1) high-intensity readings become much more important than low-intensity
1095 and possibly highly fractionated and/or imprecise readings in determining the isotope ratio of
1096 the inclusion (isotopic ratios based on individual readings show enhanced variance, and
1097 results may be distorted if isotopic beams behave non-proportionally across the ablation
1098 interval), (2) the effect of bias in amplifier response largely cancels out when the entire signal

1099 is integrated; hence, instrument-specific amplifier response correction is not a prerequisite for
1100 obtaining accurate bulk inclusion isotopic data at useful precision, and (3) laser ablation
1101 induced isotope fractionation also cancels out for bulk signal integration of fluid inclusions
1102 (Pettke et al., 2011). However, bulk signal integration does not provide a straightforward
1103 means to determine analytical uncertainties, e.g., mean and standard error as commonly
1104 obtained from sets of reading-by-reading ratio evaluation in solution-based isotope ratio
1105 measurements. Minimum uncertainties for isotope ratios calculated by bulk signal integration
1106 for an individual inclusion can, however, be estimated from a Gaussian combination of ion
1107 statistics and baseline noise.

1108 **Figure 12** documents a set of 20 compositionally identical fluid inclusions containing
1109 SRM 981 Pb individually analyzed for Pb isotopic ratios. As with element concentration data,
1110 it is best practice to determine the average and associated uncertainty for a given fluid
1111 inclusion assemblage. For the synthetic fluid inclusions containing 0.01 - 0.1 ng Pb per
1112 inclusion, 2 standard deviation uncertainties on inclusion-to-inclusion reproducibility are ca.
1113 0.08 % for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, and ca. 0.5 % on ratios normalized to ^{204}Pb , the lower
1114 precision of the latter resulting from the low intensity ^{204}Pb ion beam. The analyses are
1115 accurate at these uncertainties. Natural fluid inclusion assemblages containing up to 1 wt%
1116 Pb were since analyzed even more precisely, with ca. 0.05 % 2 SD (n=11) for $^{208}\text{Pb}/^{206}\text{Pb}$ and
1117 $^{207}\text{Pb}/^{206}\text{Pb}$, and ca. 0.13% for Pb isotope ratios normalized to mass 204. Acceptably
1118 reproducible results (± 0.1 % and 0.7 %, respectively) can be obtained for inclusions
1119 containing as little as 0.005 ng Pb with the current procedure and using Faraday detectors for
1120 data recording.

1121 In a first application (Pettke et al., 2010), brine inclusions from successive Cu±Au and Mo
1122 ore-forming stages of the late Eocene giant porphyry-type Cu-Mo-Au deposit of Bingham
1123 Canyon, Utah, were analyzed to investigate the common inference that Mo, unlike Cu and Au,
1124 originates from lower crustal sources, a model largely based on research performed on
1125 Climax-type Mo deposits. The Bingham porphyry deposit is exceptionally well suited for such
1126 an investigation because molybdenite precipitated in late veins cutting the Cu-Au stockwork
1127 veining and associated dike emplacement; hence, the two ore stages are texturally well
1128 separated.

1129 The constant Cu±Au and Mo ore-forming fluid Pb isotope signature (**Fig. 13**)
1130 demonstrates a common source for these ore metals, however. The Pb isotopic signatures
1131 are conspicuously non-radiogenic, with averages for individual fluid inclusion assemblages
1132 restricted to $17.494 < ^{206}\text{Pb}/^{204}\text{Pb} < 17.534$, $15.553 < ^{207}\text{Pb}/^{204}\text{Pb} < 15.588$, $38.204 <$
1133 $^{208}\text{Pb}/^{204}\text{Pb} < 38.311$, $0.88805 < ^{207}\text{Pb}/^{206}\text{Pb} < 0.88955$, and $2.1803 < ^{208}\text{Pb}/^{206}\text{Pb} < 2.1853$.
1134 Such a non-radiogenic Pb isotopic composition plotting to the left of the Geochron is rare for
1135 Phanerozoic rocks and has never been reported for Cenozoic, classical subduction-related
1136 calc-alkaline magmas, with or without associated porphyry-type ore deposits.

1137 A U-Th-Pb evolution model (Fig. 14), in which the parental magma is derived by melting a
1138 subcontinental lithospheric mantle that had been metasomatized by subduction fluids about
1139 1.8 billion years ago, reproduces the Pb isotope signatures measured in the ore fluids, while
1140 satisfying independent geochemical and geodynamic boundary conditions. Importantly, such
1141 a model provides an alternative view to the commonly-held assumption of a lower crustal Mo
1142 source, and it accounts for the apparent richness in incompatible elements and for the
1143 alkaline affinity of the ore-forming magmatic-hydrothermal system at Bingham. Consequently,
1144 this source of ancient, metasomatized mantle may be key to this globally most prominent Mo
1145 ore province located in the Rocky Mountains.

1146

1147 **Strontium isotope ratio analysis of individual fluid inclusions**

1148 This section summarizes the results of our pilot investigation on the feasibility and
1149 systematics of Sr isotope ratio analysis of individual fluid inclusions. In contrast to lead
1150 isotope ratio analysis described above, correction for instrumental mass bias of Sr does not a
1151 priori require external bracketing by a reference standard or admixture of an element of
1152 neighbouring mass possessing an invariant isotope ratio. The existence of invariant isotope
1153 ratios such as $^{88}\text{Sr}/^{86}\text{Sr}$ allows for internal mass bias correction, which enhances the precision
1154 and accuracy of the results. This advantage is however partially offset by the presence of
1155 isobaric interferences at essentially all Sr masses. In a recent review of Sr isotope ratio
1156 measurement by LA-ICP-MS, Vroon et al. (2008) have summarized published work that
1157 stresses the importance of proper correction for such interferences. Among the interfering ion
1158 species listed, Rb, Kr, Ca argides and/or Ca dimers can play a major role for ratio bias,
1159 because Ar used as a plasma gas typically contains non-negligible, variable amounts of Kr,
1160 and Rb and Ca are present in a wide range of geologic materials, including fluid inclusions.
1161 Doubly charged ions of Dy, Er, Yb, Lu or oxides of Zn and Ga may also be important.

1162 In addition to these problems, analysis of Sr in fluid inclusions has to cope with very
1163 limited sample amounts resulting in fast transient ion signals biased by amplifier response, as
1164 is the case for the Pb measurements described above. In this feasibility study, we have
1165 produced and analyzed synthetic fluid inclusions in quartz, prepared from various mixtures of
1166 NIST SRM 987 Sr and variable amounts of ultrapure RbCl in NaCl solution matrices.
1167 Inclusions were trapped in quartz at 700 °C and 1 kbar using a conventional hydrothermal
1168 cold seal apparatus. Several synthetic inclusion standards were produced at these conditions,
1169 with Sr concentrations ranging from ~3000-7000 ppm and Rb concentrations ranging from
1170 ~100-900 ppm ($^{87}\text{Sr}/^{87}\text{Rb}$ ranging from ~1 to 14). CaCl_2 was added in one experiment (Ca/Na
1171 = 2.2 and Ca/Sr = 11) to simulate the compositions of natural brine inclusions. Isotope
1172 geochemical applications require an accurate measurement of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which then,
1173 in the case of older samples, needs to be combined with an accurate determination of the
1174 Rb/Sr ratio in order to determine initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios or formation age information (via
1175 isochron dating). The following presentation of our current methods will be confined to the

1176 measurement of sample $^{87}\text{Sr}/^{86}\text{Sr}$. Discussion of approaches to accurately correct for in-situ
1177 produced ^{87}Sr is presented elsewhere (Hanley et al., in preparation).

1178 Laser ablation is carried out as described for Pb analysis above. Simultaneous Faraday
1179 readings at masses 88, 87, 86, 85, 84 and 83 are continuously recorded at 0.2 s integration
1180 intervals in time-resolved mode, covering first a baseline section measured on-mass for ca.
1181 60 s with laser-beam off, which yields combined information on gas and electronic
1182 backgrounds. Then the laser beam is switched on, generating an aerosol from host quartz,
1183 which modifies the gas background (e.g., lowering Kr beam intensities) and initially may also
1184 contain contaminants from the sample surface. When the fluid inclusion becomes exposed a
1185 transient signal generated from its contents is superimposed on the host quartz signals, the
1186 readings being recorded until the inclusion becomes completely exhausted.

1187 Based on this record, data reduction is then carried out off-line according to the following
1188 steps:

1189 (i) Corrections for incongruent amplifier response to signal variation are applied to the
1190 sequence of individual reading channels using procedures detailed in Pettke et al. (2011;
1191 “quadratic tau correction”). This minimizes ratio trends correlating with steep signal intensity
1192 gradients (Fig. 15).

1193 (ii) The tau-corrected data are corrected for background by subtraction of the mean signal
1194 intensities determined for the data section recorded with laser off. This correction removes
1195 electronic offsets and steady-state blank contributions, in particular the bulk of Kr interference
1196 at masses 83, 84 and 86. Such an on-peak background correction has the advantage of not
1197 requiring assumptions regarding the mass fractionations state of the ionic species involved.

1198 (iii) The Kr ion intensities are suppressed in the presence of laser ablation aerosol, resulting in
1199 negative baseline-corrected ^{83}Kr values for the fluid inclusion signal. These are then used for
1200 compensation of this effect on all masses interfered by Kr and for cancelling random
1201 fluctuations of Kr beam intensities during ablation (e.g. Waight et al., 2002; Burla et al., 2009).

1202 This is done by the peak-stripping technique, for which Kr isotopic composition is
1203 approximated by that of air and instrumental mass bias by that simultaneously determined for
1204 Sr. If Ca is also present at higher concentrations, such as in carbonates or certain brine
1205 inclusions, the ratio triplet 88/86, 84/86 and 83/86 can be used for simultaneous correction of
1206 interference by Ca argides (or Ca dimers) and Kr, and determination of the mass fractionation
1207 coefficient for Sr (see Burla et al., 2009, supporting online information). This technique
1208 expands earlier approaches by Woodhead et al. (2005) and Jackson and Hart (2006). We
1209 note that for our fluid inclusion measurements the $(^{46}\text{Ca}^{40}\text{Ar})^+$ contribution to mass 86 was of
1210 the order of a few ppm only and thus not significant. In contrast, interference of $(^{43}\text{Ca}^{40}\text{Ar})^+$ on
1211 ^{83}Kr is important and, if neglected, would result in strongly biased Kr interference corrections.

1212 (iv) After elimination of isobaric interferences by Kr and Ca compounds, Rb contribution at
1213 mass 87 is removed by the peak stripping technique, based on the net ^{85}Rb intensity and
1214 mass bias determined for Sr.

1215 **Figure 15** shows results obtained from a reading-by-reading evaluation of the
1216 measurements based on the above scheme, both for a synthetic fluid inclusion (**Fig. 15A,B**)
1217 and for a natural brine inclusion originating from the Sudbury Igneous Complex (Hanley et al.,
1218 2005a, and in preparation; **Fig. 15C,D**). The synthetic fluid inclusion (**Fig. 15A,B**) is
1219 characterized by a relatively high measured bulk $^{85}\text{Rb}/^{86}\text{Sr}$ ratio of 1.98, which requires a
1220 substantial interference correction of 107% on average for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio relative to the
1221 corrected value (0.710245 for SRM 987). We note that the baseline- and Kr-corrected ^{86}Sr
1222 and ^{85}Rb beam intensities show two maxima during ablation at roughly similar locations, but
1223 show considerable variation in proportion across the ablation sequence. The initial rise of
1224 ^{85}Rb is faster than that of ^{86}Sr , and the proportions of the two beams at their maxima are
1225 disparate (comparable to the behaviour of Tl and Pb reported in Pettke et al., 2011),
1226 suggesting that Rb and Sr are not equally distributed across the inclusion, with Rb
1227 predominantly residing in the fluid and Sr partially forming solid phases (e.g. SrCl_2), as
1228 confirmed by SEM. In view of the large corrections required by Rb interference it is of interest
1229 to examine whether such variation in Rb/Sr could potentially lead to bias in the interference-
1230 corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Such bias, however, is not evident from the tau-corrected data
1231 displayed **Fig. 15B**, at least not at the limited precision of the LA data. The inhomogeneous
1232 signal structure of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for tau-uncorrected data (**Fig. 15A**), in contrast, does not
1233 allow to evaluate whether bias is introduced by the ^{87}Rb correction.

1234 In the case of natural fluid inclusions from old geological environments such as from the
1235 1.85 Ga old Sudbury Igneous Complex (**Fig. 15CD**), Sr in fluids and precipitates may not be in
1236 isotopic equilibrium due to contrasting radiogenic increments by radioactive decay of ^{87}Rb in
1237 phases characterized by distinct Rb/Sr ratios (unless the inclusions were completely
1238 homogenized using microthermometry prior to LA analysis, which is not the case for the
1239 inclusions addressed here). Whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ data in **Fig. 15C** show pronounced
1240 variation correlating with signal structure, the flat distribution of the ratios after tau correction
1241 (**Fig. 15D**) suggests Sr isotopic equilibrium among the ablated phases, at least to the degree
1242 of current analytical resolution. Whether such apparent Sr isotopic equilibrium is a primary
1243 feature of this particular inclusion (as possibly supported by the approximately proportional
1244 trends of both ^{86}Sr and ^{85}Rb) or whether polyphase fluid inclusion contents have recently
1245 equilibrated internally remains open.

1246 Further information on the accuracy of Sr isotope ratio determination in fluid inclusions
1247 can be gained from a set of 51 on synthetic fluid inclusion analyses displayed in **Fig. 16**. In
1248 order to enhance the precision of the mean values obtained for individual inclusions, data
1249 reduction steps (i) to (iv) as outlined above were applied to baseline-corrected ion beam
1250 currents integrated over selected signal sections rather than to individual readings (bulk signal
1251 integration; cf. Pettke et al., 2011). As this procedure just produces a single data set per
1252 individual inclusion, expected analytical uncertainties (shown as 2 s error bars in **Fig. 16**)
1253 were calculated by Monte Carlo techniques, assigning normally distributed random errors to
1254 all input readings based on counting and baseline stability statistics. As all phases contained

1255 in a *synthetic* fluid inclusion can safely be assumed to be in Sr isotopic equilibrium, the
1256 uncertainty of $^{87}\text{Sr}/^{86}\text{Sr}$ can be minimized by selection of an optimal interval from the ablation
1257 sequence, e.g. by a simple numerical search algorithm, avoiding the low precision tails of the
1258 measurements. For Sr, an optimized data section will be characterized by elevated Sr beam
1259 intensities and, in the case of samples with elevated Rb contents and non-proportional
1260 behaviour of Rb and Sr during ablation, by lower than average Rb/Sr ratios. Applied to the
1261 fluid inclusion data shown in Fig. 15A,B for example, the algorithm has thus given more
1262 weight to the second signal maximum as indicated by the lower cut-off value of ^{86}Sr on its
1263 down-going slope as compared to that of the rising slope of the first maximum.

1264 From the positive correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ with $^{85}\text{Rb}/^{86}\text{Sr}$ in Fig. 16 it is evident that final
1265 calculated $^{87}\text{Sr}/^{86}\text{Sr}$ results are not fully invariant with respect to Rb/Sr. This conclusion is
1266 supported by an error weighted least squares linear fit, which results in a slope of $0.00088 \pm$
1267 0.00036 , significantly different from zero slope. The best fit line intersects the ordinate at
1268 0.71028 ± 0.00019 , identical to the nominal value of SRM 987 (0.710245). Furthermore, the
1269 MSWD value of 0.91 indicates good agreement between statistical expectation (based on our
1270 Monte Carlo approach) and observed variance of the data. The correlation between $^{87}\text{Sr}/^{86}\text{Sr}$
1271 and $^{85}\text{Rb}/^{86}\text{Sr}$ could be eliminated, if an adjusted $^{85}\text{Rb}/^{87}\text{Rb}$ value of 2.58676 rather than the
1272 canonical value of 2.59265 for SRM 984 Rb (Catanzaro et al., 1969) were used for
1273 interference correction on mass 87. The adjusted value is very close to the value of 2.5875
1274 determined by Jackson and Hart (2006) for their laser ablation experiments on melt
1275 inclusions. Such a lower $^{85}\text{Rb}/^{87}\text{Rb}$ value could either indicate that the isotopic composition of
1276 SRM 984 Rb is actually heavier than the canonical value, or that there is a minor systematic
1277 difference between the exponential mass bias coefficients (β values) for Sr and Rb. The
1278 former explanation is rather unlikely, as Nebel et al. (2005) did not find any significant
1279 deviations from the SRM 984 standard value in their study of potential isotopic fractionation of
1280 Rb in natural materials. If the deviations result from distinct β values, then $\beta_{\text{Rb}} = \beta_{\text{Sr}} + 0.098$
1281 holds on average for our data set. Such an offset in mass bias between the two elements is
1282 relatively small compared to average β_{Sr} values of ca. -1.85 determined for our sample set,
1283 but has serious implications for the accuracy of interference-corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in
1284 samples with high Rb/Sr, and, in the case of geologically older samples, for correction of in-
1285 situ accumulated radiogenic ^{87}Sr .

1286 Our results document that individual fluid inclusions can be analyzed accurately for
1287 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios for Rb-poor fluids (i.e., for Rb/Sr ratios smaller than about 0.13). Laser
1288 ablation ICP-MS data of individual fluid inclusion are less precise than those of other phases
1289 such as carbonates, largely resulting from fast transient signal recording of relatively low
1290 signal intensities as well as from uncertainty contribution by interference corrections. In the
1291 case of low Rb/Sr calcic brine inclusions, however, this method may become a powerful tool
1292 for tracing ancient fluid flow and source(s) given the analytical precision provides for sufficient
1293 resolution between possible sources (e.g., Hanley et al., in preparation).

1294 PROSPECTS

1295 We currently identify five major areas where significant progress in the LA-ICP-MS
1296 analysis of fluid inclusions could be achieved. They are (i) improving the data recording
1297 efficiency (i.e., duty cycle) of ICP-MS instruments, (ii) improved ion production and
1298 transmission in the ICP-MS, (iii) a better control on the processes of inclusion ablation and
1299 aerosol production, (iv) improvements in data quantification and, finally, (v) a better
1300 characterization of standard reference materials for concentrations of elements (e.g., Te, Br,
1301 Cl, Ga) that are often important in fluid inclusion research but not commonly used in LA-ICP-
1302 MS.

1303 (i) As with any single collector instrument, only one analyte is recorded at any point in
1304 time; hence, all other analytes pass unrecorded. Multiple collector ICP-MS instruments allow
1305 for simultaneous recording of analytes, although only in a rather limited mass (or precisely
1306 m/z) range. It would be ideal to record all analytes of interest simultaneously, e.g. from Li to U
1307 for fluid inclusion analysis. While optical emission spectrometers record all light emissions
1308 simultaneously, their sensitivity and thus detection power is inadequate for fluid inclusion
1309 trace element analysis (cf. Pettke et al., 2000b). Time-of-flight mass spectrometry allows for
1310 quasi-simultaneous recording of all analytes but also suffers from inappropriate detection
1311 limits (e.g., Bleiner et al., 2000) and abundance sensitivity problems (Tanner & Günther,
1312 2009). Most recently, a new sector field ICP-MS has been launched (in late 2010; Spectro
1313 Analytical Instruments, GmbH) that simultaneously records the mass spectra for all elements
1314 from lithium to uranium in 4800 channels. This would dramatically improve on representative
1315 recording of fast transient signals and on analyte duty cycles and, thus, can become
1316 extremely interesting. It remains to be seen whether this instrument will achieve or surpass
1317 the performance of other state-of-the art instruments.

1318 (ii) Improvements in ion production and notably transmission have remained a long-held
1319 desire amongst analytical chemists, notably because still far more than 99 % of analyte is lost
1320 during measurement. To our knowledge, there is no anticipated breakthrough in the near
1321 future, however. Alternatively, for MC-ICP-MS, the use of multiple ion counters can
1322 significantly reduce the amount of analyte required for isotope analysis, but accuracy has
1323 been shown to be somewhat limited (to ca. ± 0.1 % uncertainty) due to multiplier gain stability
1324 and linearity issues (Paul et al., 2005). This is about an order of magnitude higher than the
1325 analytical precision obtained for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios on SRM 610 glass (Pettke
1326 et al., 2011); hence, ion counting, would be of advantage for the analysis of very low-Pb
1327 samples and ratios involving ^{204}Pb only.

1328 (iii) Femtosecond-laser ablation (fs-LA) has been the hope for breakthrough in laser-
1329 ablation based analytical techniques for several years. While advantages over nanosecond
1330 (ns) laser systems have been documented for isotope ratio analysis using MC-ICP-MS (e.g.,
1331 Horn et al., 2007), the results remain inconclusive with regard to fast transient signal analysis
1332 using single collector ICP-MS (e.g., Koch et al., 2007). To our knowledge, a rigorous

1333 evaluation for fluid inclusion analysis is still due. While fs laser ablation likely minimizes heat
1334 dissipation into the sample and thus heating of the inclusion prior to opening, other
1335 phenomena cast doubt on whether such a laser source will provide a better controlled
1336 inclusion ablation process. Problems may arise from cracking of the material at the crater
1337 bottom (for monazite: Seydoux-Guillaume et al., 2010), probably associated with the process
1338 of phase explosion, which potentially represents a disadvantage for ablation control. More
1339 importantly, Glaus et al. (2010) report that fs-LA-generated aerosols consist of a bimodal
1340 mixture of agglomerated nanoparticles and larger, spherical particles, irrespective of matrix
1341 and wavelength used for ablation. These different particle types may be chemically distinct;
1342 hence, their total decomposition and ionization in the ICP would be essential to obtaining a
1343 non-biased compositional result. For such a large range in particle sizes (a few nanometer to
1344 several hundred nm diameter) current ICPs may not achieve complete ionization at a given
1345 ion extraction depth in the plasma. Therefore, the possibility of ICP-induced element
1346 fractionation cannot be excluded to date; hence, non-matrix-matched calibration strategies as
1347 required for fluid inclusions may thus be severely compromised for fs-LA-ICP-MS.

1348 Nevertheless, Volk et al. (2010) claim that fs laser pulses can be used to liberate
1349 unaltered oil from individual inclusions hosted in quartz, emphasizing that pyrolysis artefacts
1350 were not observed. The considerable amount of material deposited in and around the ablation
1351 crater shown in their Figure 2c might indicate, however, that there might be disadvantages
1352 with respect to metal solute analyses on aqueous fluid inclusions. Borisova et al. (2008)
1353 report analytical results by fs laser ablation for melt inclusions fully enclosed in host to a
1354 precision of 0.0X µg/g, without having performed a host mineral correction on the mixed
1355 inclusion plus host analysis. This makes it hard to conclude whether the use of fs laser
1356 ablation may indeed be beneficial compared to ns laser ablation for melt inclusion analysis.

1357 (iv) Fluid inclusion data quantification requires the accurate knowledge of one element
1358 abundance in the inclusion to be used as the internal standard, as determined by an
1359 independent method. Particle-induced X-ray emission (PIXE) has repeatedly been used to
1360 quantify element concentrations in fluid inclusions. This is a very laborious approach, and
1361 assumptions on the shape and dimensions of a given inclusion (to obtain its mass of liquid at
1362 the temperature of analysis) and on depth below sample surface lead to considerable
1363 analytical uncertainty that, in an ideal case, was claimed to be no better than ±10 % (probably
1364 1 σ ; Kurosawa et al., 2003). The determination of the Na concentration in a given fluid
1365 inclusion by combined microthermometry and salt correction based on the actual LA-ICP-MS
1366 analysis (Heinrich et al., 2003) is accurate for fluid compositions that closely correspond to
1367 pure (Na-K-Ca-Cl) solution; hence, the mean and analytical uncertainty determined on an
1368 assemblage average is representative. For chemically more complex aqueous and aqueo-
1369 carbonic fluid inclusions, a more accurate multi-component description of the liquidus surface
1370 of ice and the final dissolution of clathrate, hydrohalite and halite would be highly desirable,
1371 but equations of state for fluids with >3 components are not available to date. Instead, Allan et
1372 al. (2005) proposed that a charge balance data reduction approach may be superior to the

1373 use of Na as the internal standard; this, however, requires accurate determination of Cl in the
1374 fluid inclusion, which is a difficult task. Similarly, the quantification of high-P silicate rich fluid
1375 compositions is also difficult because of the inability to determine one element concentration
1376 in the inclusion by a non-destructive method as required for internal standardization. One way
1377 is to estimate an element concentration within the inclusion based on experimentally
1378 determined element distribution coefficients between fluid and host mineral; however, the
1379 uncertainty remains whether the experimental conditions are truly representative for the
1380 sample material investigated. Novel approaches for the determination of the internal standard
1381 required for deriving absolute element concentration data from LA-ICP-MS analysis of
1382 individual inclusions are needed to improve data accuracy for chemically complex fluid
1383 inclusions.

1384 (v) The accuracy of element concentration data for the external calibration materials
1385 may limit the accuracy of fluid inclusion analysis, notably for poorly characterized elements
1386 such as Te, Ga, Ge, Re, Au, W when using SRM 610 and 612 glass from NIST. For other
1387 elements like Cl, S, Br, the SRM glasses are not suitable, because calibration signals are not
1388 much different from background levels. Alternative, well-determined calibration materials are
1389 therefore required (e.g., homogeneous sulphide standards for sulphide-hosted inclusions),
1390 and it would thus be desirable that such materials become generally available.

1391

1392 **ACKNOWLEDGMENTS**

1393 TP thanks Henry Longerich, who cautioned about the possibility that the sequence of data
1394 report in the Elan ICP-MS instruments may not correspond to the sequence of data
1395 acquisition during measurement. MG thanks Martin Tanner for discussing LOD calculation.
1396 We thank Chris Heinrich for great input and discussion throughout the past years. We
1397 acknowledge the initiative of Murray Allan to program a fluid inclusion data reduction scheme
1398 (in Matlab) that has become the SILLS package. We thank Brian Rusk and Sebastien Meffre
1399 for their reviews that helped to clarify aspects in the manuscript. Continued funding by the
1400 Swiss National Science Foundation (current project PP00P2-124370 to TP) is greatly
1401 acknowledged. ACS thanks the US NSF (grant EAR 0609550) and the UNLV High Pressure
1402 Science and Engineering Center (HiPSEC) via the U.S. Department of Energy Cooperative
1403 Agreement Nos. DE-FC08-01NV14049 and DE-FC8806NA2768.
1404

1405 References

- 1406 Allan, M.M., Yardley, B.W.D., 2007. Tracking meteoric infiltration into a magmatic-hydrothermal system: A
1407 cathodoluminescence, oxygen isotope and trace element study of quartz from Mt. Leyshon, Australia. *Chemical*
1408 *Geology* 240, 343-360.
- 1409 Allan, M.M., Morrison, G.W., Yardley, B.W.D., 2011. Physicochemical Evolution of a Porphyry-Breccia System: A
1410 Laser Ablation ICP-MS Study of Fluid Inclusions in the Mount Leyshon Au Deposit, Queensland, Australia.
1411 *Economic Geology* 106, 413-436.
- 1412 Allan, M.M., Yardley, B.W.D., Forbes, L.J., Shmulovich, K.I., Banks, D.A., Shepherd, T.J., 2005. Validation of LA-ICP-
1413 MS fluid inclusion analysis with synthetic fluid inclusions. *American Mineralogist* 90, 1767-1775.
- 1414 Anderson, G.M., Burnham, C.W., 1965. The solubility of quartz in supercritical water. *American Journal of Science*
1415 263, 494-511.
- 1416 Appelblad, P.K., Rodushkin, I., Baxter, D.C., 2001. Sources of uncertainty in isotope ratio measurements by
1417 inductively coupled plasma mass spectrometry. *Analytical Chemistry* 73, 2911-2919.
- 1418 Audétat, A., Lowenstern, J.B., 2011. Melt inclusions, *Treatise on Geochemistry* 12 (in review).
- 1419 Audétat, A., 2010. Source and evolution of molybdenum in the porphyry Mo-(Nb) deposit at Cave Peak, Texas.
1420 *Journal of Petrology* 51, 1739-1760.
- 1421 Audétat, A., Günther, D., 1999. Mobility and H₂O loss from fluid inclusions in natural quartz crystals. *Contributions to*
1422 *Mineralogy and Petrology* 137, 1-14.
- 1423 Audétat, A., Pettke, T., 2003. The magmatic-hydrothermal evolution of two barren granites: a melt and fluid inclusion
1424 study of the Rito del Medio and Canada Pinabete plutons in northern New Mexico (USA). *Geochimica et*
1425 *Cosmochimica Acta* 67, 97-121.
- 1426 Audétat, A., Günther, D., Heinrich, C.A., 1998. Formation of a magmatic-hydrothermal ore deposit: insights with LA-
1427 ICP-MS analysis of fluid inclusions. *Science* 279, 2091-2094.
- 1428 Audétat, A., Günther, D., Heinrich, C.A., 2000a. Magmatic-hydrothermal evolution in a fractionating granite: a
1429 microchemical study of the Sn-W-F-mineralized Mole Granite (Australia). *Geochimica et Cosmochimica Acta* 64,
1430 3373-3393.
- 1431 Audétat, A., Günther, D., Heinrich, C.A., 2000b. Causes for large-scale metal zonation around mineralized plutons:
1432 Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Economic Geology* 95, 1563-1581.
- 1433 Audétat, A., Pettke, T., Heinrich, C.A., Bodnar, R.J., 2008. The composition of magmatic-hydrothermal fluids in
1434 barren versus mineralized intrusions. *Economic Geology* 103, 877-908.
- 1435 Baker, J., Peate, D., Waight, T., Meyzen, C., 2004. Pb isotopic analysis of standards and samples using a Pb-207-
1436 Pb-204 double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chemical*
1437 *Geology* 211, 275-303.
- 1438 Baker, T., Van Achtenberg, E., Ryan, C., Lang, J.R., 2004. Composition and evolution of ore fluids in a magmatic-
1439 hydrothermal skarn deposit. *Geology* 32, 117-120.
- 1440 Bakker, R.J., Jansen, J.B.H., 1991. Experimental post-entrapment water loss from synthetic CO₂-H₂O inclusions in
1441 natural quartz. *Geochimica et Cosmochimica Acta* 55, 2215-2230.
- 1442 Bali, E., Audétat, A., Keppler, H., 2011. The mobility of U and Th in subduction zone fluids: an indicator of oxygen
1443 fugacity and fluid salinity. *Contributions to Mineralogy and Petrology* 161, 597-613.
- 1444 Banks, D.A., Davies, G.R., Yardley, B.W.D., McCaig, A.M., Grant, N.T., 1991. The chemistry of brines from an Alpine
1445 thrust system in the central Pyrenees: an application of fluid inclusion analysis to the study of fluid behaviour in
1446 orogenesis. *Geochimica et Cosmochimica Acta* 55, 1021-1030.
- 1447 Bennett, J.N., Grant, J.N., 1980. Analysis of fluid inclusions using a pulsed laser micro-probe. *Mineralogical*
1448 *Magazine* 43, 945-947.
- 1449 Berry, A.J., Harris, A.C., Kamenetsky, V.S., Newville, M., Sutton, S.R., 2009. The speciation of copper in natural fluid
1450 inclusions at temperatures up to 700 degrees C. *Chemical Geology* 259, 2-7.
- 1451 Berry, A.J., Hack, A.C., Mavrogenes, J.A., Newville, M., Sutton, S.R., 2006. A XANES study of Cu speciation in high-
1452 temperature brines using synthetic fluid inclusions. *American Mineralogist* 91, 1773-1782.
- 1453 Bertelli, M., Baker, T., Cleverley, J.S., Ulrich, T., 2009. Geochemical modelling of a Zn-Pb skarn: Constraints from
1454 LA-ICP-MS analysis of fluid inclusions. *Journal of Geochemical Exploration* 102, 13-26.
- 1455 Beuchat, S., Moritz, R., Pettke, T., 2004. Fluid evolution in the W-Cu-Zn-Pb San Cristobal vein, Peru: fluid inclusion
1456 and stable isotope evidence. *Chemical Geology* 210, 201-224.
- 1457 Bleiner, D., Hametner, K., Günther, D., 2000. Optimization of a laser ablation-inductively coupled plasma "time of
1458 flight" mass spectrometry system for short transient signal acquisition. *Fresenius Journal of Analytical Chemistry*
1459 368, 37-44.
- 1460 Bodnar, R.J., 2003. Re-equilibration of fluid inclusions. In: *Fluid inclusions: Analysis and interpretation* (Samson, I.M.,
1461 Anderson, A., Marshall, D., eds.). *Mineralogical Association of Canada Short Course Series Volume* 32, 213-
1462 231.

- 1463 Bodnar, R.J., Sterner, S.M., 1985. Synthetic fluid inclusions in natural quartz. II. Application to PVT studies.
1464 *Geochimica et Cosmochimica Acta* 49, 1855-1859.
- 1465 Bodnar, R.J., Sterner, S.M., 1987. Synthetic fluid inclusions. In: *Hydrothermal Experimental Techniques*, (Ulmer,
1466 G.C., Barnes, H.L., eds.). John Wiley & Sons, New York, 423-457.
- 1467 Bodnar, R.J., Burnham, C.W., Sterner, S.M., 1985. Synthetic fluid inclusions in natural quartz. III. Determination of
1468 phase equilibrium properties in the system H₂O-NaCl to 1000C and 1500 bars. *Geochimica et Cosmochimica*
1469 *Acta* 49, 1861-1873.
- 1470 Borisova, A.Y., Freyrier, R., Polve, M., Salvi, S., Candaudap, F., Aigouy, T., 2008. In situ multi-element analysis of
1471 the Mount Pinatubo quartz-hosted melt inclusions by NIR femtosecond laser ablation-inductively coupled
1472 plasma-mass spectrometry. *Geostandards and Geoanalytical Research* 32, 209-229.
- 1473 Bottrell, S.H., Yardley, B., Buckley, F., 1988. A modified crush-leach method for the analysis of fluid inclusion
1474 electrolytes. *Bulletin de Minéralogie* 111, 279-290.
- 1475 Bourcier, W.L., Barnes, H.L., 1987. Rocking autoclaves for hydrothermal experiments I. The flexible reaction-cell
1476 system. In: *Hydrothermal experimental techniques* (Ulmer, G. C., Barnes, H. L. eds.). Hydrothermal
1477 experimental techniques. John Wiley & Sons.
- 1478 Bouse, R.M., Ruiz, J., Titley, S.R., Tosdal, R.M., Wooden, J.L., 1999. Lead isotope compositions of Late Cretaceous
1479 and early Tertiary igneous rocks and sulfide minerals in Arizona: Implications for the sources of plutons and
1480 metals in porphyry copper deposits. *Economic Geology* 94, 211-244.
- 1481 Burla, S., Oberli, F., Heimhofer, U., Wiechert, U., Weissert, H., 2009. Improved time control on Cretaceous coastal
1482 deposits: new results from Sr isotope measurements using laser ablation. *Terra Nova* 21, 401-409.
- 1483 Candela, P.A., Holland H.D., 1984. The partitioning of copper and molybdenum between silicate melts and aqueous
1484 fluids. *Geochimica et Cosmochimica Acta* 48, 373-380.
- 1485 Catchpole, H., Kouzmanov, K., Fontbote, L., Guillong, M., Heinrich, C.A., 2011. Fluid evolution in zoned Cordilleran
1486 polymetallic veins - Insights from microthermometry and LA-ICP-MS of fluid inclusions. *Chemical Geology* 281,
1487 293-304.
- 1488 Catanzaro, E.J., Murphy T.J., Garner, E.L., Shields, W.R., 1969. Absolute isotopic abundance ratio and atomic
1489 weight of terrestrial rubidium. *Journal of Research of the National Bureau of Standards, Sect. A*, 73A, 511-516.
- 1490 Ciobanu C.L., Cook N.J., Damian F., Damian G., 2006. Gold scavenged by bismuth melts: an example from Alpine
1491 shear-remobilizates in the Highis massif, Romania. *Mineralogy and Petrology* 87, 351-384.
- 1492 Chou, I.C., Eugster, H.P., 1977. Solubility of magnetite in supercritical chloride solutions. *American Journal of*
1493 *Science* 277, 1296-1314.
- 1494 Currie, L.A., 1968. Limits for qualitative detection and quantitative determination. *Analytical Chemistry* 40, 586-593.
- 1495 Currie, L.A., 1995. Nomenclature in evaluation of analytical methods including detection and quantification
1496 capabilities (IUPAC Recommendations 1995). *Pure & Applied Analytical Chemistry* 67, 1699-1723.
- 1497 Czamanske, G.K., Roedder, E., Burns, F.C., 1963. Neutron activation analysis of fluid inclusions for copper,
1498 manganese, and zinc. *Science* 140(356), 401-403.
- 1499 Danyushevsky, L.V., McNeill, A.W., Sobolev, A.V., 2002. Experimental and petrological studies of melt inclusions in
1500 phenocrysts from mantle-derived magmas: an overview of techniques, advantages and complications. *Chemical*
1501 *Geology* 183, 5-24.
- 1502 Diamond, L.W., 1990. Fluid inclusion evidence for P-V-T-X evolution of hydrothermal solutions in late-Alpine gold-
1503 quartz veins at Brusson, northwest Italian Alps. *American Journal of Science* 290, 912-958.
- 1504 Diamond, L.W., 1992. Stability of CO₂ clathrate hydrate+CO₂ liquid+CO₂ vapour+aqueous KCl-NaCl solutions -
1505 experimental determination and application to salinity estimates of fluid inclusions. *Geochimica et*
1506 *Cosmochimica Acta* 56, 273-280.
- 1507 Diamond, L.W., Jackman, J.A., Charoy, B., 1991. Cation ratios of fluid inclusions in a gold-quartz vein at Brusson, Val
1508 d'Ayas, northwestern Italian Alps: comparison of bulk crush-leach results with SIMS analyses of individual
1509 inclusions. *Chemical Geology* 90, 71-78.
- 1510 Doe, B.R., Tilling, R.I., Hedge, C.E., Klepper, M.R., 1968. Lead and strontium isotope studies of the Boulder
1511 Batholith, southwestern Montana. *Economic Geology* 63, 884-906.
- 1512 Douglas N., Mavrogenes J., Hack A., England R., 2000. The liquid bismuth collector model: an alternative gold
1513 deposition mechanism. 15th Australian Geological Convention, Geological Society of Australia, Abstract 135.
- 1514 Duc-Tin, Q., Audétat, A., Keppler, H., 2007. Solubility of tin in (Cl, F)-bearing aqueous fluids at 700 degrees C, 140
1515 MPa: a LA-ICP-MS study on synthetic fluid inclusions. *Geochimica et Cosmochimica Acta* 71(13), 3323-3335.
- 1516 Eggins, S.M., Kinsley, L.P.J., Shelley, J.M.G., 1998. Deposition and element fractionation processes during
1517 atmospheric pressure laser sampling for analysis by ICP-MS. *Applied Surface Science* 129, 278-286.
- 1518 Evans, R.D., Hintelmann, H., Dillon, P.J., 2001. Measurement of high precision isotope ratios for mercury from coals
1519 using transient signals. *Journal of Analytical Atomic Spectrometry* 16, 1064-1069.

- 1520 Fabre, C., Boiron, M.C., Dubessy, J., Chabiron, A., Charoy, B., Crespo, T.M., 2002. Advances in lithium analysis in
1521 solids by means of laser- induced breakdown spectroscopy: An exploratory study. *Geochimica et Cosmochimica*
1522 *Acta* 66, 1401-1407.
- 1523 Ferrando, S., Frezzotti, M.L., Petrelli, M., Compagnoni, R., 2009. Metasomatism of continental crust during
1524 subduction: the UHP whiteschists from the Southern Dora-Maira Massif (Italian Western Alps). *Journal of*
1525 *Metamorphic Geology* 27, 739-756.
- 1526 Frank, M.R., Candela, P.A., Piccoli, P.M., Glascock, M.D., 2002. Gold solubility, speciation, and partitioning as a
1527 function of HCl in the brine-silicate melt-metallic gold system at 800 °C and 100 MPa. *Geochimica et*
1528 *Cosmochimica Acta* 66, 3719-3732.
- 1529 Frank, M.R., Simon, A., Pettke, T., Candela, P.A., Piccoli, P.M., 2011. Gold and copper partitioning between vapour
1530 and liquid at 800 °C and 100 MPa. *Geochimica et Cosmochimica Acta* 75, 2470-2482.
- 1531 Fryer, B.J., Jackson, S.E., Longerich, H.P., 1995. Design, operation and role of the laser-ablation microprobe coupled
1532 with an inductively-coupled plasma - mass-spectrometer (LAM-ICP-MS) in the earth sciences. *Canadian*
1533 *Mineralogist* 33, 303-312.
- 1534 Gagnon, J., Samson, I., Fryer, B., 2003. LA-ICP-MS analysis of fluid inclusions. In: *Fluid inclusions: Analysis and*
1535 *interpretation* (Samson, I.M., Anderson, A., Marshall, D., eds.). Mineralogical Association of Canada Short
1536 *Course Series Volume* 32, 291-318.
- 1537 Glaus, R., Kaegi, R., Krumeich, F., Günther, D., 2010. Phenomenological studies on structure and elemental
1538 composition of nanosecond and femtosecond laser-generated aerosols with implications on laser ablation
1539 inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B-Atomic Spectroscopy* 65, 812-822.
- 1540 Goldstein R.H., Reynolds T.J., 1994. Systematics of fluid inclusions in diagenetic minerals. *Society for Sedimentary*
1541 *Geology Short Course* 31, 199p.
- 1542 Green T.H., 1981. Experimental evidence for the role of accessory phases in magma genesis. *Journal of Volcanology*
1543 *and Geothermal Research* 10, 405-422.
- 1544 Guillong, M., Günther, D., 2002. Effect of particle size distribution on ICP-induced elemental fractionation in laser
1545 ablation-inductively coupled plasma-mass spectrometry. *Journal of Analytical Atomic Spectrometry* 17, 831-837.
- 1546 Guillong, M., Heinrich, C.A., 2007a. Sensitivity enhancement in laser ablation ICP-MS using small amounts of
1547 hydrogen in the carrier gas. *Journal of Analytical Atomic Spectrometry* 22, 1488-1494.
- 1548 Guillong, M., Heinrich, C.A., 2007b. La-ICP-MS analysis of inclusions: improved ablation and detection. 19th Biennial
1549 Conference "European Current Research on Fluid Inclusions, ECROFI-XIX", Bern, 82.
- 1550 Guillong, M., Latkoczy, C., Seo, J.H., Günther, D., Heinrich, C.A., 2008a. Determination of sulfur in fluid inclusions by
1551 laser ablation ICP-MS. *Journal of Analytical Atomic Spectrometry* 23, 1581-1589.
- 1552 Guillong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., Yardley, B.W.D., 2008b. SILLS: A MATLAB-based program for
1553 the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. In: *Laser ablation ICP-*
1554 *MS in the Earth Sciences: Current practices and outstanding issues* (Sylvester, P., ed.). Mineralogical
1555 *Association of Canada Short Course Series Volume* 40, 328-333.
- 1556 Guillong, M., Pettke, T., Danyushevsky, L., 2011. Fluid inclusion analysis by Laser ablation ICPMS: How consistent
1557 are element ratios? Abstract. Goldschmidt 2011 Conference, Prague, August 14-19.
- 1558 Günther, D., 2001. Quantitative fluid inclusion analysis using a 193 nm Excimer laser-ablation system coupled to ICP-
1559 MS. In: *Laser ablation ICP-MS in the Earth Sciences* (Sylvester, P., ed.). Mineralogical Association of Canada
1560 *Short Course Series Volume* 29, 47-62.
- 1561 Günther, D., Hattendorf, B., 2005. Solid sample analysis using laser ablation inductively coupled plasma mass
1562 spectrometry. *TRAC - Trends in Analytical Chemistry* 24, 255-265.
- 1563 Günther, D., Heinrich, C.A., 1999. Enhanced sensitivity in laser ablation-ICP mass spectrometry using helium-argon
1564 mixtures as aerosol carrier - Plenary Lecture. *Journal of Analytical Atomic Spectrometry* 14, 1363-1368.
- 1565 Günther, D., Audétat, A., Frischknecht, R., Heinrich, C.A., 1998. Quantitative analysis of major, minor and trace
1566 elements in fluid inclusions using laser ablation inductively coupled plasma mass spectrometry. *Journal of*
1567 *Analytical Atomic Spectrometry* 13, 263-270.
- 1568 Günther, D., Frischknecht, R., Heinrich, C.A., Kahlert, H.J., 1997. Capabilities of an argon fluoride 193 nm Excimer
1569 laser for laser ablation inductively coupled plasma mass spectrometry microanalysis of geological materials.
1570 *Journal of Analytical Atomic Spectrometry* 12, 939-944.
- 1571 Hack, A.C., Mavrogenes, J.A., 2006. A synthetic fluid inclusion study of copper solubility in hydrothermal brines from
1572 525 to 725 °C and 0.3 to 1.7 GPa. *Geochimica et Cosmochimica Acta* 70, 3970-3985.
- 1573 Halter, W., Pettke, T., Heinrich, C.A., 2002a. The origin of Cu/Au ratios in porphyry type ore deposits. *Science* 296,
1574 1844-1846.
- 1575 Halter, W.E., Pettke, T., Heinrich, C.A., Rothen-Rutishauser, B., 2002b. Major to trace element analysis of melt
1576 inclusions by laser-ablation ICP-MS: methods of quantification. *Chemical Geology* 183, 63-86.
- 1577 Hanley, J.J., Mungall, J.E., Pettke, T., Spooner, E.T.C., Bray, C.J., 2005a. Ore metal redistribution by hydrocarbon-
1578 brine and hydrocarbon-halide melt phases, North Range footwall of the Sudbury Igneous Complex, Ontario,
1579 Canada. *Mineralium Deposita* 40, 237-256.

- 1580 Hanley, J.J., Pettke, T., Mungall, J.E., Spooner, E.T.C., 2005b. Investigations of the behavior and distribution of
1581 platinum and gold in silicate melt – brine mixtures at 1.5 kbar, 600 to 800°C using synthetic fluid inclusions
1582 methods: a laser ablation ICPMS pilot study. *Geochimica et Cosmochimica Acta* 69, 2593-2611.
- 1583 Hanley, J.J., Mungall, J.E., Pettke, T., Spooner, E.T.C., Bray, C.J., 2008. Fluid and halide melt inclusions of
1584 magmatic origin in the ultramafic and lower banded series, Stillwater Complex, Montana, USA. *Journal of*
1585 *Petrology* 49, 1133-1160.
- 1586 Heijlen, W., Banks, D.A., Muchez, P., Stensgard, B.M., Yardley, B.W.D., 2008. The nature of mineralizing fluids of the
1587 Kipushi Zn-Cu deposit, Katanga, Democratic Republic of Congo: quantitative fluid inclusion analysis using laser
1588 ablation ICP-MS and bulk crush-leach methods. *Economic Geology* 103, 1459-1482.
- 1589 Heinrich C.A., Günther D., Audétat A., Ulrich T., Frischknecht R., 1999. Metal fractionation between magmatic brine
1590 and vapor, determined by microanalysis of fluid inclusions. *Geology* 27, 755-758.
- 1591 Heinrich, C.A., Pettke, T., Halter, W.E., Aigner-Torres, M., Audétat, A., Günther, D., Hattendorf, B., Bleiner, D.,
1592 Guillon, M., Horn, I., 2003. Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-
1593 ablation inductively-coupled-plasma mass- spectrometry. *Geochimica et Cosmochimica Acta* 67, 3473-3497.
- 1594 Heinrich, C.A., Ryan, C.G., Mernagh, T.P., Eadington, P.J., 1992. Segregation of ore metals between magmatic brine
1595 and vapor - a fluid inclusion study using PIXE microanalysis. *Economic Geology* 87, 1566-1583.
- 1596 Hemley, J.J., Cygan, G.L., Fein, J.B., Robinson, G.R., d'Angelo, W.M., 1992. Hydrothermal ore-forming processes in
1597 the light of studies in rock-buffered systems: I. Iron-copper-zinc-lead sulfide solubility relations. *Economic*
1598 *Geology*, 87, 1-22.
- 1599 Hirata, T., Hayano, Y., Ohno, T., 2003. Improvements in precision of isotopic ratio measurements using laser
1600 ablation-multiple collector-ICP-mass spectrometry: reduction of changes in measured isotopic ratios. *Journal of*
1601 *Analytical Atomic Spectrometry* 18, 1283-1288.
- 1602 Horn, I., von Blanckenburg, F., 2007. Investigation on elemental and isotopic fractionation during 196 nm
1603 femtosecond laser ablation multiple collector inductively coupled plasma mass spectrometry. *Spectrochimica*
1604 *Acta Part B-Atomic Spectroscopy* 62, 410-422.
- 1605 Jackson, M.G., Hart, S.R., 2006. Strontium isotopes in melt inclusions from Samoan basalts: Implications for
1606 heterogeneity in the Samoan plume. *Earth and Planetary Science Letters* 245, 260-277.
- 1607 Jochum, K. P., and 11 others. Determination of reference values for NIST SRM 610-617 glasses following ISO
1608 guidelines. *Geostrand. Geoanal. Res.*, doi: 10.1111/j.1751-908X.2011.00120.x
- 1609 Johnson, C.M., Lipman, P.W., Czamanske, G.K., 1990. H, O, Sr, Nd, and Pb isotope geochemistry of the Latir
1610 Volcanic Field and cogenetic intrusions, New-Mexico, and relations between evolution of a continental magmatic
1611 center and modifications of the lithosphere. *Contributions to Mineralogy and Petrology* 104, 99-124.
- 1612 Kamenetsky, V.S., Wolfe, R.C., Eggins, S.M., Mernagh, T.P., Bastrakov, E., 1999. Volatile exsolution at the Dinkidi
1613 Cu-Au porphyry deposit, Philippines: A melt-inclusion record of the initial ore-forming process. *Geology* 27, 691-
1614 694.
- 1615 Kamenetsky V.S., Danyushevsky L.V., 2005. Metals in quartz-hosted melt inclusions: natural facts and experimental
1616 artifacts. *American Mineralogist* 90, 1674-1678.
- 1617 Klemm, L., Pettke, T., Graeser, S., Mullis, J., Kouzmanov, K., 2004. Fluid mixing as the cause of sulphide
1618 precipitation at Albrunpass, Binn Valley, Central Alps. *Schweizerische Mineralogische und Petrographische*
1619 *Mitteilungen* 84, 189-212.
- 1620 Klemm, L.M., Pettke, T., Heinrich, C.A., Campos, E., 2007. Hydrothermal evolution of the El Teniente deposit, Chile:
1621 porphyry Cu-Mo ore deposition from low-salinity magmatic fluids. *Economic Geology* 102, 1021-1045.
- 1622 Klemm, L.M., Pettke, T., Heinrich, C.A., 2008. Fluid and source magma evolution of the Questa porphyry Mo deposit,
1623 New Mexico, USA. *Mineralium Deposita* 43, 533-552.
- 1624 Koch, J., Günther, D., 2007. Femtosecond laser ablation inductively coupled plasma mass spectrometry:
1625 achievements and remaining problems. *Analytical and Bioanalytical Chemistry* 387, 149-153.
- 1626 Kostova, B., Pettke, T., Driesner, T., Petrov, P., Heinrich, C.A., 2004. LA ICP-MS study of fluid inclusions in quartz
1627 from the Yuzhna Petrovitsa deposit, Madan ore field, Bulgaria. *Schweizerische Mineralogische und*
1628 *Petrographische Mitteilungen* 84, 25-36.
- 1629 Kouzmanov, K., Pettke, T., Heinrich, C.A., 2010. Direct analysis of ore-precipitating fluids: combined IR microscopy
1630 and LA-ICP-MS study of fluid inclusions in opaque ore minerals. *Economic Geology* 105, 351-373.
- 1631 Kramers, J.D., Tolstikhin, I.N., 1997. Two terrestrial lead isotope paradoxes, forward transport modelling, core
1632 formation and the history of the continental crust. *Chemical Geology* 139, 75-110.
- 1633 Kurosawa, M., Shimano, S., Ishii, S., Shima, K., Nakajima, T., Kato, T., 2003. Quantitative PIXE analysis of single
1634 fluid inclusions in quartz vein: Chemical composition of hydrothermal fluids related to granite. *Nuclear*
1635 *Instruments, Methods in Physics Research Section B- Beam Interactions with Materials and Atoms* 210, 464-
1636 467.
- 1637 Lambrecht, G., Diamond, L.W., Pettke, T., 2008. Modification of gas speciation in quartz-hosted fluid inclusions by
1638 stray laser radiation during LA-ICPMS analysis. *American Mineralogist* 93, 1187-1190.

- 1639 Landtwing, M.R., Furrer, C., Redmond, P.B., Pettke, T., Guillong, M., Heinrich, C.A., 2010. The Bingham Canyon
1640 porphyry Cu-Mo-Au deposit. III. Zoned copper-gold ore deposition by magmatic vapor expansion. *Economic*
1641 *Geology* 105, 91-118.
- 1642 Landtwing, M.R., Pettke, T., Halter, W.E., Heinrich, C.A., Redmond, P.B., Einaudi, M.T., Kunze, K., 2005. Copper
1643 deposition during quartz dissolution by cooling magmatic-hydrothermal fluids: the Bingham Porphyry. *Earth and*
1644 *Planetary Science Letters* 235, 229-243.
- 1645 Leach A.M., Hieftje G.M., 2000. Methods for shot-to-shot normalization in laser ablation with an inductively coupled
1646 plasma time-of-flight mass spectrometer. *Journal of Analytical Atomic Spectrometry* 15, 1121-1124.
- 1647 Lerchbaumer, L., Audétat, A., 2009. Partitioning of Cu between vapor and brine – An experimental study based on
1648 LA-ICP-MS analysis of synthetic fluid inclusions. 19th Annual VM Goldschmidt Conference, Davos, Switzerland,
1649 A744.
- 1650 Li, Y., Audétat, A., 2009. A method to synthesize large fluid inclusions in quartz at controlled times and under
1651 favorable growth conditions. *American Mineralogist* 94, 367-371.
- 1652 Li, Y., Audétat, A., Lerchbaumer, L., Xiong, X.L., 2009. Rapid Na, Cu exchange between synthetic fluid inclusions
1653 and external aqueous solutions: evidence from LA-ICP-MS analysis. *Geofluids* 9, 321-329.
- 1654 Longerich, H.P., Jackson, S.E., Günther, D., 1996. Laser ablation inductively coupled plasma mass spectrometric
1655 transient signal data acquisition and analyte concentration calculation. *Journal of Analytical Atomic*
1656 *Spectrometry* 11, 899-904.
- 1657 Loucks, R.R., Mavrogenes, J.A., 1999. Gold solubility in supercritical hydrothermal brines measured in synthetic fluid
1658 inclusions. *Science* 284, 2159-2163.
- 1659 Lüders, V., Reutel, C., Hoth, P., Banks, D.A., Mingram, B., Pettke, T., 2005. Fluid and gas migration in the North
1660 German Basin: fluid inclusion and stable isotope constraints. *International Journal of Earth Sciences* 94, 990-
1661 1009.
- 1662 Mank, A.J.G., Mason, P.R.D., 1999. A critical assessment of laser ablation ICP-MS as an analytical tool for depth
1663 analysis in silica-based glass samples. *Journal of Analytical Atomic Spectrometry* 14, 1143-1153.
- 1664 Manning, C.E., 1994. The solubility of quartz in H₂O in the lower crust and upper mantle. *Geochimica et*
1665 *Cosmochimica Acta* 58, 4831-4839.
- 1666 Manning, C.E., Boettcher, S.L., 1994 Rapid-quench hydrothermal experiments at mantle pressures and
1667 temperatures. *American Mineralogist* 79, 1153-1158.
- 1668 Marschall, H.R., Ludwig, T., 2004. The low-boron contest: minimising surface contamination and analysing boron
1669 concentrations at the ng/g-level by secondary ion mass spectrometry. *Mineralogy and Petrology* 81, 265-278.
- 1670 Mason, P.R.D., Nikogosian, I.K., vanBergen, M.J., 2008. Major and trace element analysis of melt inclusions by laser
1671 ablation ICP-MS. In: *Laser ablation ICP-MS in the Earth Sciences: Current practices and outstanding issues*
1672 (Sylvester, P., ed). Mineralogical Association of Canada Short Course Series Volume 40, 219-240.
- 1673 Mavrogenes, J.A., Bodnar, R.J., 1994. Hydrogen movement into and out of fluid inclusions in quartz: experimental
1674 evidence and geologic implications. *Geochimica et Cosmochimica Acta* 58, 141-148.
- 1675 Moissette, A., Shepherd, T.J., Chenery, S.R., 1996. Calibration strategies for the elemental analysis of individual
1676 aqueous fluid inclusions by laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical*
1677 *Atomic Spectrometry* 11, 177-185.
- 1678 Mutchler, S.R., Fedele, L., Bodnar, R.J., 2008. Analysis management system (AMS) for reduction of laser ablation
1679 ICP-MS data. In: *Laser ablation ICP-MS in the Earth Sciences: Current practices and outstanding issues*
1680 (Sylvester, P., ed). Mineralogical Association of Canada Short Course Series Volume 40, 328-333.
- 1681 Nagaseki, H., Hayashi, K-I., 2008. Experimental study of the behavior of copper and zinc in a boiling hydrothermal
1682 system. *Geology* 36, 27-30.
- 1683 Nambu M., Sato T., 1981. The analysis of fluid inclusions in the microgram range with an ion microanalyzer. *Bulletin*
1684 *de Minéralogie* 104, 827-833.
- 1685 Nathans, M.W., Leider, M.J. 1962. Studies on bismuth alloys. I. Liquidus curves of the bismuth-copper, bismuth-silver
1686 and bismuth-gold systems. *Physical Chemistry* 66, 2012-2015.
- 1687 Nebel, O., Mezger, K., Scherer, E.E., Münker, C. 2005. High precision determinations of ⁸⁷Rb/⁸⁵Rb in geologic
1688 materials by MC-ICP-MS. *International Journal of Mass Spectrometry* 246, 10–18
- 1689 Newton, R.C., Manning, C.E., 2000. Quartz solubility in concentrated aqueous NaCl solutions at deep crust-upper
1690 mantle metamorphic conditions: 2-15 kbar and 500-900 °C. *Geochimica et Cosmochimica Acta* 64, 2993-3005.
- 1691 Newton, R.C., Manning, C.E., 2002. Experimental determination of calcite solubility in H₂O-NaCl solutions at deep
1692 crust/upper mantle pressures and temperatures: implications for metasomatic processes in shear zones.
1693 *American Mineralogist* 87, 1401-1409.
- 1694 Oberthür T., Weiser T.W., 2008: Gold-bismuth-telluride-sulphide assemblages at the Viceroy mine, Harare-Bindura-
1695 Shamva greenstone belt, Zimbabwe. *Mineralogical Magazine* 72, 953-970.
- 1696 Paul, B., Woodhead, J.D., Hergt, J., 2005. Improved in situ isotope analysis of low-Pb materials using LA-MC-ICP-
1697 MS with parallel ion counter and Faraday detection. *Journal of Analytical Atomic Spectrometry* 20, 1350-1357.

- 1698 Pettke, T., 2006. In situ laser-ablation ICPMS analysis of melt inclusions and prospects for constraining subduction
1699 zone magmatism. In: Melt Inclusions in Plutonic Rocks (Webster, J. D., ed.). Mineralogical Association of
1700 Canada Short Course Series Volume 36, 51-80.
- 1701 Pettke, T., 2008. Analytical protocols for element concentration and isotope ratio measurements in fluid inclusions by
1702 LA-(MC)-ICP-MS. In: Laser ablation ICP-MS in the Earth Sciences: Current practices and outstanding issues
1703 (Sylvester, P., Ed). Mineralogical Association of Canada Short Course Series Volume 40, 189-218.
- 1704 Pettke, T., Diamond, L.W., 1995. Rb-Sr isotopic analysis of fluid inclusions in quartz: evaluation of bulk extraction
1705 procedures and geochronometer systematics using synthetic fluid inclusions. *Geochimica et Cosmochimica*
1706 *Acta* 59, 4009-4027.
- 1707 Pettke, T., Frei, R., 1996. Isotope systematics in vein gold from Brusson, Val d'Ayas (NW Italy), 1. Pb/Pb evidence for
1708 a Piemonte metaophiolite Au source. *Chemical Geology* 127, 111-124.
- 1709 Pettke, T., Diamond, L.W., Kramers, J.D., 2000a. Mesothermal gold lodes in the north-western Alps: a review of
1710 genetic constraints from radiogenic isotopes. *European Journal of Mineralogy* 12, 213-230.
- 1711 Pettke, T., Halter, W.E., Webster, J.D., Aigner-Torres, M., Heinrich, C.A., 2004. Accurate quantification of melt
1712 inclusion chemistry by LA-ICPMS: a comparison with EMP and SIMS and advantages and possible limitations of
1713 these methods. *Lithos* 78, 333-361.
- 1714 Pettke, T., Heinrich, C.A., Ciocan, A.C., Günther, D., 2000b. Quadrupole mass spectrometry and optical emission
1715 spectroscopy: detection capabilities and representative sampling of short transient signals from laser-ablation.
1716 *Journal of Analytical Atomic Spectrometry* 15, 1149-1155.
- 1717 Pettke, T., Oberli, F., Audétat, A., Wiechert, U., Heinrich, C.A., 2011. Quantification of transient signals in multiple
1718 collector inductively coupled plasma mass spectrometry: Accurate lead isotope ratio determination by laser
1719 ablation of individual fluid inclusions. *Journal of Analytical Atomic Spectrometry* 26, 475-492.
- 1720 Pettke, T., Oberli, F., Heinrich, C.A., 2010. The magma and metal source of giant porphyry-type ore deposits, based
1721 on lead isotope microanalysis of individual fluid inclusions. *Earth and Planetary Science Letters* 296, 267-277.
- 1722 Portnyagin, M., Almeev, R., Matveev, S., Holtz, F., 2008. Experimental evidence for rapid water exchange between
1723 melt inclusions in olivine and host magma. *Earth and Planetary Science Letters* 272, 541-552.
- 1724 Ramsey, M.H., Coles, B.J., Wilkinson, J.J., Rankin, A.H., 1992. Single fluid inclusion analysis by laser ablation
1725 inductively coupled plasma atomic emission spectrometry - quantification and validation. *Journal of Analytical*
1726 *Atomic Spectrometry* 7, 587-593.
- 1727 Rankin, A.H., Ramsey, M.H., Coles, B., Vanlangevelde, F., Thomas, C.R., 1992. the composition of hypersaline, iron-
1728 rich granitic fluids based on laser-ICP and synchrotron-XRF microprobe analysis of individual fluid inclusions in
1729 topaz, Mole Granite, eastern Australia. *Geochimica et Cosmochimica Acta* 56, 67-79.
- 1730 Redmond, P.B., Einaudi, M.T., Inan, E.E., Landtwing, M.R., Heinrich, C.A., 2004. Copper deposition by fluid cooling
1731 in intrusion-centered systems: New insights from the Bingham porphyry ore deposit, Utah. *Geology* 32, 217-220.
- 1732 Richard, A., Pettke, T., Cathelineau, M., Boiron, M.C., Mercadier, J., Cuney, M., Derome, D., 2010. Brine-rock
1733 interaction in the Athabasca basement (McArthur River U deposit, Canada): consequences for fluid chemistry
1734 and uranium uptake. *Terra Nova* 22, 303-308.
- 1735 Roedder, E., 1984. Fluid Inclusions. In: *Reviews In Mineralogy* (Ribbe, P.H., ed.) Mineralogical Society of America,
1736 Volume 12, 646p.
- 1737 Rusk, B., Reed, M., Dilles, J.H., 2008. Fluid inclusion evidence for magmatic-hydrothermal fluid evolution in the
1738 porphyry copper-molybdenum deposit, Butte, Montana. *Economic Geology* 103, 307-334.
- 1739 Rusk, B.G., Reed, M.H., Dilles, J.H., Klemm, L.M., Heinrich, C.A., 2004. Compositions of magmatic hydrothermal
1740 fluids determined by LA-ICP-MS of fluid inclusions from the porphyry copper-molybdenum deposit at Butte, Mt.
1741 *Chemical Geology* 210, 173-199.
- 1742 Rusk, B., Koenig, A., Lowers, H., 2011. Visualizing trace element distribution in quartz using cathodoluminescence,
1743 electron microprobe, and laser ablation-inductively coupled plasma-mass spectrometry. *American Mineralogist*
1744 96, 703-708.
- 1745 Scambelluri, M., Bottazzi, P., Trommsdorff, V., Vannucci, R., Hermann, J., Gomez-Pugnaire, M.T., Vizcaino, V.L.S.,
1746 2001a. Incompatible element-rich fluids released by antigorite breakdown in deeply subducted mantle. *Earth*
1747 *and Planetary Science Letters* 192, 457-470.
- 1748 Scambelluri, M., Muntener, O., Ottolini, L., Pettke, T., Vannucci, R., 2004a. The fate of B, Cl and Li in the subducted
1749 oceanic mantle and in the antigorite breakdown fluids. *Earth and Planetary Science Letters* 222, 217-234.
- 1750 Seo, J.H., Guillong, M., Heinrich, C.A., 2009. The role of sulphur in the formation of magmatic-hydrothermal copper-
1751 gold deposits. *Earth and Planetary Science Letters* 282, 323-328.
- 1752 Seo, J.H., Guillong, M., Aerts, M., Zajacz, Z., Heinrich, C.A., 2011. Microanalysis of S, Cl, and Br in fluid inclusions by
1753 LA-ICP-MS. *Chemical Geology* 284, 35-44.
- 1754 Seydoux-Guillaume, A.M., Freydier, R., Poitrasson, F., d'Abzac, F.X., Wirth, R., Datas, L., 2010. Dominance of
1755 mechanical over thermally induced damage during femtosecond laser ablation of monazite. *European Journal of*
1756 *Mineralogy* 22, 235-244.

- 1757 Seyfried, W.E. jr., Janecky, D.R., Berndt, M.E., 1987. Rocking autoclaves for hydrothermal experiments II. Fixed-
1758 volume systems. In: Hydrothermal experimental techniques (Ulmer, G.C., Barnes, H.L. eds.). Hydrothermal
1759 experimental techniques. John Wiley & Sons.
- 1760 Shepherd, T.J., Chenery, S.R., 1995. Laser-ablation ICP-MS elemental analysis of individual fluid inclusions - an
1761 evaluation study. *Geochimica et Cosmochimica Acta* 59, 3997-4007.
- 1762 Simon, A.C., Pettke, T., 2009. Platinum solubility and partitioning in a felsic melt – vapor – brine assemblage.
1763 *Geochimica et Cosmochimica Acta* 73, 438-454.
- 1764 Simon, A.C., Candela, P.A., Piccoli, P.M., Englander, L., 2008a. The effect of crystal – melt partitioning on the budgets
1765 of copper, gold, and silver. *American Mineralogist* 93, 1437-1448.
- 1766 Simon, A.C., Frank, M.R., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2005. Gold partitioning in melt-
1767 vapor-brine systems. *Geochimica et Cosmochimica Acta* 69, 3321-3335.
- 1768 Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2004. Magnetite solubility and iron transport in
1769 magmatic-hydrothermal environments. *Geochimica et Cosmochimica Acta* 68, 4905-4914.
- 1770 Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2006. Copper partitioning in sulphur bearing
1771 magmatic systems. *Geochimica et Cosmochimica Acta* 70, 5583-5600.
- 1772 Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2007. The partitioning behavior of As and Au in a
1773 haplogranite - vapor at magmatic conditions in sulphur-free and sulphur bearing systems. *Geochimica et*
1774 *Cosmochimica Acta* 71, 1764-1782.
- 1775 Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2008b. The partitioning behavior of silver in a
1776 vapor – brine – rhyolite melt assemblage. *Geochimica et Cosmochimica Acta* 72, 1638 -1659.
- 1777 Spandler, C., Mavrogenes, J., Hermann, J., 2007. Experimental constraints on element mobility from subducted
1778 sediments using high-P synthetic fluid/melt inclusions. *Chemical Geology* 239, 228-249.
- 1779 Stein, H.J., Hannah, J.L., 1985. Movement and origin of ore fluids in Climax-type systems. *Geology* 13, 469-474.
- 1780 Sterner, S.M. (1992). Synthetic fluid inclusions: Part XI. Notes on the application of synthetic fluid inclusions to high
1781 P-T experimental aqueous geochemistry. *American Mineralogist* 77, 156-167.
- 1782 Sterner, S.M., Bodnar, R.J., 1984. Synthetic fluid inclusions in natural quartz: I. Compositional types synthesized and
1783 applications to experimental geochemistry. *Geochimica et Cosmochimica Acta* 48, 2659-2668.
- 1784 Sterner, S.M., Bodnar, R.J., 1989. Synthetic fluid inclusions. 7. Re-equilibration of fluid inclusions in quartz during
1785 laboratory-simulated metamorphic burial and uplift. *Journal of Metamorphic Geology* 7, 243-260.
- 1786 Stoffell, B., Wilkinson, J.J., Jeffries, T.E., 2004. Metal transport and deposition in hydrothermal veins revealed by
1787 213nm UV laser ablation microanalysis of single fluid inclusions. *American Journal of Science* 304, 533-557.
- 1788 Stoffell, B., Appold, M.S., Wilkinson, J.J., McClean, N.A., Jeffries, T.E., 2008. Geochemistry and evolution of
1789 Mississippi Valley-Type mineralizing brines from the Tri-state and Northern Arkansas Districts determined by
1790 LA-ICP-MS microanalysis of fluid inclusions. *Economic Geology* 103, 1411-1435.
- 1791 Su, W.C., Heinrich, C.A., Pettke, T., Zhang, X.C., Hu, R.Z., Xia, B., 2009. Sediment-hosted gold deposits in Guizhou,
1792 China: products of wall-rock sulfidation by deep crustal fluids. *Economic Geology* 104, 73-93.
- 1793 Tanner, M., 2010. Shorter signals for improved signal to noise ratio, the influence of Poisson distribution. *Journal of*
1794 *Analytical Atomic Spectrometry* 25, 405-407.
- 1795 Tanner, M., Günther, D., 2009. Short transient signals, a challenge for inductively coupled plasma mass
1796 spectrometry, a review. *Analytica Chimica Acta* 633, 19-28
- 1797 Tooth, B., Brugger J., Ciobanu C., Liu W., 2008. Modeling of gold scavenging by bismuth melts coexisting with
1798 hydrothermal fluids. *Geology* 36, 815-818.
- 1799 Tsui, T.F., Holland, H.D., 1979. Analysis of fluid inclusions by laser microprobe. *Economic Geology* 74, 1647-1653.
- 1800 Ulrich, T., Günther, D., Heinrich, C.A., 1999. Gold concentrations of magmatic brines and the metal budget of
1801 porphyry copper deposits. *Nature* 399, 676-679.
- 1802 Ulrich, T., Günther, D., Heinrich, C.A., 2002. Evolution of a porphyry Cu-Au deposit, based on LA-ICP-MS analysis of
1803 fluid inclusions: Bajo de la Alumbrera, Argentina (Vol 96, Pg 1743, 2001). *Economic Geology* 97, 1888-1920.
- 1804 Ulrich, T., Mavrogenes, J., 2008. An experimental study of the solubility of molybdenum in H₂O and KCl-H₂O
1805 solutions from 500 degrees C to 800 degrees C, and 150 to 300 MPa. *Geochimica et Cosmochimica Acta* 72,
1806 2316-2330.
- 1807 Volk, H., Fuentes, D., Fuerbach, A., Miese, C., Koehler, W., Barsch, N., Barcikowski, S., 2010. First on-line analysis
1808 of petroleum from single inclusion using ultrafast laser ablation. *Organic Geochemistry* 41, 74-77.
- 1809 Vroon, P.Z., van der Wagt, B., Koornneef, J.M., Davies, G.R., 2008. Problems in obtaining precise and accurate Sr
1810 isotope analysis from geological materials using laser ablation MC-ICPMS. *Analytical and Bioanalytical*
1811 *Chemistry* 390, 465-476.
- 1812 Waight, T., Baker, J., Peate, D., 2002. Sr isotope ratio measurements by double-focusing MC-ICPMS: techniques,
1813 observations and pitfalls. *International Journal of Mass Spectrometry* 221, 229-244.

- 1814 Whitney, J.A., Hemley, J.J., Simon, F.O., 1985. The concentration of iron in chloride solutions equilibrated with
1815 synthetic granite compositions: the sulphur-free system. *Economic Geology* 80, 444-460.
- 1816 Wilkinson, J.J., Stoffell, B., Wilkinson, C.C., Jeffries, T.E., Appold, M.S., 2009. Anomalously metal-rich fluids form
1817 hydrothermal ore deposits. *Science* 323, 764-767.
- 1818 Williams, C.D., Ripley, E.M., Li, C.S., 2010. Variations in Os isotope ratios of pyrrhotite as a result of water-rock and
1819 magma-rock interaction: constraints from Virginia Formation-Duluth Complex contact zones. *Geochimica et*
1820 *Cosmochimica Acta* 74, 4772-4792.
- 1821 Wood, S.A., Crerar, D.A., Borcsik, M.P., 1987. Solubility of the assemblage pyrite-pyrrhotite-magnetite-sphalerite-
1822 galena-gold-stibnite-bismuthinite-argentite-molybdenite in H₂O-NaCl-CO₂ solutions from 200 to 350 °C.
1823 *Economic Geology* 82, 1864-1887.
- 1824 Woodhead, J., Swearer, S., Hergt, J., Maas, R., 2005. In situ Sr-isotope analysis of carbonates by LA-MC-ICP-MS:
1825 interference corrections, high spatial resolution and an example from otolith studies. *Journal of Analytical*
1826 *Atomic Spectrometry* 20, 22-27.
- 1827 Zacharias, J., Wilkinson, J.J., 2007) Exlam 2000: Excel VBA application for processing of transient signals from laser
1828 ablation (LA-ICP-MS) of fluid inclusions and solid phases. 19th Biennial Conference "European Current
1829 Research on Fluid Inclusions, ECROFI-XIX", Bern, 194
- 1830 Zajacz, Z., Halter, W.E., Pettke, T., Guillong, M., 2008. Determination of fluid/melt partition coefficients by LA-ICPMS
1831 analysis of co-existing fluid and silicate melt inclusions: controls on element partitioning. *Geochimica et*
1832 *Cosmochimica Acta* 72, 2169-2197.
- 1833 Zajacz, Z., Hanley, J.J., Heinrich, C.A., Halter, W.E., Guillong, M., 2009. Diffusive reequilibration of quartz-hosted
1834 silicate melt and fluid inclusions: Are all metal concentrations unmodified? *Geochimica et Cosmochimica Acta*
1835 73, 3013-3027.
- 1836 Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., Heinrich, C.A., Guillong, M., 2010. Alkali metals control the release
1837 of gold from volatile-rich magmas. *Earth and Planetary Science Letters* 297, 50-56.
- 1838 Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., Tossell, J.A., 2011. The solubility of copper in high-temperature
1839 magmatic vapors: a quest for the significance of various chloride and sulfide complexes. *Geochimica et*
1840 *Cosmochimica Acta* 75, 2811-2827.
- 1841 Zartman, R.E., 1974. Lead isotopic provinces in Cordillera of western United-States and their geologic significance.
1842 *Economic Geology* 69, 792-805.

1843 Figure Captions

1844 Fig. 1 Examples of fluid inclusions. (A) illustrates a homogeneous fluid inclusion
1845 assemblage. The phase proportions of water, vapour and tiny halite crystal are
1846 uniform, indicating that the phase assemblage formed during closed-system cooling
1847 of a fluid of constant composition. (B) shows a close-up of an individual fluid
1848 inclusion with tiny daughter crystals (note also the needle in the vapour bubble) that
1849 may contain the bulk mass of certain trace elements. (C) shows a heterogeneous
1850 fluid assemblage documenting stable coexistence of a high-density, saline aqueous
1851 liquid with a low-density, low-salinity aqueous vapour. Phase proportions are
1852 variable, representing variable liquid plus vapour mixtures; only the highest and
1853 lowest salinity inclusions are representative for the compositions of the respective
1854 one-phase end members. The boiling assemblage represents an experimental run
1855 product (Frank et al., 2011).

1856 Fig. 2 Sketch illustrating the general principle and fast transient signal obtained from the
1857 LA-ICP-MS analysis of an individual inclusion (part of signal displayed in Fig. 4).
1858 Three signal intervals are mandatory for proper inclusion quantification, the signal
1859 backgrounds with laser off (interval 1), the inclusion interval and an interval of pure
1860 host mineral. The latter is taken either before the inclusion or, to minimize downhole
1861 fractionation effects and inhomogeneities in host composition, as the mean from an
1862 interval before and one after the inclusion (i.e., intervals 2 and 4). The inclusion
1863 signal (interval 3) actually represents a mixture of inclusion plus host mineral in a
1864 priori unknown proportions; hence, a host mineral correction is mandatory for
1865 obtaining accurate data, except for host minerals that do not contain any of the
1866 solutes as for example for diamond-hosted silicate inclusions.

1867 Fig. 3 Data of Table 1 plotted as (A) element concentrations (labelled to the right of the
1868 graph) and (B) element abundance ratios ($M/(Na+K+Fe)$), where M represents the
1869 metal as labelled to the right of the graph). In (A) the major cations Na, K and Fe
1870 are uniform across the 4 successively entrapped assemblages; hence, they can be
1871 used for normalization of metal abundances as shown in (B). Copper documents a
1872 ca. 95% decrease in concentration across these 4 assemblages, and Au may have
1873 a lower concentration in assemblage 4 when compared to the uniform assemblages
1874 1, 2 and 3. Note that the pattern of the data points is identical in figures (A) and (B);
1875 the pattern of data points in figure (B) can thus be obtained without the use of an
1876 internal standard because the element abundance ratios are uniquely defined by
1877 use of external standardization only (see text for discussion). Also note that outliers
1878 in assemblages can be identified quickly in both absolute concentration and
1879 element abundance ratio data. The width of the bands for Cu represents 2 standard
1880 deviation uncertainties on assemblage average concentrations.

1881 Fig. 4 Plot A illustrates the ideal signal of a multiphase fluid inclusion of ca. 45 wt% NaCl
1882 equivalent bulk salinity. The “Gaussian-shape” signal intensities of the different
1883 solutes evolve non-parallel; therefore, signal quantification can only be done by
1884 bulk signal integration. The rise and notably the decay of the inclusion analyte
1885 signals are slower than those of Si (the latter illustrates the washout speed of the
1886 ablation chamber), thus imaging the controlled layer-by-layer ablation of the fluid
1887 inclusion content. The dwell time was 10 ms except for Au for which 100 ms were
1888 employed to lower the limit of detection. Signal intensities are processed in cps
1889 (counts per second) to account for such differences in dwell time between analytes.
1890 The stepwise increase of the ^{29}Si signal (grey line) monitors the stepwise increase
1891 of beam size (black numbers, in μm) prior to fluid inclusion opening. The fluid
1892 inclusion is then liberated by the straight ablation technique, i.e., drilling through the
1893 entire inclusion without change in laser beam size. Plot B illustrates a typical signal
1894 as obtained from uncontrolled rupturing of the fluid inclusion. In this case, the
1895 inclusion exploded upon the last beam size increase as could be observed on video
1896 screen. The signal shape also provides clues to whether the inclusion ablation was
1897 controlled or not. The transient signal peak is fast with notably rapid signal decay.
1898 Note the dashed line labelled Na’ that runs parallel to the signal decay of Si after
1899 laser beam off, demonstrating that the signal decay of Na (as all other analyte
1900 signals) is entirely controlled by the washout characteristics of the ablation chamber
1901 and not the result from controlled layer-by layer ablation of the fluid inclusion. This
1902 indicates an instantaneous release of inclusion material into the ablation cell. It
1903 therefore remains unconstrained how much of the fluid inclusion material (e.g.,
1904 crystals) was lost upon explosion. Therefore, data from uncontrolled fluid inclusion
1905 ablations are likely heavily compromised. Both analyses were acquired with H_2
1906 admixed to the aerosol carrier gas.

1907 Fig. 5 Transient signal characteristically obtained from the LA-ICP-MS analysis of a mixed
1908 aqueo-carbonic fluid inclusion containing $\text{H}_2\text{O}_{\text{liq}}$, $\text{CO}_{2,\text{liq}}$ and $\text{CO}_{2,\text{vap}}$ (blue, dark and
1909 light green in the inset, respectively). “Background”, “Host” and “Inclusion” refer to
1910 the respective signal intervals used for quantification. The signal resulted from the
1911 straight ablation method, using a 44 μm beam (black numbers next to Si signal).
1912 Invariably, such aqueo-carbonic fluid inclusions show an extremely fast transient
1913 signal “spike” upon inclusion opening (see enlargement of signal in Fig. B), followed
1914 by the controlled ablation of the remaining inclusion content producing a signal
1915 hump. This initial, rapid release of most of the inclusion content results from an
1916 internal overpressure in the inclusion at room temperature that may be further
1917 increased due to laser beam heating prior to inclusion opening. Note the signal
1918 increases notably in Na and Sr upon beam size increase, testifying to surface
1919 contamination (in this case deposits from previous fluid inclusion ablations nearby)
1920 because similar signals are not observed when reducing the beam size to 44 μm for

1921 inclusion ablation. The inset illustrates the ablation procedure employed here for
1922 deep-seated inclusions. After stepwise increase of the beam size, the 60 μm beam
1923 is used to ablate excessive quartz above the inclusion in order to minimize negative
1924 side effects encountered for craters with large depth to diameter ratios and to
1925 eliminate surface contamination (sometimes referred to as "pre-ablation"). The 44
1926 μm beam is then used for fluid inclusion ablation, thereby maximizing the mass
1927 proportion of inclusion in the mixed inclusion + host signal interval. The signal
1928 shown in Fig. 4a was produced in the same way. Analysis acquired without H_2
1929 admixed to the aerosol carrier gas. Sample is from the orogenic gold district of
1930 Brusson (Diamond, 1990; Pettke et al., 2000a). Modified from Pettke (2008).

1931 Fig. 6 Comparison of results for L_C and L_D (in counts per second) as a function of
1932 background count rate for equal background intervals of 50 replicates (sweeps)
1933 each. L_C was calculated for 99.9 % confidence (equation 3 in text), thus
1934 corresponding closely to the LOD formulation of Longerich et al. (1996; equation 2
1935 in text), and L_D was calculated using equation 6 in text at 95 % confidence. Dwell
1936 time was set to 0.01s and sensitivity was kept constant.

1937 Fig. 7 Plot of "LOD"s (in $\mu\text{g/g}$) as a function of the numbers of readings (sweeps) in the
1938 sample signal interval using equations 2 and 6 (see text), employing fixed
1939 parameters as given in the figure. Note that LOD values calculated following IUPAC
1940 recommendations (equation 6) are always higher (simply because $L_D \geq 2 * L_C$),
1941 more so for short transient signals (i.e., for <100 signal readings in the sample
1942 interval).

1943 Fig. 8 Plot of LODs for Au calculated using equation 2 (at 99.9 % confidence level) and
1944 equation 6 (at 95 % confidence level) for natural fluid inclusion analyses (Tables 2
1945 and 3) as a function of the duration of the fluid inclusion signal ($N(\text{an})$). Note that
1946 equation 6 returns variably higher LOD values as documented for constant
1947 parameters in Fig. 7.

1948 Fig. 9 (A) Transient fluid inclusion signal with a constant background interval and variably
1949 long signal intervals (5 to 25 s). Data were recorded at 0.276 s duration per sweep.
1950 (B) Ratio of "LOD"s calculated by equation 2 and equation 6 as a function of the
1951 signal durations from 5 to 25 s as illustrated in Fig. A. Note that different confidence
1952 levels (equation 2, 99.9 %; equation 6, 95 %) are compared. See text for
1953 discussion.

1954 Fig. 10 LA-ICP-MS signal of a bismuth inclusion drilled out of topaz (sample *Bism3.3*;
1955 analysis 99Mz12d10). Trace element signals are inhomogeneously distributed,
1956 illustrating the presence of minor phases exsolved from the bismuth melt after
1957 entrapment. The Cu signal has been slightly shifted to the right to render it visible
1958 behind the Au signal. Their perfect overlap indicates the presence of a Cu-Au alloy

- 1959 in the Bi-inclusion at room temperature that formed upon cooling of a homogeneous
 1960 Bi melt. The signal was integrated from ~42 to ~55 seconds to obtain the bulk
 1961 composition. Gold was recorded with 30 ms dwell time, all other analytes with 10
 1962 ms.
- 1963 Fig. 11 Transient Pb isotope signal from ablation of a 20 * 20 * 15 µm synthetic Na-K-Cl
 1964 inclusion of 17 wt% bulk salinity and ca. 5700 µg g⁻¹ Pb concentration. After
 1965 recording the instrumental background, a desolvated aerosol containing SRM 997
 1966 TI required for mass bias correction is admixed to the ablation chamber gas at 85 s.
 1967 Once the TI signal is stable, laser ablation of quartz host started at 150 s, as
 1968 indicated by low, scattered Pb isotope signals originating from surface deposits of
 1969 previous inclusion ablations. The inclusion is opened at 175 s, and ablation is
 1970 terminated at 225 s. Note the steady, low background signal of Hg, allowing for
 1971 accurate quantification of ²⁰⁴Pb, too. Modified from Pettke et al. (2011).
- 1972 Fig. 12 External reproducibility plots for ²⁰⁸Pb/²⁰⁶Pb (A) and ²⁰⁷Pb/²⁰⁴Pb (B) ratios for 20
 1973 individual fluid inclusion (20-25 µm diameter) analyses. Grey data points were
 1974 discarded from the averaged data set, due to uncontrolled fluid inclusion ablation,
 1975 which may generate precise measurements of unconstrained accuracy. Thick
 1976 yellow lines represent nominal values for SRM 981 (Baker et al., 2004). The same
 1977 data set was reduced in three different ways, set (i) in blue by the individual reading
 1978 integration method (plus 2 SE measurement uncertainties), sets (ii) in green and
 1979 (iii) in red by the bulk signal integration method (with error estimates based on a
 1980 Gaussian combination of ion statistics and baseline noise). Sets (i) and (ii) use data
 1981 not corrected for amplifier response, while for (iii) they were corrected using the
 1982 stepping *tau* correction scheme (Pettke et al., 2011). Data obtained by the bulk
 1983 signal integration method (ii and iii) are significantly more accurate and scatter less
 1984 for isotope ratios normalized to ²⁰⁶Pb while this is not so obvious for isotope ratios
 1985 normalized to ²⁰⁴Pb, due to the low precision of the ²⁰⁴Pb measurements. Modified
 1986 from Pettke et al. (2011), were detailed explanations are available.
- 1987 Fig. 13 Comparison of fluid inclusion assemblage data obtained for the giant Bingham
 1988 Canyon porphyry Cu±Au-Mo deposit. A uniform Pb isotopic composition
 1989 characterizes the texturally distinct Cu-Au (red symbols) and Mo (blue symbols) ore
 1990 stages. Dashed lines separate inclusions from different samples (labels shown at
 1991 the top of the diagram), identical symbols identify inclusions from the same fluid
 1992 inclusion assemblage. Error bars are two standard error measurement uncertainties
 1993 (2 s.e.), some of them smaller than symbol size. This Pb isotopic uniformity strongly
 1994 suggests a common source for Cu, Au and Mo. Modified from Pettke et al. (2010).
- 1995 Fig. 14 Forward modelling of the uranogenic two-stage Pb isotope evolution (stage 1, solid
 1996 green line; stage 2, dashed green line) that reproduces the measured Pb isotope
 1997 signatures of Bingham ore fluids (red star at 38 Ma). μ values denote ²³⁸U/²⁰⁴Pb

1998 ratios. Ages are in million years (Ma) before present, the green stars marking the
 1999 beginning of stages 1 and 2, respectively. The dashed MORB source mantle
 2000 evolution line (Kramers and Tolstikhin, 1997) represents convecting, depleted
 2001 mantle, the dotted line depicts primitive mantle. Data for other Mo-enriched
 2002 porphyry deposits of the eastern Rocky Mountains, US (Area 1 of Zartman, 1974),
 2003 are shown for comparison (Butte: Doe et al., 1968; Henderson: Stein and Hannah,
 2004 1985; hornblende andesite associated with Questa: Johnson et al., 1990; SEAZ:
 2005 northern SE Arizona district Cu-Mo centres; Bouse et al., 1999). Modified from
 2006 Pettke et al. (2010).

2007 Fig. 15 Normalized, interference corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (black diamonds), ^{86}Sr (red
 2008 squares, corrected for Kr interference) and ^{85}Rb (blue circles) beam intensities
 2009 (right ordinate) recorded for transient LA signals from a synthetic fluid inclusion
 2010 made up of NaCl, SRM 987 Sr and Rb (A, B), and from a brine inclusion from the
 2011 Sudbury igneous complex (C, D). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios not corrected for amplifier
 2012 response (A, C) show substantial variation correlating with signal intensity
 2013 gradients, whereas tau-corrected ratios ("quadratic correction") are essentially
 2014 constant (B, D). The units on the abscissa refer to number of individual readings
 2015 integrated for 0.2 s. The dashed vertical lines delimit the signal sections which
 2016 would be selected for error optimization based on counting and baseline statistics
 2017 (see text for details).

2018 Fig. 16 Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{85}\text{Rb}/^{86}\text{Sr}$ measured on a series of 51 synthetic fluid
 2019 inclusions with variable Rb (SRM 984), Sr (SRM 987), Na and Ca contents. Both
 2020 ratios were internally corrected for isobaric interference by Kr and Rb and
 2021 normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for individual fluid inclusions
 2022 were calculated by data integration and optimization. The results show a significant
 2023 residual sloping trend (solid line; least squares parameters) as a function of Rb/Sr,
 2024 intersecting the ordinate at 0.71028 ± 0.00019 , identical to the nominal value of
 2025 0.710245 for SRM 987 (dashed horizontal line). The dependence on Rb/Sr
 2026 suggests that mass 87 was undercorrected for contributions of ^{87}Rb , which in turn
 2027 suggests that the assumption of identical fractionation coefficients for Rb and Sr
 2028 may not be valid (see text for details). All errors given at 95% c.l.

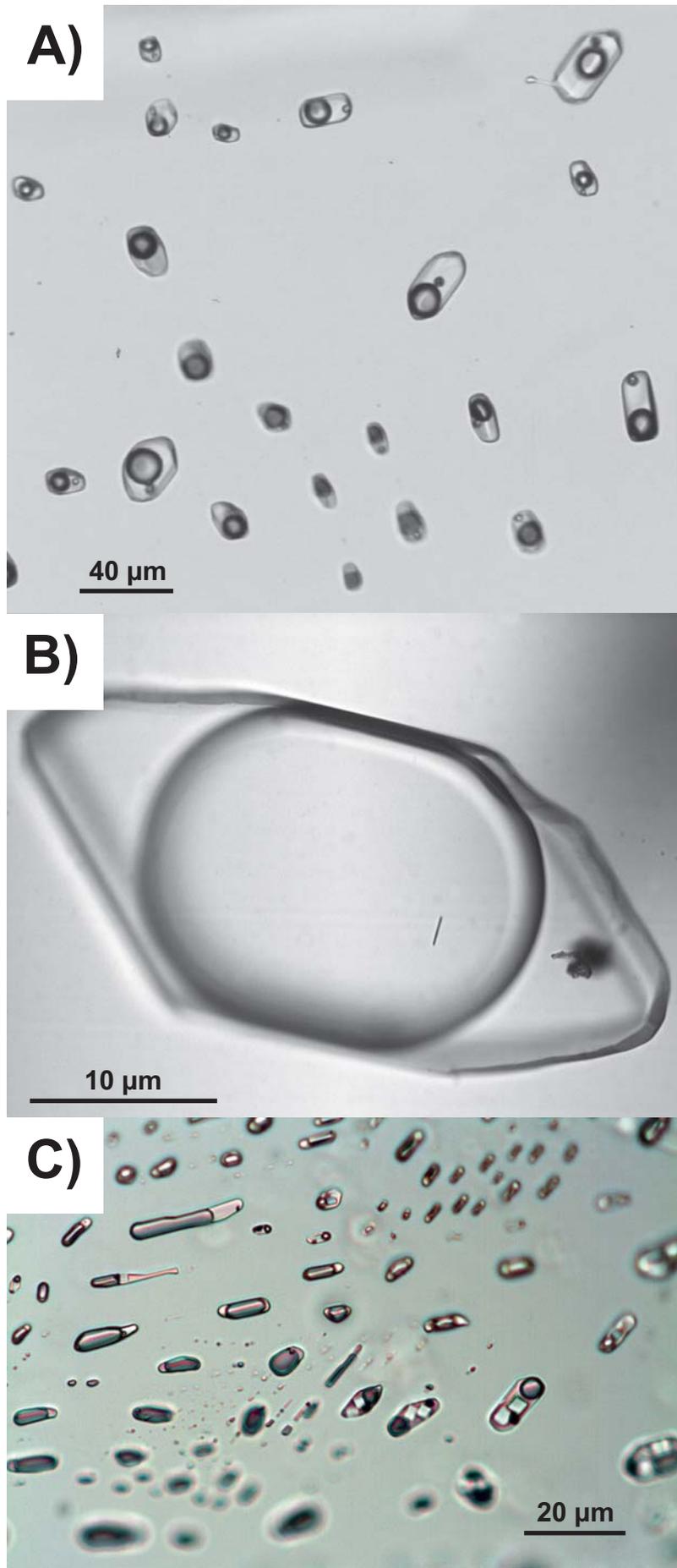


Figure 1

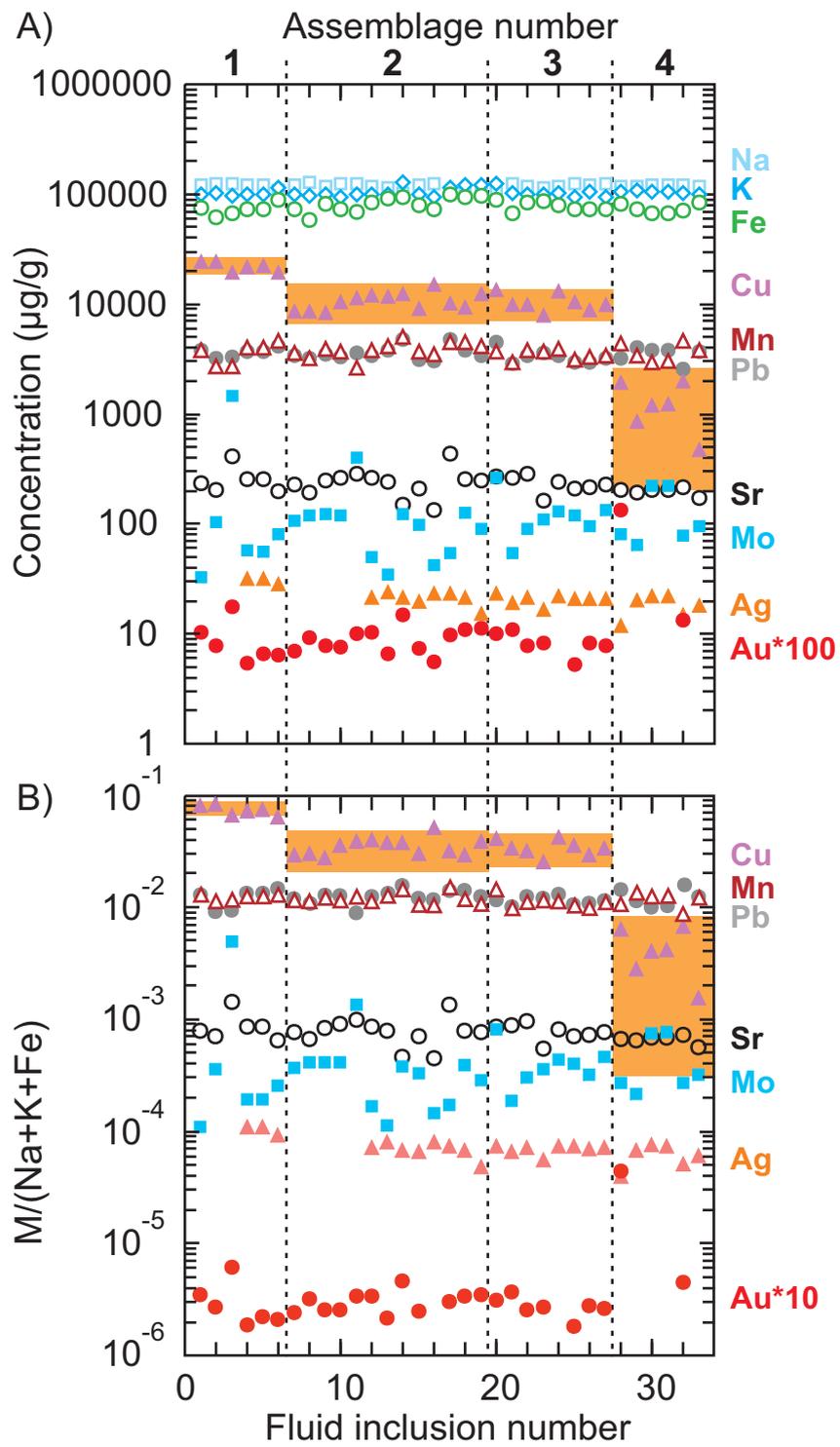


Figure 3

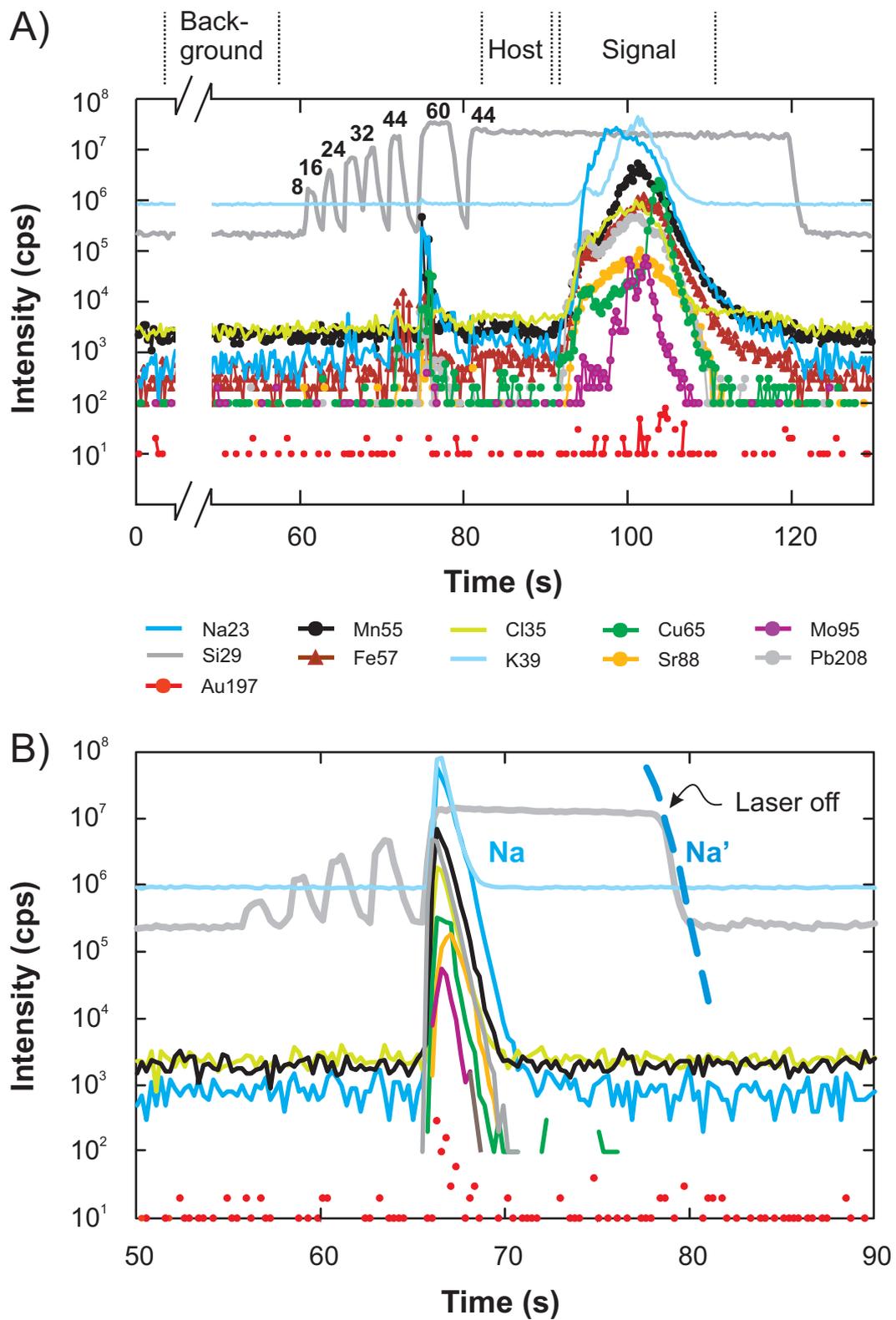


Figure 4

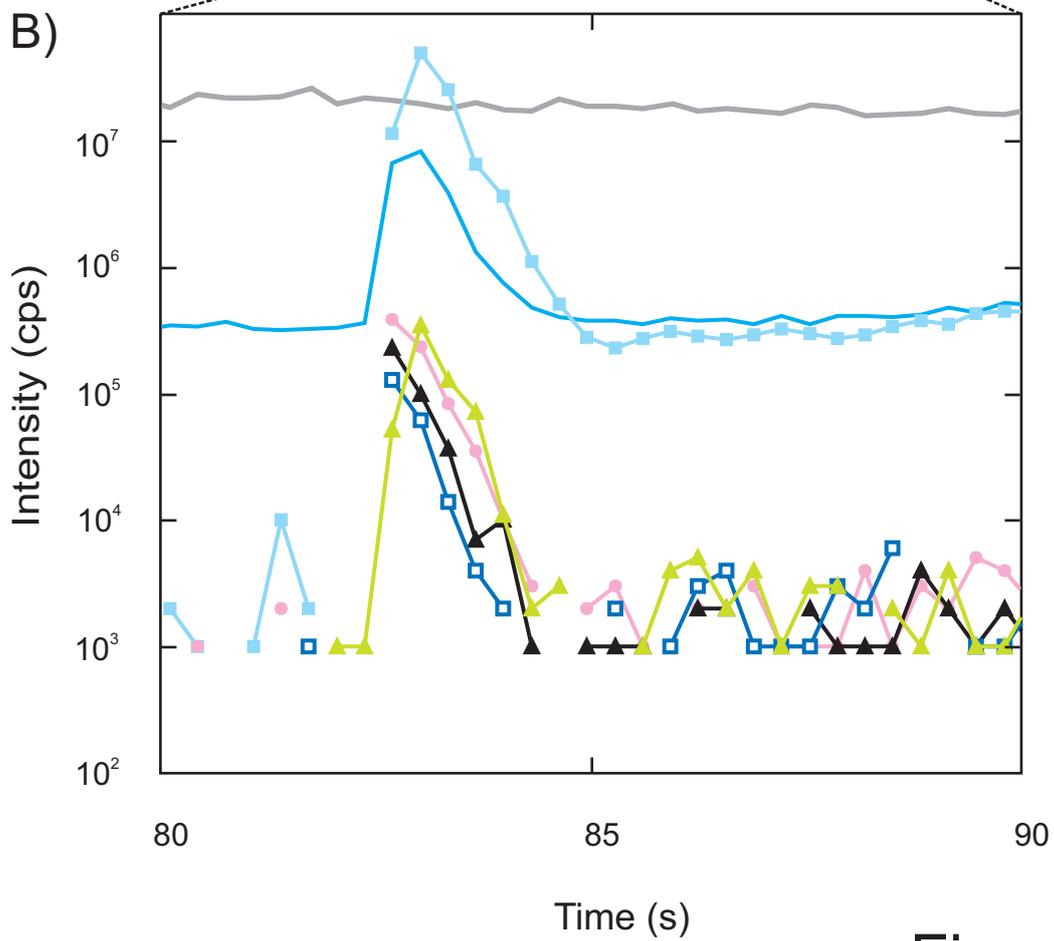
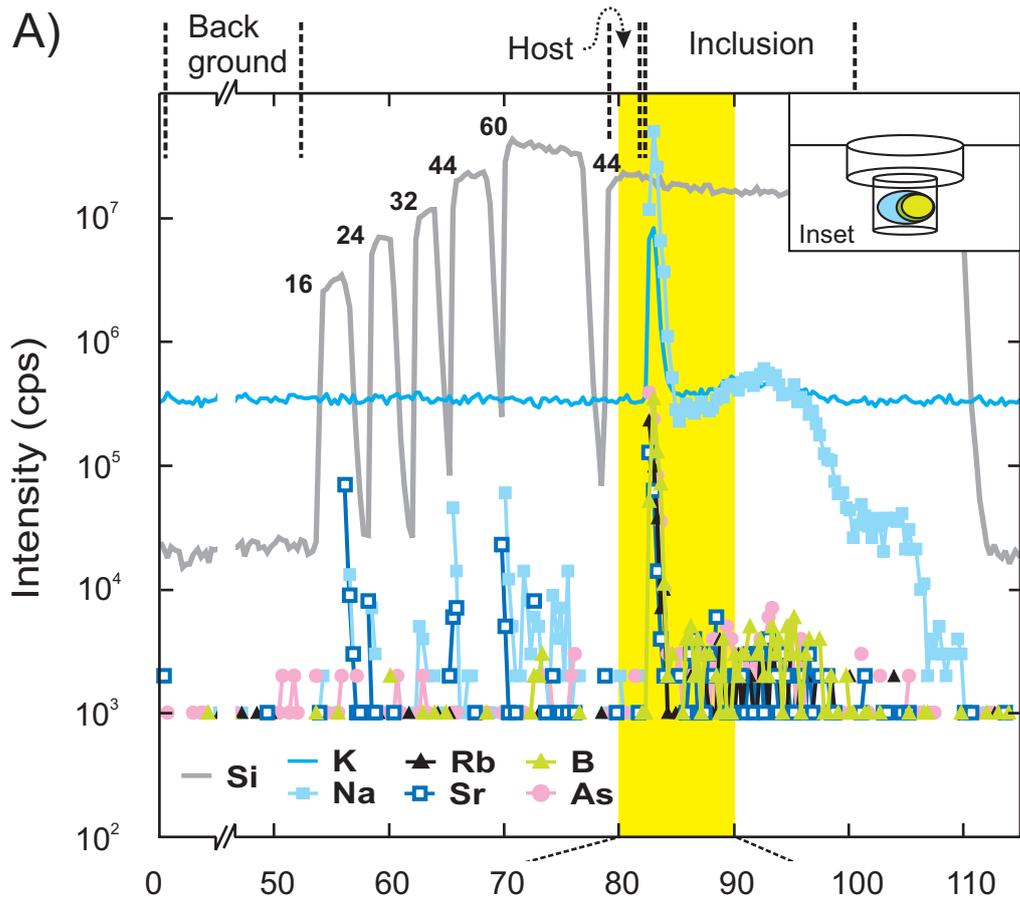


Figure 5

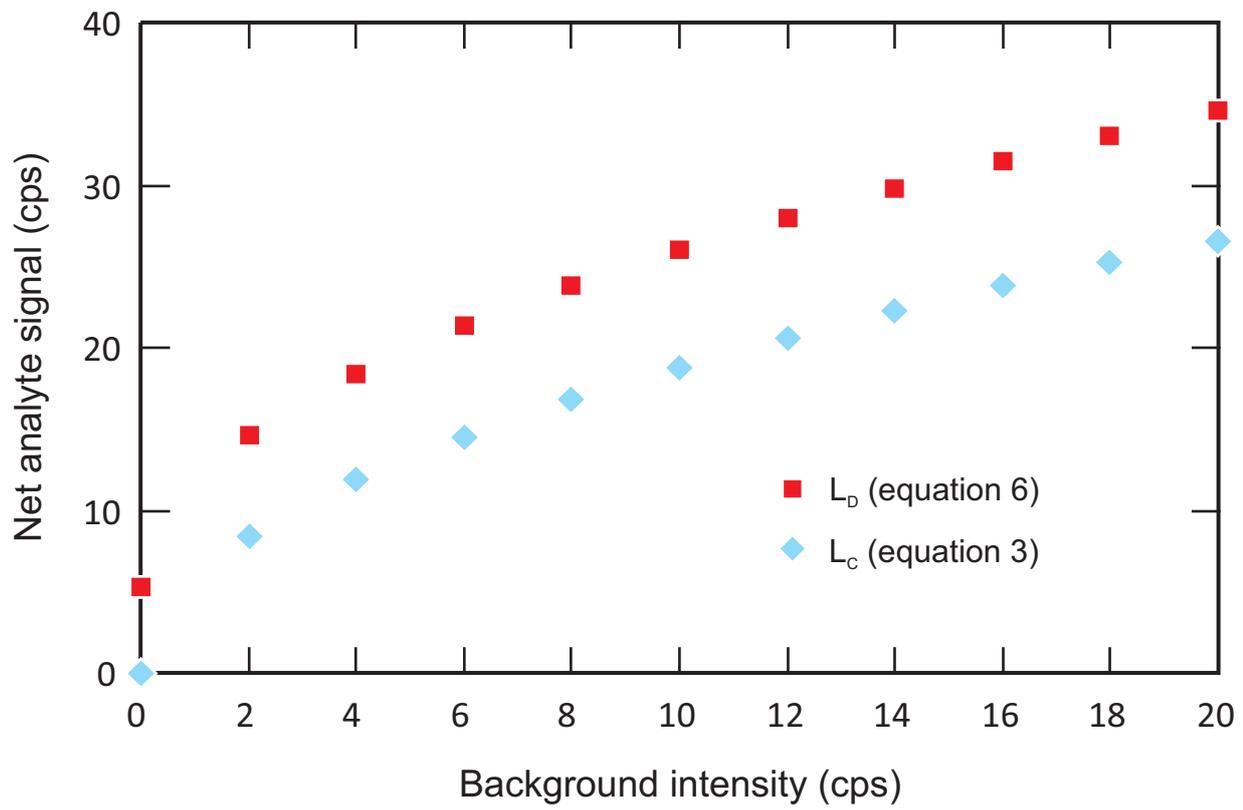


Figure 6

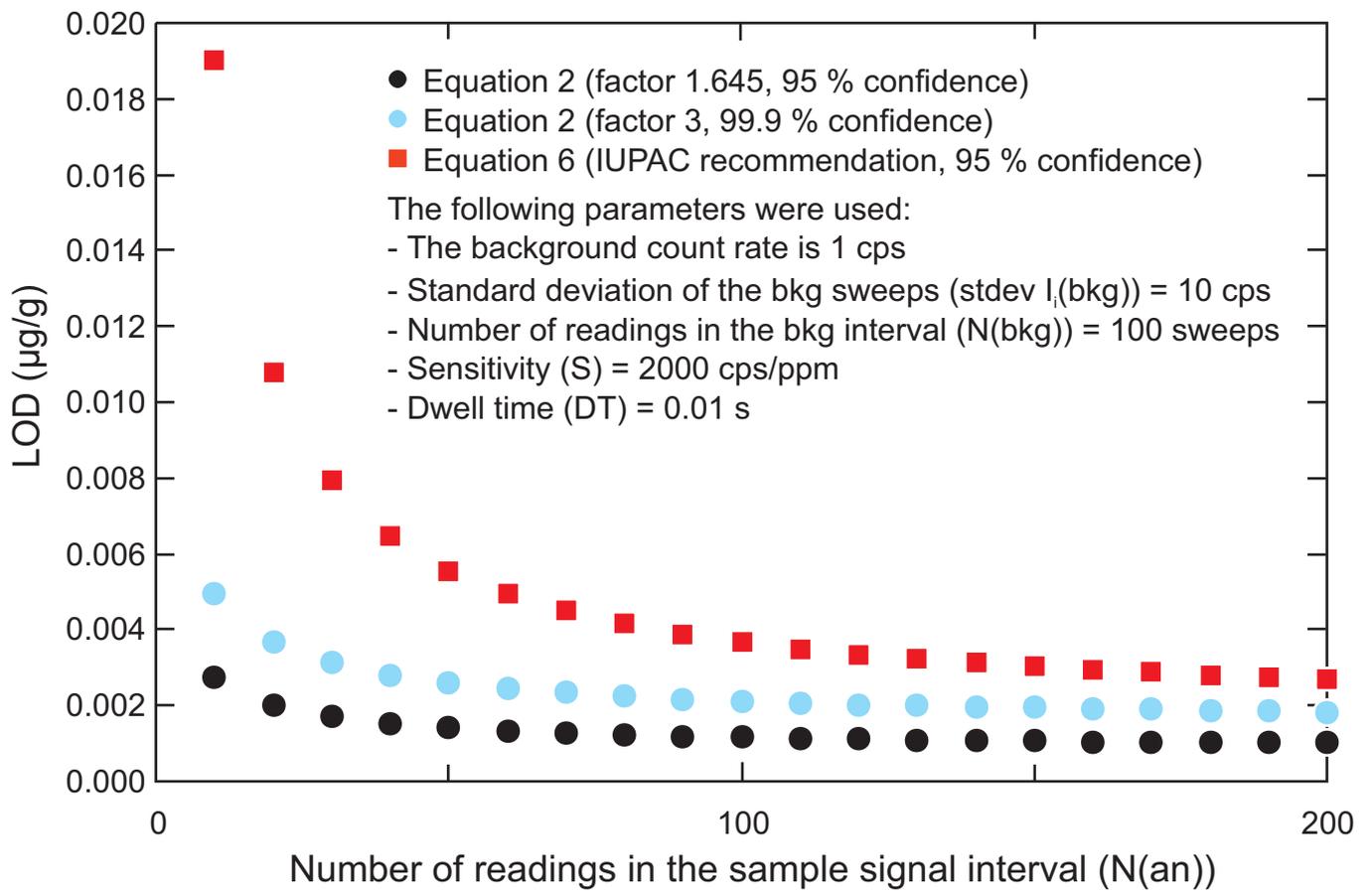


Figure 7

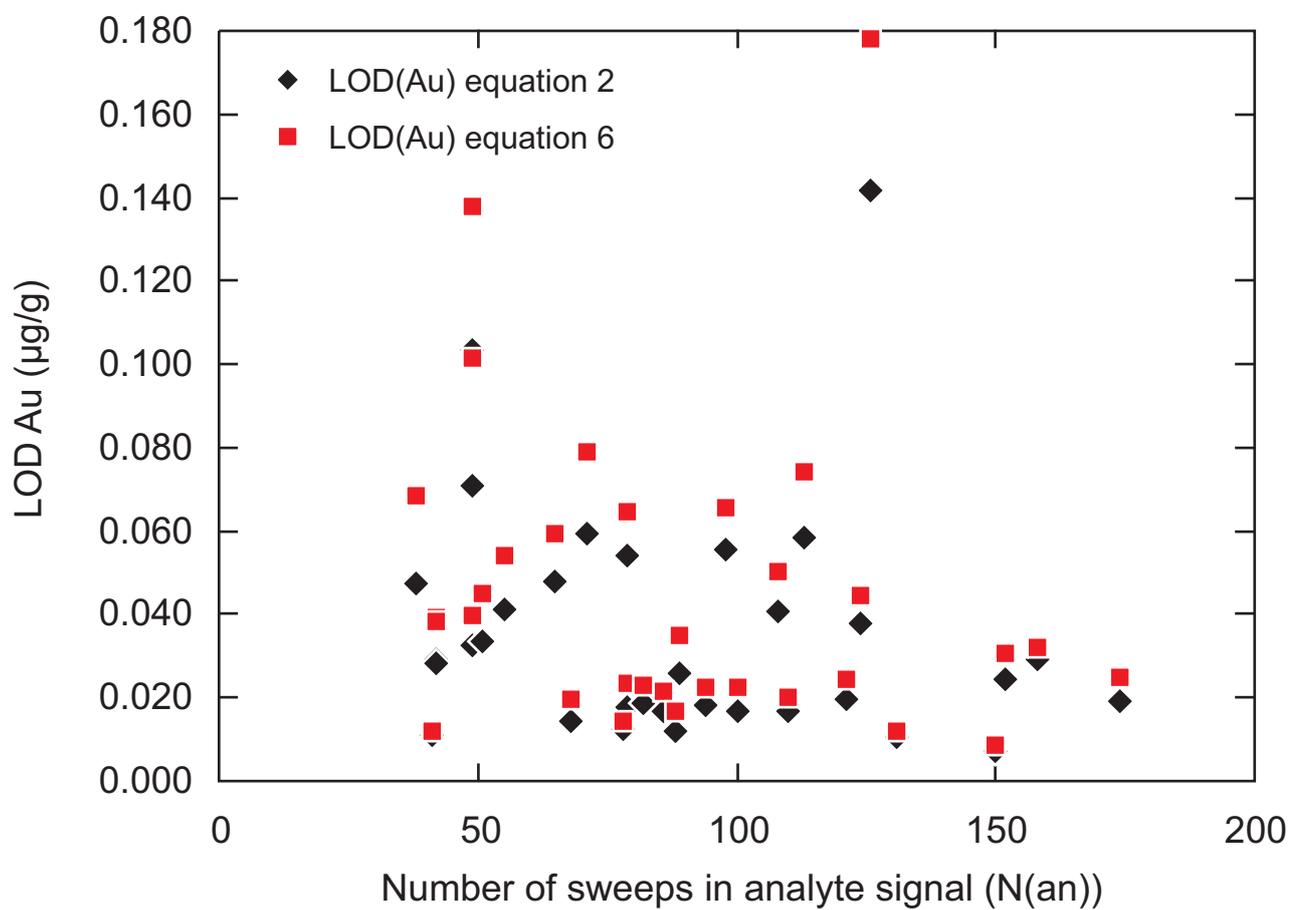


Figure 8

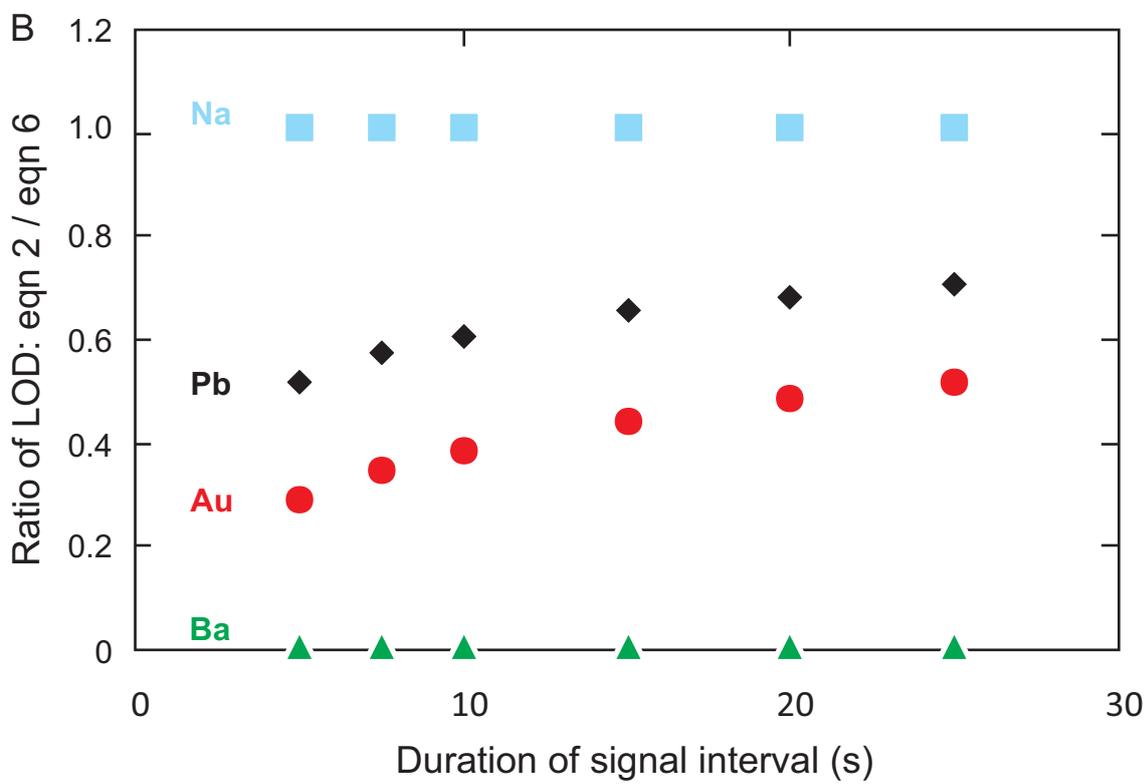
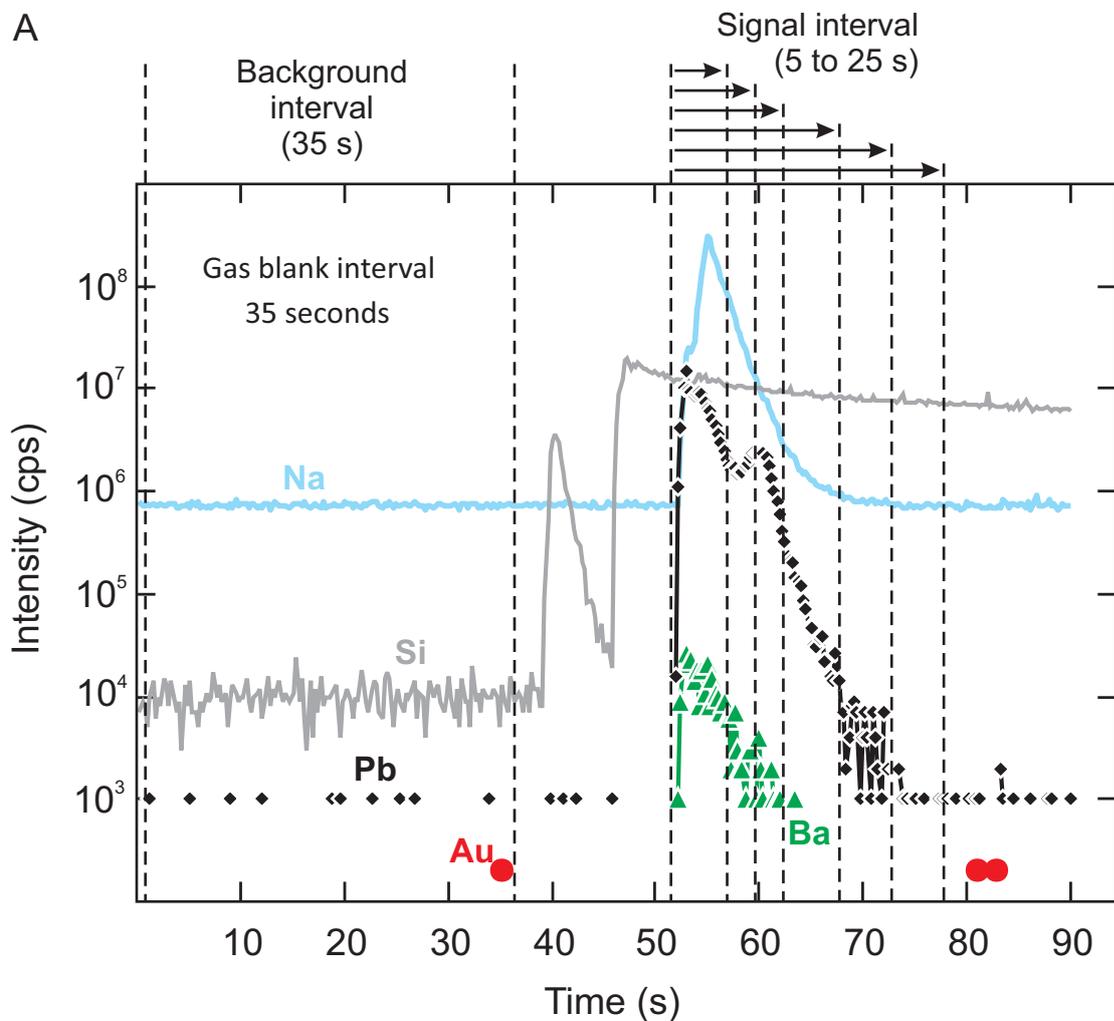


Figure 9

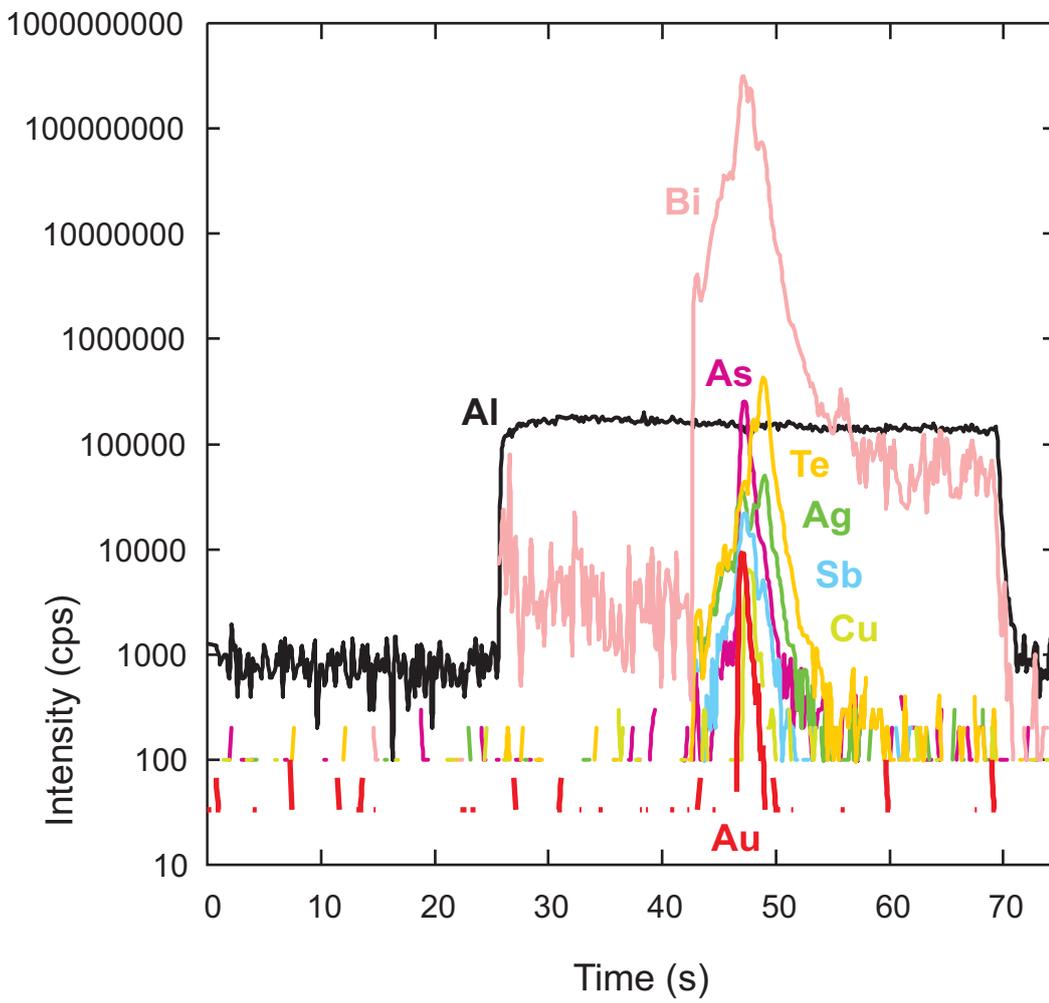


Figure 10

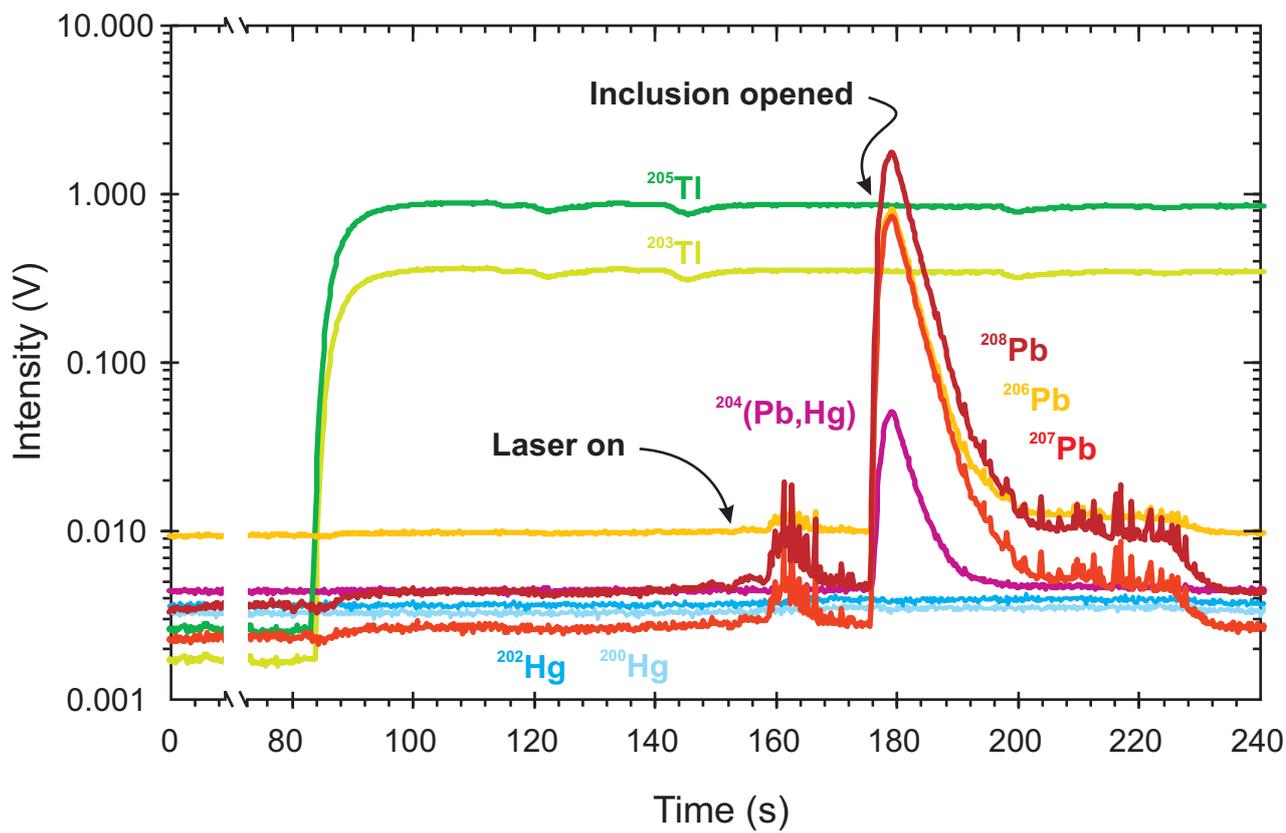


Figure 11

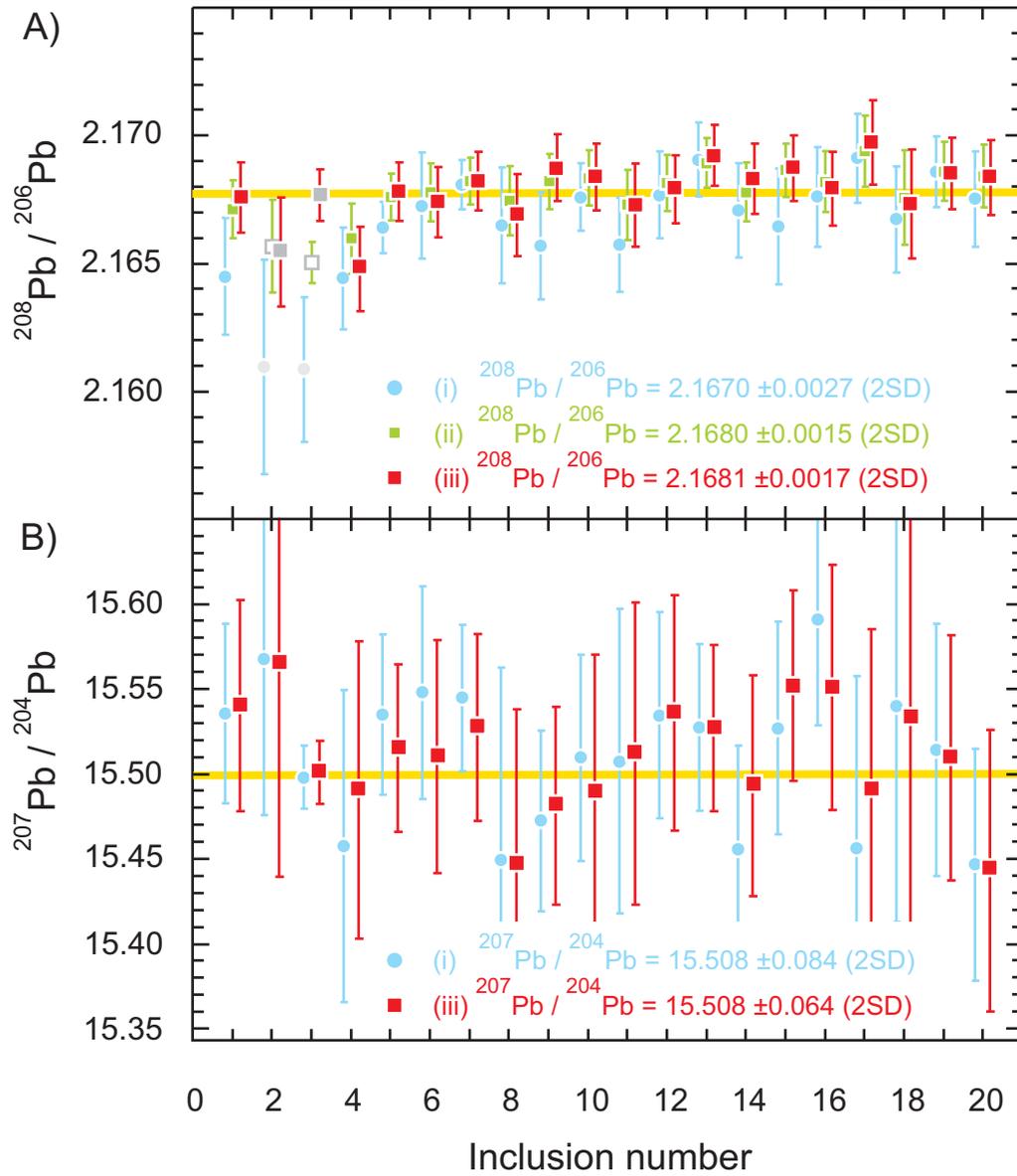


Figure 12

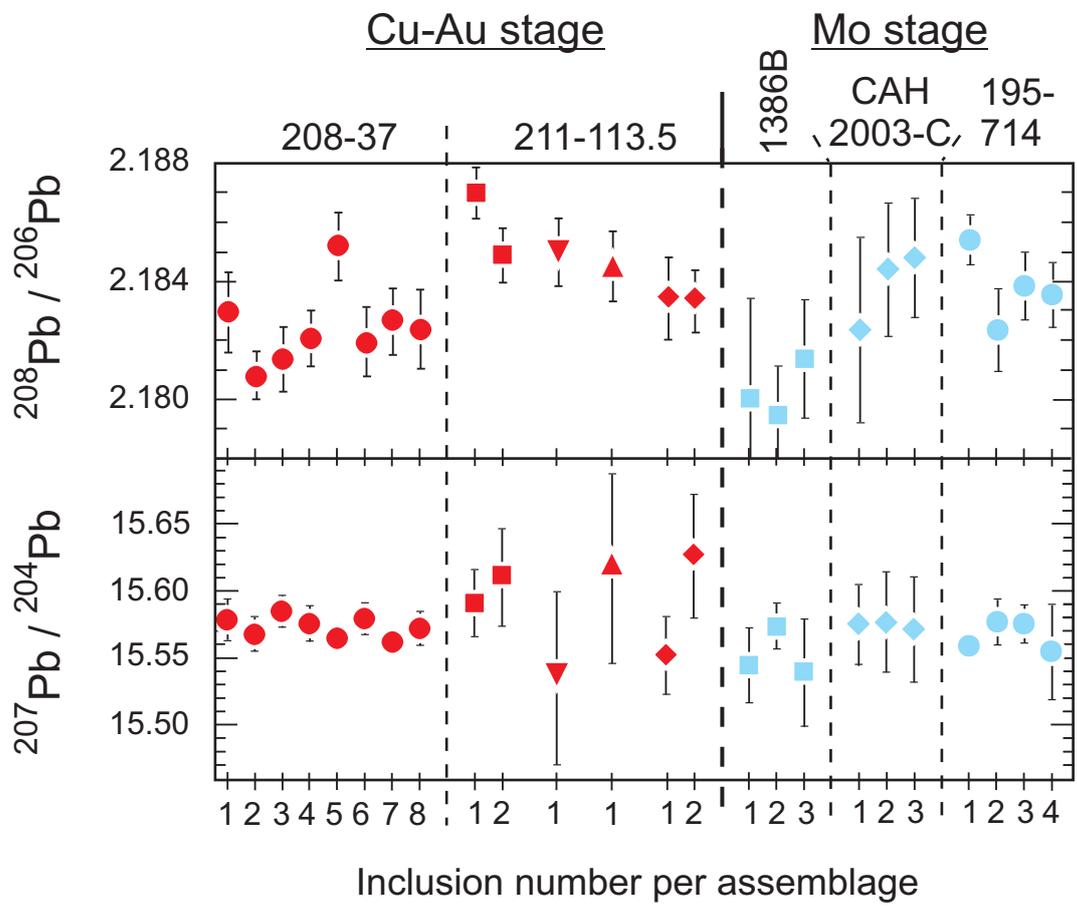


Figure 13

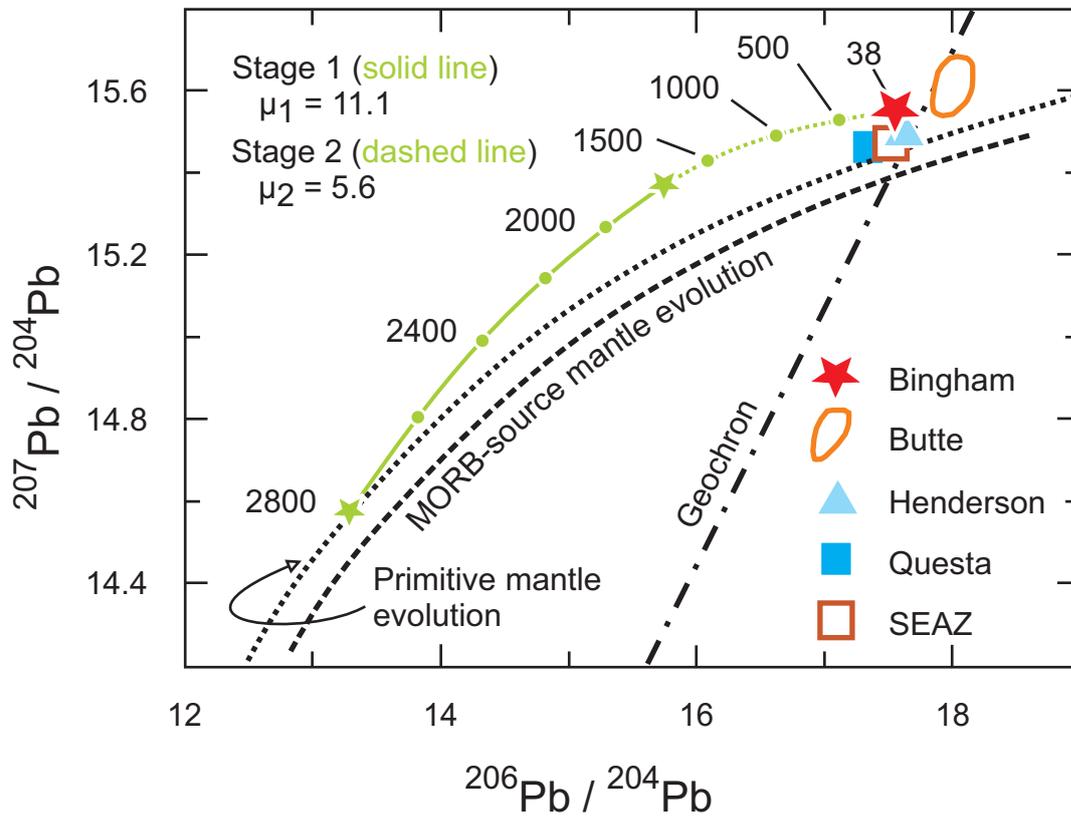


Figure 14

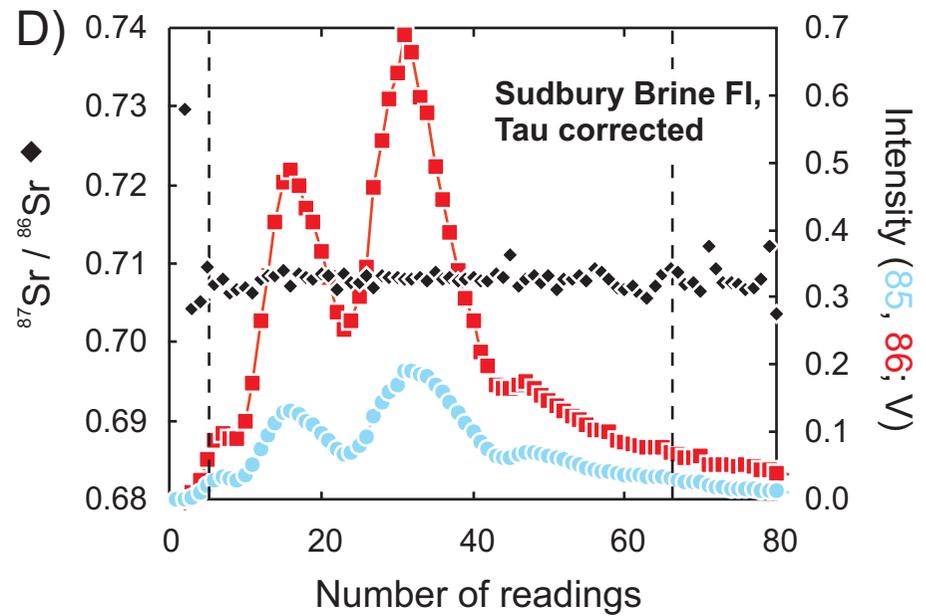
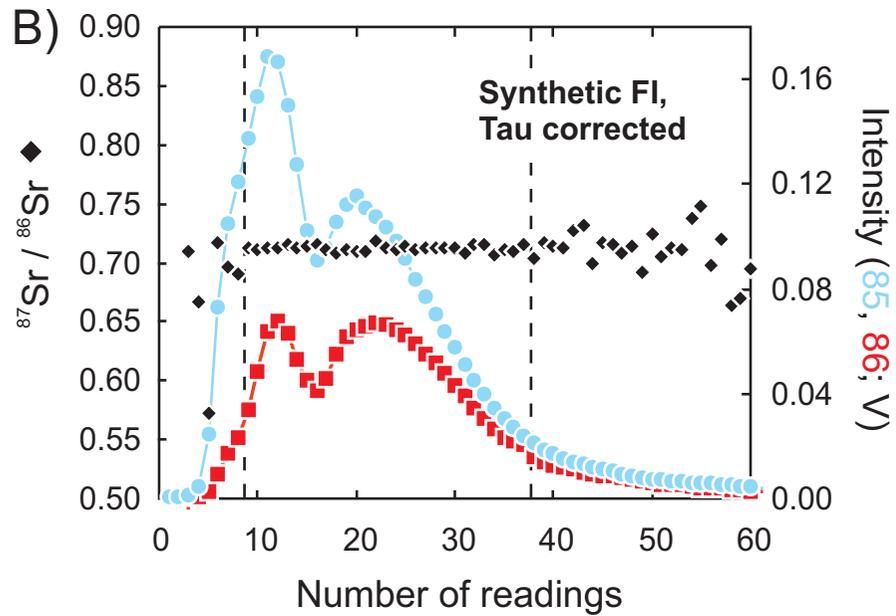
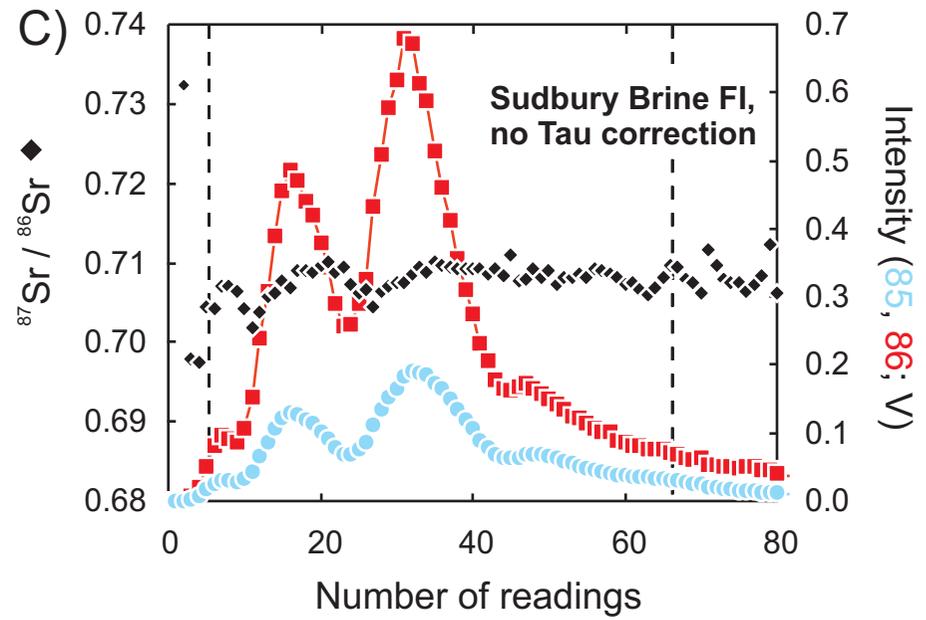
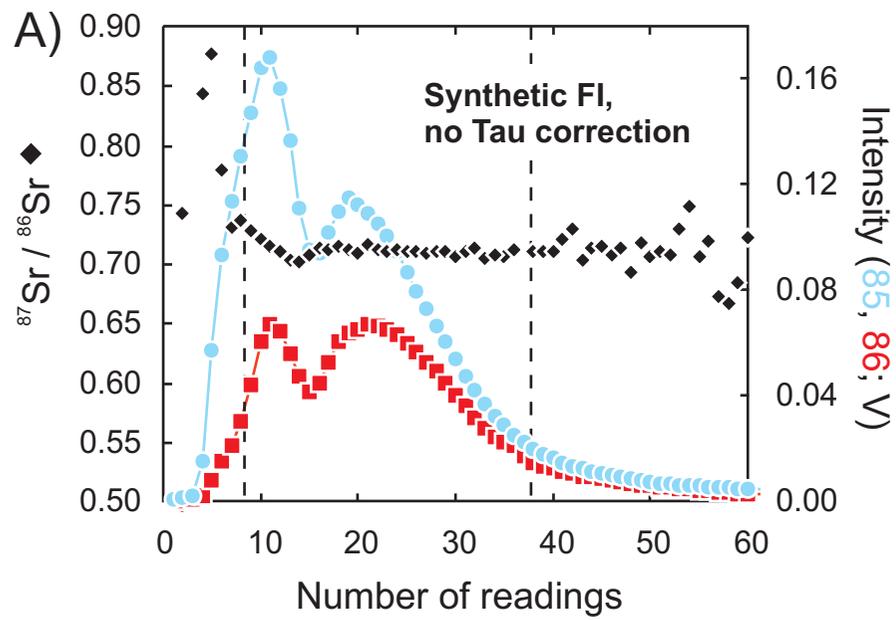


Figure 15

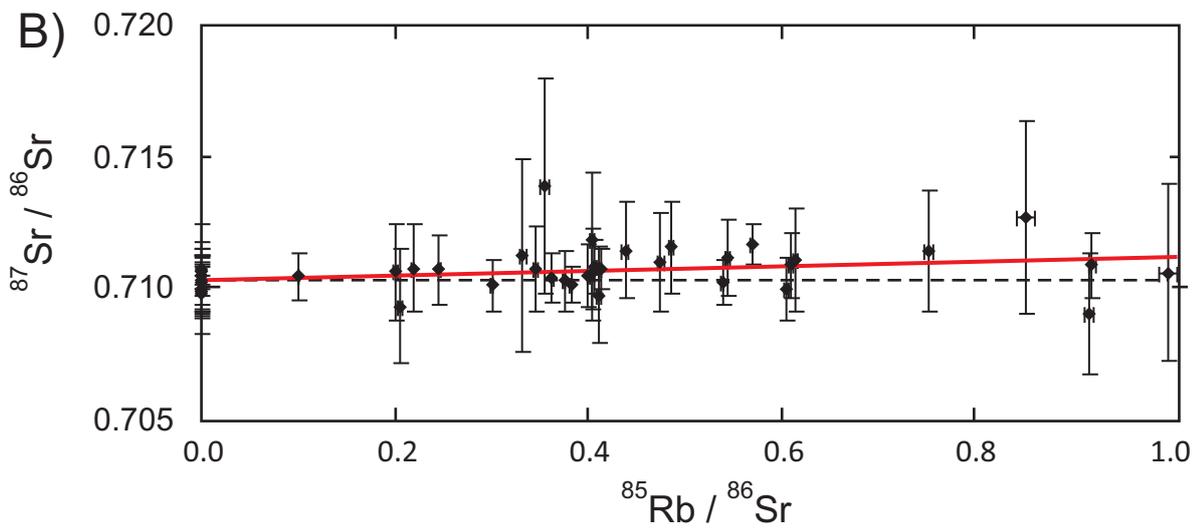
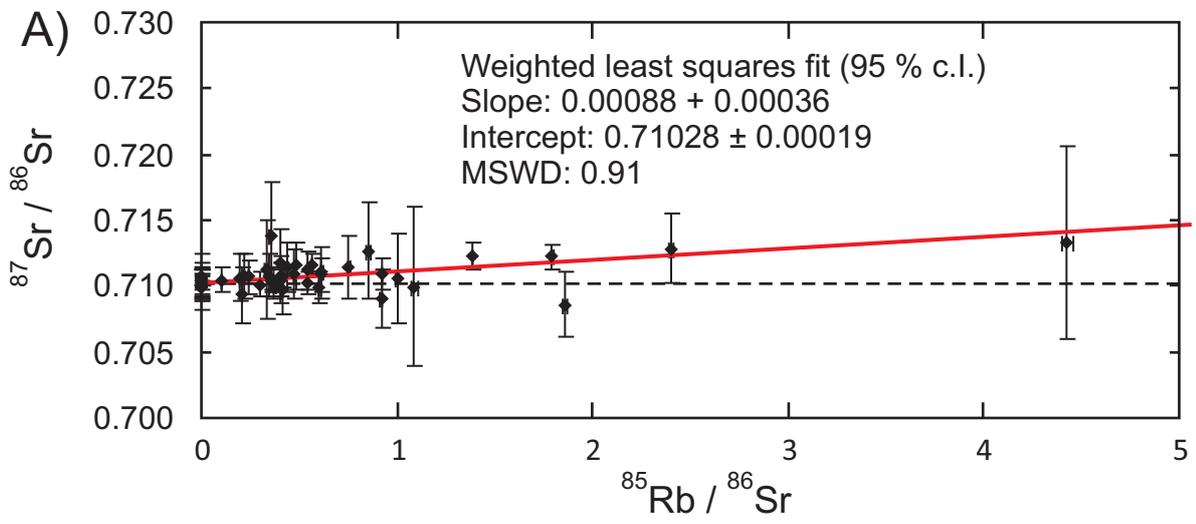


Figure 16

Table 1: Element concentration data of individual fluid inclusions of 4 successively entrapped fluid inclusion assemblages from a porphyry stage quartz vein of Bingham

Analysis number	Assemblage	Ablation quality	FI size µm	Na (23) µg/g	K (39) µg/g	Mn (55) µg/g	Fe (57) µg/g	Cu (65) µg/g	Sr (88) µg/g	Mo (95) µg/g	Ag (109) µg/g	Pb (208) µg/g
14fre07	1	+++	35	120400	100200	3820	74800	24200	240	33	—	3840
14fre16	1	+++	30	125800	103000	2680	61500	24200	200	103	—	3240
14fre17	1	+++	40	125400	96400	2740	67900	19700	410	1442	—	3340
26jib06	1	+++	38	122600	99800	3980	72100	21600	260	57	32	3730
26jib07	1	++(+)	38	122500	99700	4000	72500	22200	260	56	32	3730
26jib10	1	+++	25	<i>109005</i>	<i>115500</i>	<i>4610</i>	<i>89300</i>	<i>19500</i>	<i>200</i>	<i>80</i>	<i>29</i>	<i>4120</i>
		average		123300	99800	3440	69800	22400	240	62	32	3580
		1 SD		2250	2340	680	5250	1900	28	29	0	270
		1 SD (%)		2	2	20	8	8	12	47	0	8
14frc12	2	+++	20	122000	98700	3560	72700	8610	230	110	—	3410
14fre06	2	+++	40	129200	96500	3170	58800	8650	190	120	—	3230
14fre08	2	+++	40	117400	99500	3930	81900	8430	250	120	—	3540
14fre15	2	+++	18	123100	95000	3660	73300	10600	270	120	—	3340
14fre18	2	++(+)	45	123300	100600	2620	69200	11400	290	397	—	3580
26jia07	2	++(+)	40	117400	100600	3780	83500	12210	260	50	22	3380
26jia12	2	++(+)	25	114300	99900	4130	90600	11720	240	34	24	3860
26jib03	2	++(+)	28	<i>102800</i>	<i>126600</i>	<i>5080</i>	<i>93600</i>	<i>12270</i>	<i>150</i>	<i>120</i>	<i>22</i>	<i>4750</i>
26jib04	2	++(+)	35	120100	98500	3690	79200	9080	210	100	20	3170
26jib08	2	++(+)	25	124100	95000	3460	73300	15320	130	43	23	3020
26jib09	2	++	24	105100	114400	4500	98600	10210	430	55	23	4780
26jib13	2	++(+)	28	104100	122100	4490	95000	9390	250	130	21	3800
26jib14	2	+++	26	104300	120500	4110	96100	12570	250	91	15	3400
		average		117000	103400	3760	81000	10680	230	88	21	3540
		1 SD		8460	9730	540	12300	2070	44	36	3	460
		1 SD (%)		7	9	14	15	19	19	41	14	13
26jic04	3	++	38	<i>105800</i>	<i>123800</i>	<i>3680</i>	<i>89200</i>	<i>13300</i>	270	260	23	4550
26jic05	3	++	42	124000	102900	2990	66900	10000	260	54	19	2870
26jic06	3	+++	20	117800	100100	3850	83000	9790	290	91	21	3360
26jic07	3	+++	18	115500	100800	3730	87400	7920	160	110	17	3580
26jic08	3	+++	22	118800	102500	3880	78700	13000	240	130	22	3430
26jic09	3	++	30	124900	93500	3100	72900	10430	210	120	21	2990
26jic10	3	++	40	120600	103900	3290	73800	8890	220	94	21	2960
26jic11	3	++(+)	35	124500	95300	3420	72100	9860	230	130	21	3190
		average		120900	99900	3470	76400	9990	230	104	20	3200
		1 SD		3700	3970	360	7040	1570	41	27	2	270
		1 SD (%)		3	4	10	9	16	18	26	9	8
26jia03	4	++(+)	35	116600	105200	4420	81400	1920	200	81	12	3230
26jia17	4	+++	35	118900	109200	3400	72500	850	190	64	20	4030
26jib11	4	+++	40	122800	104700	3000	67500	1200	200	220	22	3780
26jib12	4	++(+)	40	122500	105000	3020	68000	1230	200	224	22	3770
26jib15	4	++(+)	25	122800	101000	4590	71400	2000	220	79	15	2600
26jic03	4	+++	13	117600	99200	3800	83900	470	170	95	18	3670
		average		120200	104100	3700	74100	1280	200	80	18	3510
		1 SD		2840	3520	690	6930	600	16	13	4	520
		1 SD (%)		2	3	19	9	47	8	16	22	15

Sample used is 208-37. Equivalent NaCl concentration used as the internal standard for signal quantification is 49.1 wt-%.

Masses analyzed are listed in brackets in the table header

Fluid inclusion data are corrected for host quartz contribution, and salt correction (Heinrich et al., 2003) was effected for KCl, FeCl₂ and PbCl₂

Values *in italics* are outliers and thus were not used for statistical calculations

+++ Indicates perfect ablation of fluid inclusion as judged on TV screen

++(+)
++ Indicates good ablation of fluid inclusion with a very minor problem (e.g., signal tailing because the fluid inclusion was deep)

++ Indicates acceptable ablation, with problems such as surficial quartz breakout or unclear signal boundary, e.g.,

because an underlying inclusion was hit before the first signal ended

— Analyte was not recorded

Table 2: Gold concentration data, LODs and uncertainties of individual fluid inclusions from Bingham Canyon porphyry Cu-Au-Mo deposit

Analysis number	Assemblage	Ablation quality	Fl size (µm)	Au signal visible †	bkg (cps)	stdev I (bkg) (cps)	DT (s)	N(bkg)	N(an)	S(Au) (cps/(µg/g))	Au app. (197) (µg/g)	LOD(Au) eqn 2 (99.9%) (µg/g)	LOD(Au) eqn 2 (95%) (µg/g)	LOD(Au) eqn 6 (95%) (µg/g)	Au final (µg/g)	CSU Au (%)
14fre07	1	+++	35	Y	6	7.9	0.1	343	78	242.9	0.084	0.013	0.007	0.015	0.084	8
14fre16	1	+++	30	Y	4.167	6.6	0.1	267	131	204.5	0.064	0.011	0.006	0.012	0.064	8
14fre17	1	+++	40	Y	3.956	6.2	0.1	283	150	261.0	0.069	0.008	0.004	0.009	0.069	5
26jib06	1	+++	38	Y	1.868	4.2	0.1	182	68	124.6	0.055	0.014	0.008	0.019	0.055	15
26jib07	1	+++	38	Y	1.858	4.2	0.1	183	152	56.4	0.065	0.025	0.013	0.031	0.065	13
26jib10	1	+++	25	Y	2.081	4.4	0.1	197	38	49.2	0.065	0.048	0.026	0.069	(0.065)	29
average															0.072	0.068
1 SD															0.010	0.010
1 SD (%)															14	15
14frc12	2	+++	20	Y	4.518	7.0	0.1	197	49	102.8	0.071	0.033	0.018	0.040	0.071	15
14fre06	2	+++	40	Y	5.762	9.0	0.1	374	41	402.3	0.075	0.012	0.006	0.012	0.075	9
14fre08	2	+++	40	Y	6.667	8.2	0.1	367	110	158.4	0.063	0.019	0.009	0.020	0.063	9
14fre15	2	+++	18	Y	4.733	7.1	0.1	384	79	48.7	0.062	0.056	0.030	0.064	(0.062)	21
14fre18	2	+++	45	Y	4.506	7.2	0.1	302	158	72.9	0.082	0.033	0.016	0.032	0.082	10
26jia07	2	+++	40	Y	2.24	4.7	0.1	183	86	109.2	0.102	0.017	0.009	0.022	0.102	10
26jia12	2	+++	25	Y	1.881	4.3	0.1	218	71	29.6	0.065	0.060	0.033	0.079	(0.065)	27
26jib03	2	+++	28	Y	2.402	4.9	0.1	229	42	85.0	0.151	0.029	0.016	0.039	0.151	14
26jib04	2	+++	35	Y	2.021	4.3	0.1	188	79	98.6	0.073	0.018	0.010	0.024	0.073	13
26jib08	2	+++	25	Y	2.024	4.8	0.1	168	98	33.0	0.053	0.055	0.030	0.065	(0.053)	—
26jib09	2	+++	24	Y	2.457	4.6	0.1	175	49	31.5	0.097	0.071	0.039	0.101	(0.097)	26
26jib13	2	+++	28	Y	2.286	5.0	0.1	175	65	45.6	0.108	0.048	0.026	0.059	0.108	18
26jib14	2	+++	26	Y	1.913	4.3	0.1	183	113	26.4	0.112	0.058	0.032	0.074	0.112	17
average															0.073	0.076
1 SD															0.010	0.012
1 SD (%)															13	16
26jic04	3	++	38	Y	2.934	5.3	0.1	167	42	97.5	0.099	0.028	0.015	0.038	0.099	16
26jic05	3	+++	42	Y	1.839	4.3	0.1	174	121	77.8	0.109	0.020	0.011	0.024	0.109	10
26jic06	3	+++	20	Y	1.842	4.4	0.1	190	55	49.0	0.077	0.041	0.023	0.054	0.077	22
26jic07	3	+++	18	Y	2.544	5.0	0.1	169	49	23.5	0.083	0.103	0.057	0.138	(0.083)	32
26jic08	3	+++	22	N	1.864	4.1	0.1	220	89	60.1	0.014	0.026	0.014	0.035	<0.035	—
26jic09	3	++	30	Y	2.635	5.3	0.1	167	124	50.0	0.053	0.038	0.021	0.044	0.053	18
26jic10	3	++	40	Y	2.148	4.4	0.1	149	100	100.7	0.083	0.017	0.009	0.022	0.083	11
26jic11	3	+++	35	Y	2	4.6	0.1	155	82	101.7	0.077	0.019	0.010	0.023	0.077	12
average															0.080	0.079
1 SD															0.020	0.026
1 SD (%)															25	33
26jia03	4	+++	35	Y	1.667	4.2	0.1	204	108	36.9	1.333	0.041	0.022	0.050	1.33 †	4
26jia17	4	+++	35	N	1.713	4.3	0.1	181	94	89.9	0.018	0.018	0.010	0.022	<0.022	—
26jib11	4	+++	40	N	2.045	4.2	0.1	176	88	135.7	0.008	0.012	0.007	0.017	<0.017	—
26jib12	4	+++	40	N	2.011	4.2	0.1	184	174	69.5	0.010	0.019	0.011	0.025	<0.025	—
26jib15	4	+++	25	Y	2.34	4.8	0.1	188	51	67.5	0.134	0.034	0.018	0.045	0.134 †	15
26jic03	4	+++	13	N	3.046	5.3	0.1	174	126	13.1	0.028	0.142	0.078	0.178	<0.178	—
average															—	—
1 SD															—	—
1 SD (%)															—	—

Sample used is 208-37; same inclusions as in Table 1. ¹⁹⁷Au was analyzed. CSU refers to counting statistics uncertainty for Au.

Values in *italic* are deemed outliers based on bulk fluid inclusion data (Table 1) and thus were not used for statistical calculations.

Definition of ablation quality: see Table 1

† Indicates whether a gold signal is visible by eye in the transient signal plot (Y) or not (N)

<value i Indicates that the concentration value is below the LOD as discussed in text

‡ Considered to be an outlier based on within assemblage statistics and thus not used for statistical calculations

Au app. Represents the calculated Au concentration prior to LOD filtering

LOD(Au) LODs were calculated using equations 2 and 6 as explained in text (with different confidence levels for equation 2)

Au final Gold values in round brackets represent a gold signal visible by eye but below LOD (equation 6). Not used for statistical calculations.

Note that these apparent Au concentrations are only slightly below the 95% confidence LOD calculated using equation 6

CSU Au Reports the counting statistics uncertainty for the Au signal

Average and 1 SD values reported in the column "Au final" are simple averages, those in column "CSU Au" are counting statistics uncertainty weighted mean values at 95% confidence

Table 3. Experimental studies that used synthetic fluid inclusions to trap and recover aqueous fluid(s) at elevated pressure and temperature to constraining metal solubilities and speciation.

Phase Assemblage	Fluid	Element of Interest	Fluid inclusion host	T (°C)	P (MPa)	f_{O_2}	f_{S_2}	Bulk salinity	Vapor salinity	Brine Salinity	Major Findings	Reference
brine, po-mt ±py	H-O-S-KCl-FeCl ₂ -HCl	Au	quartz	550 - 725	110 - 400	po-mt-py, po-mt	$a_{H_2S} = 12.1 - 46.4$	0 to 1 m HCl + KCl		0 to 1 m HCl + KCl	solubility of Au in brine increases significantly with increasing f(H ₂ S)	Loucks and Mavrogenes, 1999
granite melt + mt + vapor + brine	O-H-NaCl-KCl-FeCl ₂	Fe	quartz	800	110, 130, 140, 145	NNO	S-free	1,8 – 20 wt. % NaCl eq.	2.1 to 19.2 wt. % NaCl eq.	35 – 58 wt. % NaCl eq.	$D_{Fe}^{v/si-mt} = 0.22, 0.92, 1.94, 3.8$ $D_{Fe}^{b/si-mt} = 4.6, 6.6, 7.1, 6.7$ $D_{Fe}^{v/b} = 0.05, 0.14, 0.27, 0.56$	Simon et al., 2004
peraluminous granite melt, supercritical O-H-Cl fluid	NaCl, KCl, HCl	Pt	silicate glass	800	150	NNO	S-free	20 and 50 wt. % NaCl eq.			$D_{Pt}^{v/si-mt} = 6.6 \times 10^3$ to 5.2×10^4 $D_{Pt}^{b/si-mt} = 1 \times 10^2$ to 2.6×10^2 $D_{Au}^{v/si-mt} = 4.2 \times 10^3$ to 1.2×10^4	Hanley et al., 2005b
granite melt + mt + vapor + brine	O-H-NaCl-KCl-FeCl ₂	Au	quartz	800	110, 130, 140, 145	NNO	S-free	1,8 – 20 wt. % NaCl eq.	2.1 to 19.2 wt. % NaCl eq.	35 – 58 wt. % NaCl eq.	$D_{Au}^{v/si-mt} = 10, 8, 56, 72$ $D_{Au}^{b/si-mt} = 58, 56, 80, 100$ $D_{Au}^{v/b} = 0.21, 0.18, 0.80, 0.72$	Simon et al., 2005
Cu + cpr + tc + qz; Cl added as CuCl ₂ or Cu + Mt + Hm + Kf + Qz + Sil; Cl added as KCl	O-H-Cl	Cu	quartz	630, 700	313, 338, 341	NR	S-free	14.6 – 29.3 wt. % Cl			Cu speciation in aqueous fluid at elevated T: Cu speciated as [CuCl ₂] in KCl-fluid with Cu:Cl = 1:6, and in K-free fluid possibly as [CuCl ₄] ³⁻ in KCl-solutions with Cu:Cl = 1:6	Berry et al., 2006
tc + qtz + cpr + O-H-Cl fluid + Cu ₂ O	O-H-CuCl ₂ -	Cu	quartz	524 to 710	313 to 1703	NR	S-free	0.775 to 13.4 wt. % Cl		0.775 to 13.4 wt. % Cl	Cu solubility in aqueous brine is ~15 wt. % at 630C and 0.34 GPa; modeled Cu speciation as $CuCu(HCl)_{n-1}^0$ where $n \leq 4$	Hack and Mavrogenes, 2006
granite melt + mt + vapor + brine + CuCl ± po	O-H-NaCl-KCl-HCl ± S	Cu	quartz and silicate glass	800	140	NNO	runs with S: log $f_{S_2} = -3$ bars	20 wt. % NaCl eq.	8 – 9 wt. % NaCl eq.	41 – 45 wt. % NaCl eq.	$D_{Cu}^{v/si-mt} = 60 \pm 30$ $D_{Cu}^{b/si-mt} = 240 \pm 80$ $D_{Cu}^{v/b} = 0.27 \pm 0.10$ S-bearing	Simon et al., 2006

											$D_{Cu}^{v/si-mt} = 320 \pm 20$ $D_{Cu}^{b/si-mt} = 440 \pm 70$ $D_{Cu}^{v/b} = 0.69 \pm 0.16$	
pelite + H ₂ O; solid phases included zrn, ap, grt, rt	H ₂ O	Al, Ca, Na, K, Ti, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Gd, Yb, Ta, Pb, Th, U	quartz	600 - 750	1000, 1500, 2200	NNO	NR	4 - 5.5 wt. % total solutes			quantified $D_i^{v/solids}$ for Al, Ca, Na, K, Ti, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Gd, Yb, Ta, Pb, Th, U	Spandler et al., 2007
granite melt + mt + vapor + apy	O-H-NaCl- KCl-HCl ± S	Au, As	silicate glass	800	120	NNO	runs with S: log $f_{S_2} = -3$ bars	1.8 wt. % NaCl eq.	1.8 wt. % NaCl eq.		<u>S-free</u> $D_{Au}^{v/si-mt} = 15 \pm 2.5$ $D_{As}^{v/si-mt} = 1 \pm 0.1$ <u>S-bearing</u> $D_{Au}^{v/si-mt} = 12 \pm 0.3$ $D_{As}^{v/si-mt} = 2.5 \pm 0.3$	Simon et al., 2007
Supercritical fluid + cst (±NaF melt)	O-H-NaCl- NaF-HF-HCl	Sn	quartz	700	140	NNO	S-free	5-35 wt. % NaCl eq.; 0.5-3.2 m HF; 0.8- 0.5-4.4 m HCl			$D_{Sn}^{fluid/si-mt} = 0.1 - 4$, controlled primarily by HCl concentration of the fluid; Sn solubility up to 11 wt% in HCl-rich fluids; formation of Sn- rich melt phase in NaF-bearing experiments; Sn dissolution likely as Sn(OH)Cl, SnCl ₂ and SnF ₂	Duc-Tin et al., 2007
granite melt + vapor + brine	O-H-NaCl- KCl-HCl	Ag	quartz and silicate glass	800	100, 140	NNO	S free	1.8, 5.5, 20 wt. % NaCl eq.	1.2 - 9.7 wt. % NaCl eq.	41 - 67 wt. % NaCl eq.	<u>100 MPa</u> $D_{Ag}^{v/si-mt} = 32 \pm 30$ $D_{Ag}^{b/si-mt} = 1150 \pm 240$ $D_{Ag}^{v/b} = 0.026 \pm 0.004$ <u>140 MPa</u> $D_{Ag}^{v/si-mt} = 32 \pm 10$ $D_{Ag}^{b/si-mt} = 410 \pm 170$ $D_{Ag}^{v/b} = 0.06 \pm 0.03$	Simon et al., 2008

Mo-KCl-H ₂ O	O-H-KCl	Mo	quartz	500-800	150-300	NNO	S-free	1 - 24 wt % KCl	NA	NA	Mo solubilities up to 1.6 wt % in KCl-solutions; up to 0.8 wt % in pure H ₂ O; solubilities are pressure independent but temperature dependent and correlate positively with KCl, likely as molybdc acid and Mo-oxo-chloride complexes	Ulrich and Mavrogenes, 2008
S-anthracene	H-O-S-CuCl-ZnCl ₂ -NaCl, HCl	Cu	quartz	600, 700	50, 100	NNO	buffered by bn + iss @ NNO	brine / vapor density 2.0 to 8.0	NR	NR	$D_i^{v/b} = \leq 0.39$ and ≤ 0.18 H ₂ S was not observed to enhance solubility of Cu in vapor relative to brine at experimental conditions	Lerchbaumer and Audétat, 2009
bn-iss-bt-mt-or- and ±ab,±anh	H-O-S-KCl-FeCl ₂ -HCl ±NaCl	Cu	quartz	600, 700	50, 100	NNO	buffered by bn + iss @ NNO	NR	NR	NR	$D_{Cu}^{v/b} = 0.1$ to 0.2	Lerchbaumer and Audétat, 2009
S-anthracene	H-O-S-NaCl, CuCl-ZnCl ₂ -HCl	Cu, Zn	quartz	500, 600, 650	140 to 167	NR	NR	brine / vapor density 2.03 to 7.85	NR	NR	$D_{Cu}^{v/b} = 0.026$ (n=1) to 32 ± 4 $D_{Zn}^{v/b} = 0.006$ (n=1) to 0.13 ± 0.89 H ₂ S enhances solubility of Cu in vapor relative to brine at experimental conditions	Nagaseki and Hayashi, 2009
granite melt, vapor, brine	NaCl, KCl, HCl	Pt	silicate glass	800	100	NNO	S-free	10 wt. % NaCl eq.	2 wt. % NaCl eq.	63 wt. % NaCl eq.	$D_{Pt}^{v/si-mt} = 2.9 \pm 1.0$ $D_{Pt}^{b/si-mt} = 6.8 \pm 2.4$ $D_{Pt}^{v/b} = 0.15 \pm 0.05$	Simon and Pettke, 2009
granite melt, vapor, brine	NaCl, KCl, HCl	Pt	silicate glass	800	140	NNO	S-free	10 wt. % NaCl eq.	2 wt. % NaCl eq.	63 wt. % NaCl eq.	$D_{Pt}^{v/si-mt} = 1.0 \pm 0.2$ $D_{Pt}^{b/si-mt} = 70 \pm 30$ $D_{Pt}^{v/b} = 0.13 \pm 0.05$	Simon and Pettke, 2009
supercritical fluid – gold	NaCl, KCl, HCl, SO ₂ , H ₂ S	Au	quartz	1000	150	NNO-0.6 to NNO+1.9	varied f_{S_2} , f_{H_2S} , f_{SO_2}	variable NaCl, KCl, HCl; S from ~1 to ~10 wt. %			data consistent with gold-hydrosulfide complex dominating over gold-chloride complex; alkali chlorides amplify stability of gold-hydrosulfide-alkali complex	Zajacz et al., 2010
granite melt- iss-po-vapor-brine ±bn	NaCl, KCl, HCl, FeCl ₂	Cu, Au	quartz	800	100	NNO	$\log a_{S_2}^{sys} = 3.5 \times 10^{-2}$ and	5 wt. % NaCl eq.	2.7 – 3.6 wt. % NaCl eq.	66.5 – 68.5 wt. % NaCl eq.	Increasing activity of S in fluid correlated with increase in measured Au and Cu concentrations in the fluid; Cu and Au behave similar with no observed fractionation	Frank et al., 2011

							$\log a_{S_2}^{sys}$ = 1,2x 10^{-4}					
supercritical fluid – gold	NaCl, KCl, HCl, FeCl ₂ SO ₂ , H ₂ S	Cu	quartz	1000	150	NNO-0.6 to NNO+1.9	varied f_{S_2} , f_{H_2S} , f_{SO_2}	variable NaCl, KCl, HCl; S from ~1 to ~10 wt. %			Solubility of Cu in the aqueous fluid increases with increasing f_{O_2} ; addition of S to a Na/K/H/Fe-Cl fluid does not result in increased Cu solubility relative to a S-free alkali- chloride fluid	Zajacz et al., 2011
Uraninite, thorite, supercritical fluid	H-O-NaCl- Cs-Rb-Ba- Co	U, Th	Quartz	800	710 - 2610	Fe-FeO, Co-CoO, Ni-NiO, Re-ReO ₂	S-free	0 – 14.1 wt. % NaCl eq.			U solubility increases with f_{O_2} and NaCl; Th solubility in fluid independent of NaCl and little dependent on f_{O_2} ; data indicate that degassing of subducted slab can fractionate U/Th at QFM-0.5 to QFM+3.35	Bali et al., 2011
liquid only, and vapor only	Liquid: NaCl, Na ₂ SO ₄ *10(H ₂ O), NaBr, CsCl Vapor: H ₂ O, S, NaCl, NaBr, CsCl, RbCl	S, Cl, Br	Quartz	liquid at 600, vapor at 160- 170	950- 1000	NR	H ₂ S dominant	3.6 – 9.0 wt. % total dissolved solids			Quantification of S, Br, Cl in synthetic fluid inclusions can be performed with good accuracy; analytical uncertainty for S is 17- 44% RSD, and 6-26% for Br/Cl ratios. LODs are in the range of 60 ppm for S, 250 ppm for Cl, 15 ppm for Br	Seo et al., 2011

NR = not reported; NNO = NiNiO; IW = iron-wüstite; CCO = CoCoO; RRO = ReReO; f = fugacity; a = activity; v = vapor; b = brine; si-mt = silicate melt; bn = bornite; iss = intermediate solid solution; ab = albite; and = andalusite; anh = anhydrite; ap = apatite; apy = arsenopyrite; bn = bornite; bt = biotite; cst = cassiterite; grt = garnet; or = orthoclase; rt = rutile; zrn = zircon; anthracene is a reductant with the formula C₁₄H₁₀

Table 4: Bismuth inclusion element concentration data for 3 localities in the Sn-W mineralized Mole Granite, NSW, Australia

Analysis number	Sample	host mineral	Ablation quality	Bi (209) wt%	As (75) wt%	Te (126) wt%	Te (128) wt%	Co (59) ppm	Ni (61) ppm	S (32) ppm	S (34) ppm	Cu (65) ppm	Zn (66) ppm	Ga (69) ppm	Ge (72) ppm	Se (78) ppm	Ag (107) ppm	Cd (111) ppm	In (115) ppm	Sn (118) ppm	Sb (121) ppm	W (182) ppm	Au (197) ppm	Pb (208) ppm
99Mz17b03	Taro20 incl.1	Fluorite	exploded	95.1	3.4	1.5	1.5	8800	7100	n.a.	n.a.	310	<200	<30	n.a.	n.a.	4150	n.a.	<21	840	3900	270	34	1580
99Mz17b04	Taro20 incl.2	Fluorite	*	97.3	1.4	1.3	1.3	3900	5500	n.a.	n.a.	180	<120	<20	n.a.	n.a.	2350	n.a.	<15	530	1660	<58	19	520
99Mz17b07	Taro20 incl.5	Fluorite	***	99.0	0.1	0.9	1.0	5200	3400	n.a.	n.a.	<18	<46	13	n.a.	n.a.	4890	n.a.	<5	460	2060	130	<1	640
99Mz17b08	Taro20 incl.6	Fluorite	*	94.7	3.9	1.4	1.4	38200	44000	n.a.	n.a.	1370	350	<26	n.a.	n.a.	1660	n.a.	<22	2100	2420	1890	42	420
99Mz17b09	Taro20 incl.7	Fluorite	***	97.3	1.5	1.2	1.2	1110	1140	n.a.	n.a.	270	<64	<8	n.a.	n.a.	1710	n.a.	<6	230	2120	210	28	660
99Mz17b10	Taro20 incl.8	Fluorite	***	97.4	1.5	1.2	1.1	11200	10200	n.a.	n.a.	250	<190	<30	n.a.	n.a.	1600	n.a.	<22	1210	2090	460	29	670
99Mz17b11	Taro20 incl.9	Fluorite	*****	96.8	2.0	1.2	1.2	2650	3100	n.a.	n.a.	330	<29	<4	n.a.	n.a.	2140	n.a.	31	400	2140	220	15	610
99Mz17b12	Taro20 incl.10	Fluorite	**	96.9	1.7	1.4	1.4	28400	23600	n.a.	n.a.	350	950	<41	n.a.	n.a.	4060	n.a.	35	5400	2090	1040	15	790
Average				97.4	1.4	1.2	1.2	8700	7800			280					2800		33	570	2030	260	21	650
1 SD				0.8	0.7	0.2	0.1	10200	8300			70					1360		3	380	1820	140	7	90
99Mz12d03	Bism3.3 incl.1	Topaz	***	97.2	1.0	1.8	n.a.	n.a.	n.a.	n.a.	n.a.	530	n.a.	n.a.	n.a.	n.a.	1110	<200	n.a.	n.a.	300	n.a.	71	76
99Mz12d04	Bism3.3 incl.2	Topaz	***	97.5	0.9	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	480	n.a.	n.a.	n.a.	n.a.	1240	<120	n.a.	n.a.	270	n.a.	54	67
99Mz12d06	Bism3.3 incl.4	Topaz	*	97.6	0.9	1.6	n.a.	n.a.	n.a.	n.a.	n.a.	<1400	n.a.	n.a.	n.a.	n.a.	1400	<530	n.a.	n.a.	260	n.a.	55	<60
99Mz12d07	Bism3.3 incl.5	Topaz	**	97.5	0.9	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	500	n.a.	n.a.	n.a.	n.a.	1270	<150	n.a.	n.a.	270	n.a.	52	63
99Mz12d08	Bism3.3 incl.6	Topaz	**	97.3	1.0	1.7	n.a.	n.a.	n.a.	n.a.	n.a.	<4000	n.a.	n.a.	n.a.	n.a.	1390	<250	n.a.	n.a.	300	n.a.	48	76
99Mz12d09	Bism3.3 incl.7	Topaz	****	97.5	0.9	1.6	n.a.	n.a.	n.a.	n.a.	n.a.	520	n.a.	n.a.	n.a.	n.a.	1240	<65	n.a.	n.a.	280	n.a.	54	62
99Mz12d10	Bism3.3 incl.8	Topaz	****	97.6	0.8	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	500	n.a.	n.a.	n.a.	n.a.	1200	<51	n.a.	n.a.	280	n.a.	48	74
99Mz12e04	Bism3.3 incl.9	Topaz	*****	97.4	1.2	1.4	n.a.	n.a.	n.a.	<2100	<4100	300	<200	67	750	1600	870	<67	n.a.	n.a.	750	n.a.	49	15
99Mz12e05	Bism3.3 incl.10	Topaz	****	97.5	0.9	1.6	n.a.	n.a.	n.a.	<1100	<2700	360	<120	53	570	1100	1210	<49	n.a.	n.a.	270	n.a.	59	72
Average				97.5	1.0	1.6						460		60	660	1350	1210				330		54	63
1 SD				0.1	0.1	0.1						90		10	127	350	160				160		7	20
99Mz17a04	Gold4 incl.2	Quartz	exploded	96.2	0.10	3.8	3.8	3200	<13500	n.a.	n.a.	<810	<1880	<230	n.a.	n.a.	430	n.a.	<190	6650	<120	6700	2030	290
99Mz17a05	Gold4 incl.3	Quartz	**	95.3	<0.02	4.7	4.4	<100	<3500	n.a.	n.a.	<1900	<10000	<47	n.a.	n.a.	620	n.a.	<30	1650	410	600	990	68
99Mz17a06	Gold4 incl.4	mil Quartz	*	96.5	0.06	3.5	3.5	2000	<8600	n.a.	n.a.	<360	<830	<120	n.a.	n.a.	360	n.a.	<82	2790	110	1550	1050	330
99Mz17a08	Gold4 incl.6	Quartz	**	95.5	<0.07	4.5	4.5	840	<6300	n.a.	n.a.	<530	<1360	<150	n.a.	n.a.	1440	n.a.	<100	4520	220	5100	1780	520
99Mz17a10	Gold4 incl.8	Quartz	**	97.0	0.07	3.0	2.8	1860	<3200	n.a.	n.a.	<190	<420	87	n.a.	n.a.	940	n.a.	<37	2700	180	3700	1680	420
99Mz17a11	Gold4 incl.9	Quartz	***	97.4	<0.05	2.6	2.4	340	<4000	n.a.	n.a.	<650	<700	<110	n.a.	n.a.	790	n.a.	<81	2840	120	4300	2090	320
Average				96.3	0.07	3.7	3.5	1260									830			2900	210	3050	1520	400
1 SD				0.9	0.01	0.9	1.0	800									400			1030	120	1900	480	90

Notes: *Bism 3.3* is a large topaz crystal within quartz-topaz greisen. Bismuth inclusions formed early, at ≥ 370 °C.
Gold 4 a quartz crystal from a Bi and Au-rich vein within quartz-topaz greisen. Inclusions formed late at ca. 250 °C.
Taro 20 is a sample from a sheeted vein system above a ridge in the Mole Granite. Inclusions formed early at ≥ 390 °C.
 See Audetat et al. (2000 a,b) for more information on sample locations and characteristics.
 The numbers in brackets below the elements represent the isotopes analyzed
 The numbers of stars for ablation quality represents bad (*) to excellent (*****) as determined visually on TV screen during ablation
 Outliers (in italics) not used for further evaluation
 Inclusion compositions were normalized to 100 wt% (Bi+As+Te) for quantification.
 Inclusion size was between 8 and 20 μm .
 For locality Bism 3.3, two Te isotopes were recorded to check for interferences. Identical concentration data for ^{126}Te and ^{128}Te demonstrate that interferences are absent.
 n.a. indicates not analyzed
 Values prefixed by "<" were below LOD