

## SUPPLEMENTAL MATERIAL

### Analytical methods

#### *Fluid inclusion petrography*

For this study, doubly polished 500µm thick sections were prepared from existing rock slabs used in the studies of Miron et al. 2013, Rauchenstein-Martinek et al. 2016 and Fusswinkel et al. 2017 and given the corresponding sample names used in these studies (see Table S1). All samples are euhedral quartz crystals with clear growth features that guided fluid inclusion petrographical work. Fluid inclusion assemblages (FIA) are defined as groups of coeval fluid inclusions trapped on temporally constrained petrographic features such as growth zones or healed fractures (Goldstein and Reynolds 1994). Primary and pseudosecondary FIA are entrapped during crystal growth and preserve information on fluid compositions during a mineralization event. Secondary FIA occur in healed fractures cutting through a crystal and so may record fluid compositions that are unrelated to those that their host mineral precipitated from. In this study, only primary and pseudosecondary FIA were used.

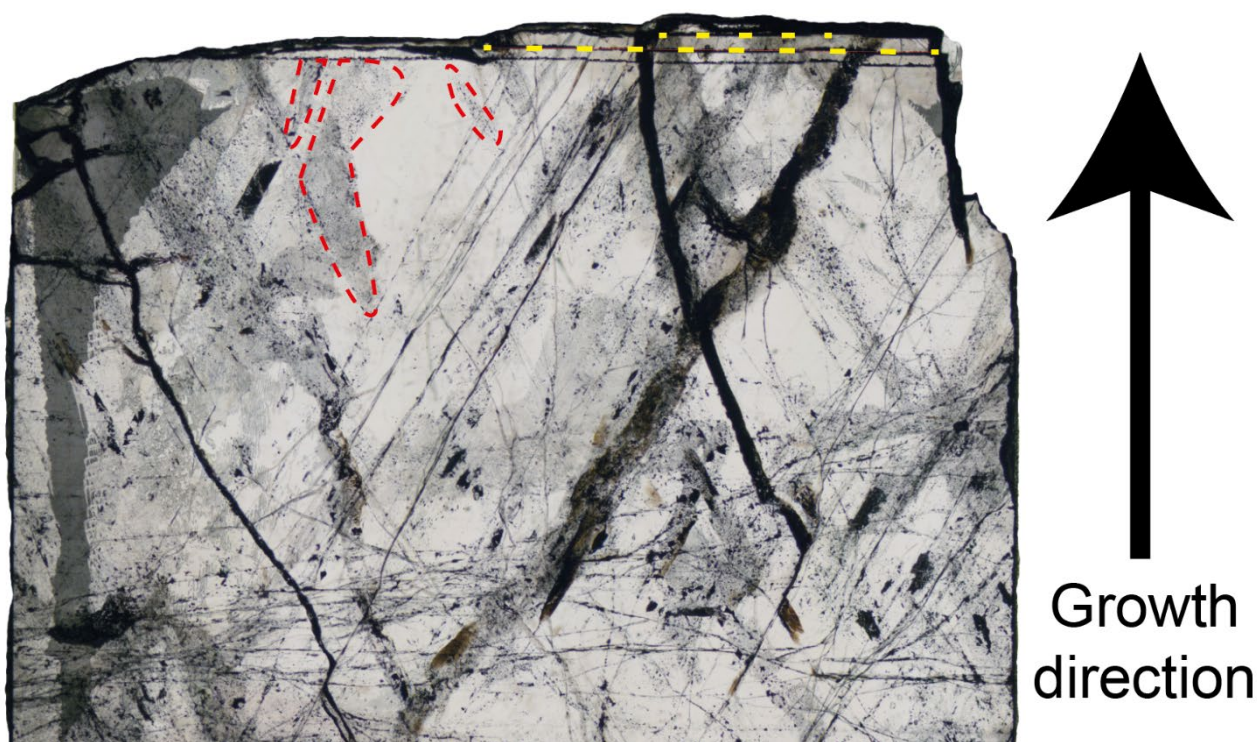


Fig. S1. Sample PAM-19 with growth zoning towards the outer edge of the crystal. The outermost two growth zones are highlighted by dashed yellow lines. Three fluid inclusion assemblages (highlighted by red dashed lines) clearly terminate against the innermost growth zone, identifying them as pseudosecondary. Other healed fractures (not highlighted) cross over the growth zones and to the edge of the crystal. Field of view ca. 2 cm.

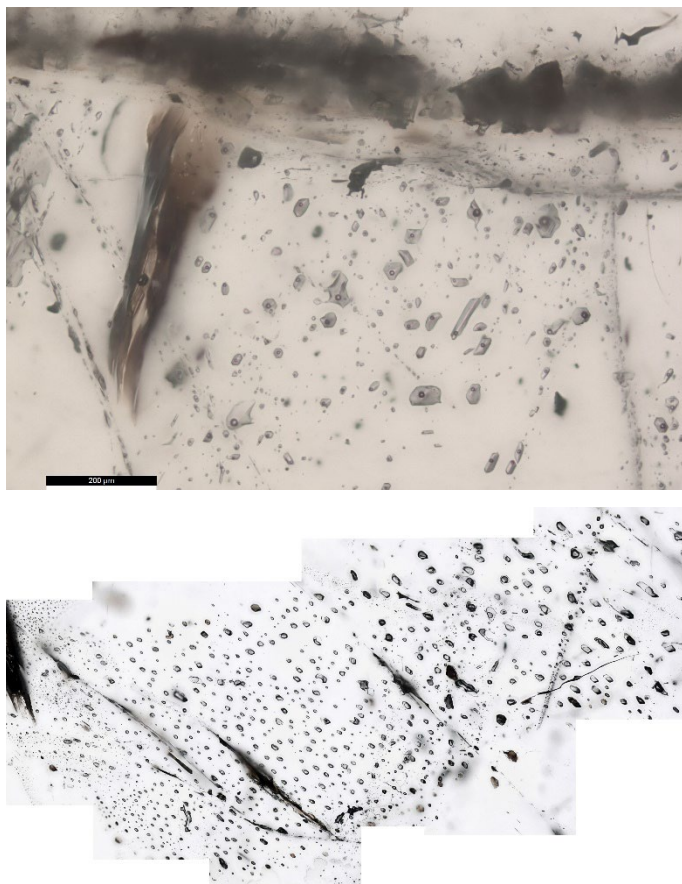


Fig. S2. Left: Sample PAM-19 (Pampalo). Focus-stacked photomicrograph showing a pseudosecondary fluid inclusion assemblage terminating against a growth zone (overgrown by opaque mineral phases) in the upper part of the image. Right: Sample KM-B3 (Bedretto). Collage showing a large pseudosecondary assemblage of aqueous-carbonic inclusions. Field of view ca. 6 mm.

### *Microthermometry*

Fluid inclusion microthermometry was conducted at RWTH Aachen University using a Linkam THMS600G heating freezing stage mounted on a Leica DM3000 petrographic microscope. The stage was calibrated against synthetic fluid inclusion standards to the melting temperature of ice (0.0 °C), the H<sub>2</sub>O-NaCl eutectic (-21.2 °C) and the H<sub>2</sub>O-CO<sub>2</sub> Q3 quadruple point (-56.6 °C) and additionally the critical point of H<sub>2</sub>O (374.1 °C).

Phase transition temperatures were monitored at heating rates of 0.5 °C/min. The reproducibility of freezing experiments is estimated at 0.1 °C. Bulk fluid inclusion compositions were calculated using the programs BULK (aqueous fluids) and Q2 (aqueous-carbonic fluids) from the Clathrates software package (Bakker 1997, 2003).

### *LA-ICP-MS triple halogen microanalysis*

LA-ICP-MS analytical work was performed at RWTH Aachen University using a Coherent GeolasHD 193nm laser ablation system coupled to an Agilent 7900 quadrupole mass spectrometer with high sensitivity s-lens ion lens configuration and operating using Pt skimmer and sampler cones. Samples were loaded into a small volume (1 cm<sup>3</sup>) fast washout ablation cell based on a design from ETH Zurich to ensure high sensitivities and low limits of detection. Instrumental accuracy was monitored using NIST613 as a secondary quality control standard. The instrument was tuned daily to optimize sensitivities, ensure low oxide (ThO/Th < 0.4 %) and doubly charged interference production rates (Ca<sup>2+</sup>/Ca < 0.3 %) as well as stable ablation, transport, and ionization conditions (U/Th = 1.00 ± 0.02). Scapolite Sca17 (Seo et al. 2013, Fusswinkel et al. 2018) was used as external standard reference material for halogen quantification. NIST611 was used to for all other elements. Sodium concentrations from microthermometry were used for internal standardization. The fluid inclusion measurements were bracketed by analysis of the reference materials in order correct for instrument drift. Quantification of LA-ICP-MS results was done using the SILLs data reduction software. The fluid inclusion LA-ICP-MS signals were corrected for quartz host element contributions by bracketing the fluid inclusion signal intervals with intervals for host correction.

The analytical protocol was designed to provide means to monitor interference effects that may affect accurate halogen quantification. Specifically, <sup>111</sup>Cd was included to provide a qualitative measure for the possible occurrence of the [<sup>111</sup>Cd<sup>16</sup>O]<sup>+</sup> interference on <sup>127</sup>I<sup>+</sup>. Low to non-existent signals on <sup>111</sup>Cd would then rule out significant contributions to the <sup>127</sup>I<sup>+</sup> signal by this oxide-based interference. <sup>125</sup>Te was included in order to monitor the magnitude of [<sup>85</sup>Rb<sup>40</sup>Ar]<sup>+</sup> as a proxy for the [<sup>87</sup>Rb<sup>40</sup>Ar]<sup>+</sup> interference on <sup>127</sup>I<sup>+</sup>. This was necessary because <sup>87</sup>Rb cannot be measured directly due to an isobaric interference with <sup>87</sup>Sr. In addition, <sup>85</sup>Rb has a higher isotopic abundance than <sup>87</sup>Rb (72.17 % vs 27.83 %, respectively), so that the magnitude of the [<sup>87</sup>Rb<sup>40</sup>Ar]<sup>+</sup> interference would be proportionally even smaller. No signals were observed on the <sup>111</sup>Cd or <sup>125</sup>Te mass, proving that no significant [<sup>85</sup>Rb<sup>40</sup>Ar]<sup>+</sup> or [<sup>87</sup>Rb<sup>40</sup>Ar]<sup>+</sup> interferences affected the iodine concentration values. <sup>162</sup>Dy was included to monitor the possible occurrence of the <sup>162</sup>Dy<sup>++</sup> doubly charged interference on <sup>81</sup>Br. Significant count rates on <sup>162</sup>Dy would lead to a proportionally contribution by the doubly charged ion on <sup>81</sup>Br count rates and deteriorate accuracy. Neither the samples nor the Sca17 reference material showed any signals on <sup>162</sup>Dy, proving that Br quantification is reliable. Please refer to Fusswinkel et al. 2018 for a more in-depth discussion of the analytical approach and the measures taken to monitor and rule out significant interference effects on halogen quantification.

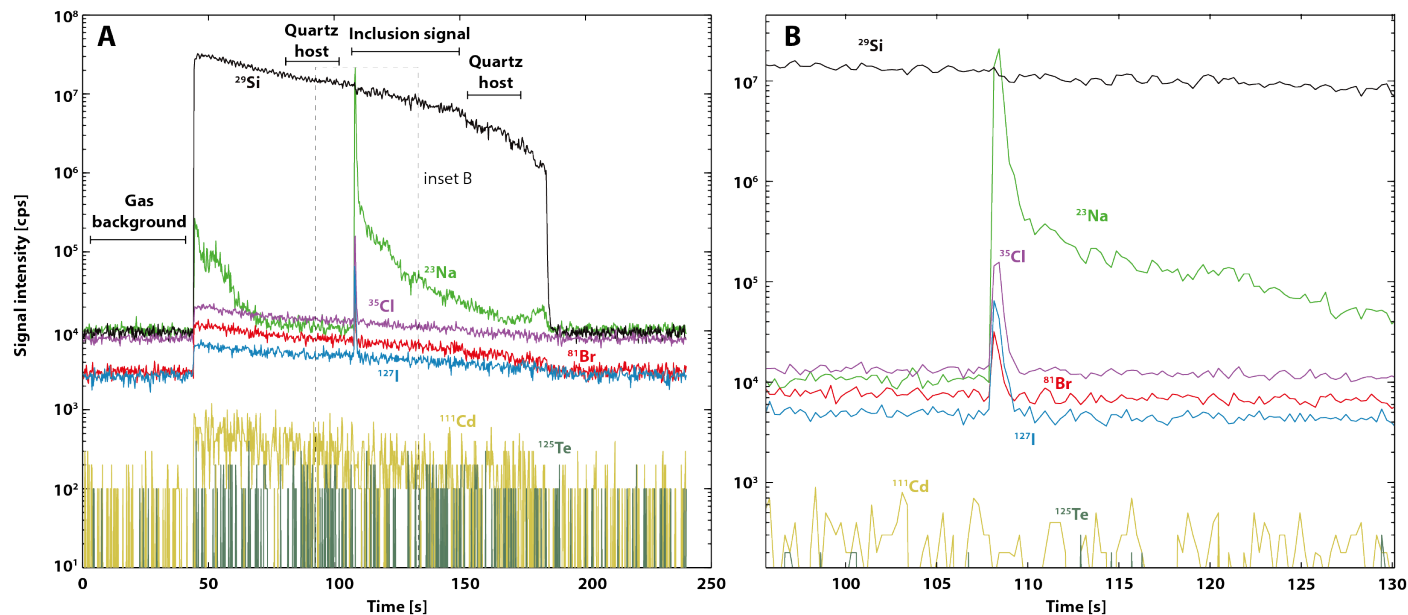


Fig. S3: Representative fluid inclusion LA-ICP-MS spectra (sample DM2A9, Thusis). A: complete spectrum showing signal intensities of Si, Na, Cl, Br, I, Cd and Te (other signals omitted for clarity) as well as signal intervals used for background correction, host correction and the fluid inclusion signal. B: Detail view of the inclusion signal.

Table S2: Instrumental parameters for LA-ICP-MS analysis

Item	Settings
<i>Laser ablation system</i>	Coherent GeolasHD 193nm
Ablation cell	Ultrafast washout small volume (~ 1 cm <sup>3</sup> ) cell
Laser energy density	10 J/cm <sup>2</sup> on all standard reference materials 15 – 25 J/cm <sup>2</sup> for quartz ablation during fluid inclusion analysis
Repetition rate	10 Hz
Crater size (all circular)	Adjusted to size of fluid inclusions
Carrier gas flow (He 5.6)	1.1 l/min
<i>ICP-MS system</i>	Agilent 7900s (Pt cone configuration)
Plasma gas flow (Ar 5.0)	15 l/min
Auxiliary gas flow (Ar 5.0)	0.85 l/min
RF Power	1550 W
U/Th	~1.00 ± 0.02
ThO/Th	< 0.4 %

Ca <sup>2+</sup> /Ca	< 0.3 %
Reference materials	NIST611 for all elements except halogens Sca17 for Cl, Br and I quantification NIST613 as secondary standard
Isotopes measured	<sup>7</sup> Li, <sup>11</sup> B, <sup>23</sup> Na, <sup>29</sup> Si, <sup>34</sup> S, <sup>35</sup> Cl, <sup>39</sup> K, <sup>44</sup> Ca, <sup>75</sup> As, <sup>81</sup> Br, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>111</sup> Cd, <sup>118</sup> Sn, <sup>121</sup> Sb, <sup>125</sup> Te, <sup>127</sup> I, <sup>128</sup> Te, <sup>133</sup> Cs, <sup>137</sup> Ba, <sup>162</sup> Dy
Dwell times	10 ms: <sup>7</sup> Li, <sup>11</sup> B, <sup>23</sup> Na, <sup>29</sup> Si, <sup>34</sup> S, <sup>39</sup> K, <sup>44</sup> Ca, <sup>75</sup> As, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>111</sup> Cd, <sup>118</sup> Sn, <sup>121</sup> Sb, <sup>125</sup> Te, <sup>128</sup> Te, <sup>133</sup> Cs, <sup>137</sup> Ba, <sup>162</sup> Dy  20 ms: <sup>35</sup> Cl, <sup>81</sup> Br  30 ms: <sup>127</sup> I

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## Additional References for Data shown in Figure 1, Figure 2 and Table 2 in the Text

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