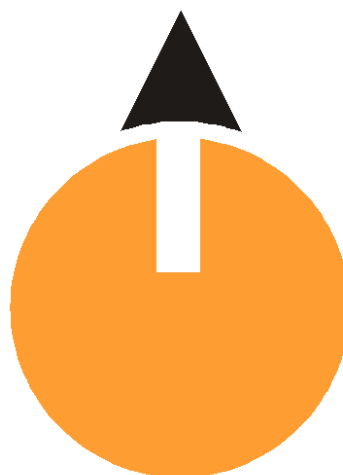




## Grant Agreement Number 608553

# IMAGE

## Integrated Methods for Advanced Geothermal Exploration



### IMAGE-D4.03

#### Final report on: *High temperature (>380°C) measurement*

Responsible author	Giovanni Ruggieri (IGG-CNR)
Responsible WP-leader	Sæunn Halldórsdóttir (ÍSOR)
Responsible SP-leader	Gylfi Páll Hersir (ÍSOR)
Contributions by:	Giovanni Ruggieri, Andrea Orlando, Laura Chiarantini, Valentina Rimondi (IGG-CNR) Tobias Björn Weisenberger (ÍSOR)



## Introduction & summary

The aim of this task is the development of a method to measure high reservoir temperature ( $\geq 380^{\circ}\text{C}$ ) by the production of synthetic fluid inclusions within an apparatus that will be placed in high-temperature geothermal wells. Super-hot geothermal systems in magmatic areas are, in fact, a possible target for the future geothermal exploration either for the direct exploitation of fluids or as a potential reservoirs of Enhanced Geothermal Systems. Reservoir temperature determination are crucial for the assessment of the geothermal resources, however, measurements of temperature (T) in high-temperature ( $>380^{\circ}\text{C}$ ) geothermal wells are difficult or impossible by using conventional logging tools. In fact, mechanical temperature sensors (KTG bi-metal, KTG LV based on bourdon tube principle) and electronic high-temperature tools (thermocouples, resistance thermometers, thermally shielded) have a maximum operating temperatures of  $380^{\circ}\text{C}$  and  $350^{\circ}\text{C}$ , respectively (HiTI, 2010). Furthermore, conventional optical fibers device can be used to maximum temperature of  $275^{\circ}\text{C}$ . For temperature  $>380^{\circ}\text{C}$  "melting tablets" with known melting temperature (Zn:  $419^{\circ}\text{C}$ ) were sometimes used, however such method gives minimum temperature of temperature ranges. Thus, un-conventional methods should be developed in order to overcome this problem.

The European HiTI project (High Temperature Instruments for Supercritical Geothermal Reservoir Characterisation & Exploitation) which was carried out in 2007-2010 developed, built and tested in the field new downhole tools and developed chemical approaches for deep high temperature boreholes. In particular, during the HiTI a wire-line temperature probe with a possible use up to  $500^{\circ}\text{C}$  was developed and was tested at temperature up to  $320^{\circ}\text{C}$ . Moreover, a PLT multi-sensor within a heat shielding flask tolerating  $400^{\circ}\text{C}$  was also developed.

In the framework of IMAGE project, we developed a possible method alternative to the above methodology for borehole high-temperature measurement by the production of synthetic fluid inclusions (F.I.) within an apparatus that will be placed in geothermal wells.

This is based on the entrapment of aqueous fluid (of known chemical composition and salinity) in pre-fractured mineral chips; for a given composition, the density and the molar volume of synthetic F.I. entrapped in the fractures will be function of Pressure (P) and T. Therefore, the density (and molar volume) of the synthetic F.I. can be obtained from microthermometry, and isochores can be computed and the T of trapping of synthetic F.I. can be estimated with a good approximation from isochores if P is known.

Synthetic F.I. as logging tools was first used for temperature measurement and fluid sampling in the Continental Scientific Drilling Program in the Valles caldera, New Mexico, U.S.A. (Bethke et al., 1990). In this case F.I. were synthesized for 21 days and their formation temperature corresponded to that measured using conventional techniques ( $293.6^{\circ}\text{C}$  at 1762 m depth). Then, Sawaki et al. (1997) utilized the synthesis of F.I. to measure temperatures and sample fluids in high-temperature geothermal wells; they tested this methodology in a hole drilled in the Kakkonda (Japan) geothermal field and after 24 days, they got temperatures measured from F.I. consistent with borehole temperatures measured by conventional logging tools.

Later, Sekine et al. (2004) through lab experiments estimated trapping conditions of fluids in pre-fractured quartz utilizing different sets of synthetic F.I. with different salinities. They got synthetic F.I. after 5 days' autoclave experiments at  $T= 375\text{-}475^{\circ}\text{C}$ ,  $P=39\text{-}62$  MPa.

The method elaborated in this task is based on the production of synthetic fluid inclusions within an apparatus that will be placed in geothermal wells. This apparatus consist of gold capsules placed within a stain steel vessel (micro-reactor), the latter will be partially filled with an amount of distilled water such that the the P-T conditions in the micro-reactor will follow the liquid-vapor curve of  $\text{H}_2\text{O}$  and critical isochore of  $\text{H}_2\text{O}$  (characterized by a density of  $0.322$  g/cm<sup>3</sup>) above the critical point of  $\text{H}_2\text{O}$ . The gold capsules contain: i) a pre-fractured quartz fragment (devoid of natural fluid inclusions) in which synthetic F.I. will be trapped, ii) an alkaline, saline aqueous solution (9.1 wt.% NaCl + 0.4 wt.% NaOH), i.e. the solution that will be trapped in the synthetic F.I. and iii) powdered silica. The utilization of alkaline aqueous solutions (in quartz) decrease the time necessary to form F.I., this is a crucial point for measurements in high-T geothermal well



(>380°C), as the resistance of the cable needed for lowering devices in geothermal wells decrease with time at high-T and with the prolonged exposure to high-T aggressive fluid. A set of experiments have been performed in the laboratory either by placing the gold capsules in an externally heated pressure vessel and by placing a commercial micro-reactor containing the gold capsules within a furnace. Such experiments demonstrated that synthetic F.I. form within a relatively short time (even in 48 hours) and that trapping temperatures of synthetic F.I. give a good estimate of the experimental temperatures. Finally, a test was carried out by lowering the apparatus in the KJ-35 geothermal well (Krafla, Iceland) at about 1750 m below the ground level, at such depth conventional method recorded a T of about 335°C. The test showed that synthetic F.I. formed and that the trapping temperature of synthetic F.I. (339-343°C) closely approach the measured temperature.

In conclusion, the proposed method can be used to measure the temperature in relatively high-temperature geothermal well (<380°C) but it can be potentially applied for temperature measurements of geothermal well with temperature up to 427°C (i.e. the working temperature limit of the utilized commercial pressure vessel). This limit can be extended to higher temperature by using different pressure vessels.



## **TABLE OF CONTENT**

<b>INTRODUCTION &amp; SUMMARY</b>	<b>2</b>
<b>Chapter 1. Description of the method</b>	<b>5</b>
<b>Chapter 2. Procedure</b>	<b>5</b>
<b>Chapter 3. Laboratory experiments</b>	<b>6</b>
<b>3.1 Preparation of gold capsules, minerals and solution used</b>	<b>7</b>
<b>3.2 Synthesis of fluid inclusions in lab using an externally heated pressure vessel</b>	<b>7</b>
<b>3.2.1 Equipment and experimental procedure</b>	<b>7</b>
<b>3.2.2 Experiments</b>	<b>7</b>
<b>3.2.3 Fluid inclusion results</b>	<b>7</b>
<b>3.2.4 Main results</b>	<b>8</b>
<b>3.3 Synthesis of fluid inclusions in lab using a micro reactor in a furnace</b>	<b>8</b>
<b>3.3.1 Equipment and experimental procedure</b>	<b>9</b>
<b>3.3.2 Experiments</b>	<b>9</b>
<b>3.3.3 Fluid inclusion results</b>	<b>10</b>
<b>3.3.4 Main results</b>	<b>11</b>
<b>Chapter 4. Experiment with the micro reactor in the KJ-35 geothermal well (Krafla, Iceland)</b>	<b>11</b>
<b>4.1 Location and description of the test</b>	<b>11</b>
<b>4.2 Fluid inclusion results</b>	<b>12</b>
<b>4.3 Comparison with present-day bore-hole measured temperature</b>	<b>12</b>
<b>Chapter 5. Errors estimate of the method</b>	<b>13</b>
<b>Chapter 6. Final remarks</b>	<b>13</b>
<b>Acknowledgements</b>	<b>14</b>
<b>References</b>	<b>14</b>
<b>Figures</b>	<b>16</b>
<b>Tables</b>	<b>36</b>



## 1. Description of the method

Synthetic F.I. were successfully produced in Experimental Mineralogy and Petrology Lab (CNR-IGG – Florence) at high T (535-540°C) after 14 days (Borrini et al., 2006). Based on these studies, we operated modifications on the procedure adopted in the previous studies in order either to protect pre-fractured crystals (which are inserted in gold capsules hosted in a stain steel vessel, i.e. micro-reactor) to be lowered in the well, to improve data reliability and to minimize the time of formation of synthetic F.I.. Our new method is a modification and simplification of the method proposed by Sekine et al. (2004).

The base of method here proposed is computation of the trapping T of synthetic F.I. from the intersection of the isochore of a saline fluid with the liquid-vapor curve of H<sub>2</sub>O or the critical isochore of H<sub>2</sub>O. This could be obtained by using a saline aqueous fluid as the fluid that will be placed in the gold capsule and which will be trapped in the synthetic F.I. and by setting the amount of distilled H<sub>2</sub>O to be introduced in micro-reactor equal to the amount of H<sub>2</sub>O corresponding to the critical density of water (0.322 g/cm<sup>3</sup>). The presence of NaCl in aqueous solution raises the critical point, thus extending the liquid-vapour field to higher T respect to pure water. Furthermore, it changes the slope of the isochores by virtue of the change of fluid density.

Pressure within the micro-reactor varies with T along the H<sub>2</sub>O liquid-vapor curve or along the critical isochore. Moreover, P and T within gold capsule is equal to those in the micro-reactor, in fact: 1) the gold capsule and the micro-reactor should be in thermal equilibrium after short time (few minutes); 2) P inside the gold capsule is nearly equal to the P in the micro-reactor because of the ductile nature of gold. Since the P and T inside the gold capsule are equal to the P and T in the micro-reactor the P-T of trapping of synthetic F.I. correspond to the intersection of the isochore of the synthetic F.I. with the isochore of H<sub>2</sub>O with critical density or the liquid vapor curve. Figure 1 shows the theoretical P-T conditions of trapping for H<sub>2</sub>O-NaCl fluid with different NaCl concentrations (10, 15 and 20 wt.%) trapped at 400, 450 and 500°C obtained from the intersections of the isochores of the H<sub>2</sub>O-NaCl fluids and the critical isochore of water.

## 2. Procedure

Prior to test the synthesis of fluid inclusions directly in the geothermal well (“in situ”) we performed experiments in the laboratory to ensure that the proposed method gives reliable results at relatively high temperature (>380°C) and that inclusions form in a relatively short time (<3 days). In particular, the time necessary for the formation of aqueous fluid inclusions generally decrease increasing T; they generally form in few days at T>600°C but they need 3-6 weeks at T<500°C (Bodnar and Sterner, 1987). However, the utilization of alkaline aqueous solutions (in quartz) should decrease the time necessary to fluid inclusions to form Sawaki et al. (1997) (see also Introduction & summary).

Thus, our research developed in three different subsequent stages:

- Laboratory experiments by using the gold capsules within an externally heated pressure vessel in order to establish if the proposed method provide reliable T of trapping of synthetic F.I. (i.e. the method can be used for T measurement >380°C) and if the method allow the formation of synthetic F.I. in a relatively short time (i.e. 48 hours).
- Laboratory experiments carried out by using a stainless steel micro-reactor in which the gold capsule was inserted together with an amount of distilled water



such that P-T conditions in the micro-reactor follow the liquid-vapor curve of H<sub>2</sub>O and critical isochore of H<sub>2</sub>O above the critical point of H<sub>2</sub>O. These experiments were conducted by leaving the micro-reactor within a furnace at temperature up to 400°C and were aimed to reproduce the condition existing in a geothermal well.

- Test in KJ-35 geothermal well (Krafla, Iceland) by lowering the stainless steel micro-reactor partially filled with distilled water and containing gold capsules (hosting pre-fractured quartz, the saline, alkaline solution and powdered silica) for 69 hours.

Each stage will be hereafter described. Common to all these phases is the preparation of the capsules, which is described in the next paragraph.

### 3. Laboratory experiments

#### 3.1 Preparation of gold capsules, minerals and solution used

The procedure used to produce synthetic fluid inclusions was mostly taken from Bodnar and Sterner (1987). Chips, aqueous solution and sealant (silica or fluorite powders) were loaded into pure gold capsules (O.D.= 4.8 mm; I.D. =4.5 mm; length= 17-28 mm, Figure 2) that were sealed using an arc welder equipped with a graphite electrode. The goodness of the welds was checked weighing capsules soon after the welding and after storing capsules overnight at 110°C.

Inclusion-free Brazilian quartz crystals (Figure 3) were cut in 2 cm thick slabs and 3-4 mm (larger size) quartz chips were thus obtained smashing slabs into a vice. Chips were stored in an oven at 350°C for 6 hours before quenching in a deionized water. This process caused the formation of many fractures radiating from the edge into the interior of the chips. The chips were put in ultrasonic bath for 5 minutes and subsequently in an oven at 110°C overnight to remove any water entered into the fractures.

During the lab tests with the externally heated pressure vessel two experiments were performed using fluorite chips, prepared with the same procedure as for quartz. Some studies (e.g. Dubessy et al., 2000; Teinturier and Pironon, 2003) have demonstrated that this mineral can be a good alternative to quartz in the production of synthetic fluid inclusions. Anyway, the utilization of fluorite was abandoned, because using our procedure we noticed that fluid inclusions forms easily in quartz respect to fluorite. A variable number of chips (1, 2 or 3) was inserted into the capsule. At the end of the experiments chips were recovered and they were polished on both sides in preparation for microthermometric analysis.

We decided to use a NaCl-containing aqueous alkaline solution as fluid to be trapped in the fractures of chips. In fact, solubility of silica in NaCl aqueous solutions is higher than in pure water and alkaline solutions also allow higher solubilities of silica (e.g. Anderson and Burnham, 1967). The increase of silica solubility allows to the fractures in the chips to be healed easily at P-T conditions of the experiment. Thus, an aqueous solution at pH=13 was prepared adding 4 g NaOH and 10 g NaCl (99.99 %, Suprapur Merck) to 1 liter of deionized water obtaining a solution with 9.5 wt.% of total dissolved salts. In the two runs in which fluorite chips were utilized the solution was prepared without adding NaOH. The amount of solution inserted in the capsules was set as close as possible to have bulk density in the gold capsule of 0.559 g/cm<sup>3</sup> i.e. the critical density of a saline (~10 wt.% NaCl) aqueous solution. Although the fracture will heal without an additional source of silica, we added silica powder (99.995+ %, Aldrich Chem. Co.) since it shortens healing times (Bodnar and Sterner, 1987). In those experiments in which fluorite chips were used (instead of



quartz), fluorite powders (grinded from the same mineral used in chips) was inserted in the capsules as sealant.

## **3.2 Synthesis of fluid inclusions in lab using an externally heated pressure vessel**

### **3.2.1 Equipment and experimental procedure**

The utilised equipment was a Leco Corp. (model HR-2B-2) cold seal pressure vessel. Capsules (prepared according to the procedure described in paragraph 3.1) were inserted in a René 41 pressure vessel (Figure 4). This is closed in the upper end by a cone-in-cone seal which always remain outside of the furnace (hence cold-seal) and allow the pressure medium (water) to enter/exit vessel. Capsule is kept in the lower end of the vessel by a solid alumina rod and vessel is positioned into a sliding vertical furnace (Figure 4). Pressure is measured by pressure gauges while temperature is controlled and monitored by K-type thermocouples (Ni-Cr)/(Ni-Al).

### **3.2.2 Experiments**

Five experiments were performed using fluorite or quartz chips at the following conditions:  $T = 280^{\circ}\text{C}$ ,  $P = 8 \text{ MPa}$  and  $T = 400^{\circ}\text{C}$ ,  $P = 30 \text{ MPa}$  (Table 1). Pressure conditions of the experiments carried below the critical temperature of pure water (i.e. at  $280^{\circ}\text{C}$ ) were fixed at about 8 MPa in order to have P-T conditions relatively close to the liquid-vapour curve of  $\text{H}_2\text{O}$  (in the liquid field). Whereas, P-T of the experiments performed above the critical temperature of pure water (i.e. at  $400^{\circ}\text{C}$ ) were set at about 30 MPa in order to have P-T conditions on the critical isochore of  $\text{H}_2\text{O}$ .

The duration of experiments varied from 48 to 140 hours. Experiments run at the same T, P and duration were performed inserting relative capsules in a single pressure vessel, since it can host up to three capsules. At the end of the experiments the vessel was extracted from the furnace and cooled in air at  $T < 80^{\circ}\text{C}$ . After that, the capsules were recovered and weighted and experiments were considered successful only if capsules did not change significantly ( $\pm 0.001 \text{ g}$ ) their weight compared to before the experiment.

### **3.2.3 Fluid inclusion results**

During the experiments synthetic F.I. systematically formed in quartz even in short time (i.e. 48 hours at  $400^{\circ}\text{C}$ ) by using alkaline, saline aqueous solution. On the other hand, synthetic F.I. in fluorite were not observed.

In quartz synthetic F.I. occurs within typical curvilinear healed fractures (Figure 5). Necking down processes (Roedder, 1984) produced several F.I. often with relatively regular shapes.

### **Microthermometry**

Microthermometric measurements were performed at Linkam THMSG600 heating-freezing stages coupled with ZEISS POL-BK microscope at CNR-IGG. The stages were calibrated by using pure  $\text{H}_2\text{O}$  with critical density, and mixed  $\text{H}_2\text{O}-\text{CO}_2$  ( $\text{CO}_2$  25% M) synthetic fluid inclusions. Accuracy was estimated to be  $\pm 0.1^{\circ}\text{C}$  for final ice melting ( $T_{m_{\text{ice}}}$ ) and  $\pm 1^{\circ}\text{C}$  for the vapour/liquid homogenization ( $T_h$ ). Salinity (expressed in wt.% NaCl equiv.) of F.I. have been computed from  $T_{m_{\text{ice}}}$  by using HOKIEFLINCS\_H2O-NACL Excel spread sheet (Steele-MacInnis et al., 2012) and the equation of Bodnar (1993).



In order to avoid the collection of data of F.I. not representative of the trapping conditions, for microthermometric measurements of F.I. produced in all experiments we selected Fluid Inclusion Assemblages (FIAs of Goldstein and Reynolds, 1992). In each FIAs we analysed at least 5 F.I.; all single FIAs are characterized by consistent microthermometric data (Figure 6), indicating that F.I. in the FIA are representative of the density (molar volume) of the original trapped fluid (i.e. they were not affected by post-trapping processes which modified the original density) and they therefore can be used for T estimate.

Microthermometric results of F.I. formed by using externally heated pressure vessel are reported in Table 2 and Figure 7. Synthetic F.I. in experiment SFI3 (P: 8 MPa, T: 280°C, duration 140 hours) showed  $T_h$  from 272 to 277°C with a mean of 274°C and a standard deviation of 1°C (Table 2, Figure 6).  $T_h$  of F.I. of experiment SFI4 (P: 30 MPa, T: 400°C, duration 48 hours) varies from 383 to 386°C (Figure 7) with a mean  $T_h$  of 384°C and standard deviation of 0.5°C, whereas F.I. of experiment SFI5 (P: 30 MPa, T: 400°C, duration 140 hours) were characterized by  $T_h$  from 360 to 363°C, with a mean value of 361°C and a standard deviation of 0.1°C (Table 2, Figure 7).  $T_{m_{ice}}$  was also measured in several F.I. of SFI3 experiment and in few F.I. of SFI4 and SFI5 experiments. All F.I. show a relatively restricted range of  $T_{m_{ice}}$  from -6.5 to -6.7°C corresponding to salinity between 9.9 and 10.1 wt.% NaCl equiv. (Table 2). These salinities are higher than the concentration expressed in wt.% of the dissolved solids in the original solution (9.1 wt.% of NaCl + 0.4 wt.% of NaOH). However, considering the wt.% of NaCl of the solution (9.1 wt.%) plus the wt.% of NaCl corresponding to the conversion from NaOH molality to NaCl molality (i.e. 0.6 wt.%) we have a total salinity expressed in wt.% of 9.7, close to the salinity indicated by F.I.. In addition, since the saline fluid introduced in the gold capsule is rather small (0.06-0.16 g.), evaporation process during capsule preparation may have also increased the salinity of the solution.

### **Temperature computation from synthetic F.I.**

Trapping temperatures of synthetic F.I. have been calculated from F.I. isochores considering the experimental pressure values (Figures 8, 9 and 10). F.I. isochores and liquid-vapour curves have been computed using the HOKIEFLINCS\_H2O-NACL Excel spread sheet (Steele-MacInnis et al.; 2012) from the mean  $T_h$  of synthetic F.I. of each experiment considering a fluid salinity of 10.0 wt.% of NaCl equiv.. For such computation the HOKIEFLINCS\_H2O-NACL Excel spread sheet (Steele-MacInnis et al., 2012) considers the data of Atkinson (2002) and Bodnar and Vityk (1994). Figures 8, 9 and 10 show that the isochores of synthetic F.I. pass very close to the experimental P-T conditions. In particular, trapping T of synthetic F.I. calculated at the experimental P differ from the experimental T of less than 7°C.

### **3.2.4 Main results**

The main results of these experiments are: 1) synthetic F.I. forms in quartz in relatively short time (48 hours at 400°C) using alkaline aqueous solution and quartz chips and 2) the estimated trapping T of synthetic F.I. is close to the actual experimental T.

## **3.3 Synthesis of fluid inclusions in lab using a micro reactor in a furnace**

After the successful experiments got through the utilization of an externally heated pressure vessel, we decided to acquire a micro-reactor with the perspective to utilize it in a geothermal well. Before doing that, it was necessary to make experiments in the laboratory inserting it in a furnace with the aim to verify: 1) if the synthetic F.I.





form by using the micro-reactor, 2) if they form in relatively short time and 3) if the T estimated from synthetic F.I. are coherent with the experimental T. Equipment and experimental procedure will be discussed in the next paragraph.

### 3.3.1 Equipment and experimental procedure

The micro-reactor should have the following features in order to fit our needs: a) internal diameter >5 mm in order to host capsules; b) external diameter as low as possible (preferably < than 30 mm) in order to be easily lowered in the geothermal wells; c) it should operate at least at 400°C and 50 MPa.

After a market research, we decided to acquire the micro-reactor model MS-15 HiP from the High Pressure Equipment Company (Erie, Pennsylvania, USA). The instrument (Figure 11) has the following features:

- Internal diameter: 7.9 mm.
- Maximum external diameter: 29.3 mm.
- Overall length: about 370 mm.
- Capacity: 15 ml.
- Material of construction: Type 316 stainless steel.
- Working T: up to 427°C. This is made possible by the metal to metal seal construction.
- Working P: up to 138 MPa.
- Weight: about 750 g.

We also added two threaded plugs to both ends of the micro-reactor in order to isolate it from the outside.

For the experiments the micro-reactor has been filled with 1 or 2 capsules (prepared according the procedure described in paragraph 3.1) and with an amount deionized water, corresponding to the critical density of water (0.322 g/cm<sup>3</sup>). Therefore, on heating the water in the micro-reactor follow the P-T of the liquid-vapour curve of H<sub>2</sub>O up to the critical point and then at higher T the critical isochore (0.322 g/cm<sup>3</sup>). For this purpose, volume of capsules was determined.

The micro-reactor was inserted in a furnace (Figure 12a) equipped with a horizontal alumina tube (diameter =5 cm; length =60 cm) and a control K thermocouple (Ni-Cr)/(Ni-Al). The insertion occurred at T<50°C of experimental T. The T was then increased up to experimental T at a 3°C/min rate. This procedure was adopted in order to avoid furnace overheating. An additional monitoring K thermocouple was inserted together with the micro-reactor (Figure 12b) in the furnace with the junction as close as possible to the capsule(s). Prior to do experiments, furnace calibration was executed (at both 350 and 400°C, Figure 13) just to individuate the hot zone of the furnace and to estimate T gradients into the furnace. This is a crucial point since furnace size is slightly larger than micro-reactor. The ideal solution would be to have a very large furnace with hot zone size comparable to micro-reactor size. Results show that hot zone is about 4 cm wide from the geometric centre of the furnace to the rear part of it. T gradients are high since T decrease of about 50°C shifting from the hot zone of ~15-20 cm (Figure 13). Due to geometric constraints of both micro-reactor and furnace, capsule was lodged at ~10 cm from the geometric centre of the furnace towards its back and this implied to set control K thermocouple of ~ +15-20°C respect to the experimental T.

At the end of experiments furnace was let to cool removing the front stopper and setting T to lab T. After ~1 h (at T<80°C) the micro reactor was removed from the furnace and chip was recovered from the capsule.

### 3.3.2 Experiments



A preliminary experiment was programmed placing the micro-reactor in the furnace with water and no capsule inside, just to test the seal capacity of the instrument at P-T conditions of the experiments. The test was positive and experiments at T in the 350-400°C range were executed (Table 3). A sketch of an experiment with T gradient in the furnace is shown in Figure 14.

Note, that the experimental T are the temperatures of the hot zone in the furnace which is only about 4 cm wide. Whereas the overall length of the micro-reactor is about 37 cm implying that the micro-reactor was subject to significant thermal gradient during the experiment (Figure 14). As a consequence, during the experiment the water in the micro-reactor was likely interested by convection that produce a significant decrease of the thermal gradient within the micro-reactor, setting the temperature at the site of the gold capsule between the highest and the lowest temperature values measured along the micro-reactor length.

Durations varied from 47 to 163 h. One, two or three quartz chips were used for each capsule. Capsule length was around 20 mm for all experiments. One experiment (SFI9) was programmed with pure water (milli Q) into the capsule, just to assess if fluid inclusions forms using such solution; anyway, it failed since capsule weight varied after the experiment. The same occurred in SFI10 experiment whose capsule was inserted together with SFI9 capsule. All the other experiments were successful.

### 3.3.3 Fluid inclusion results

Synthetic F.I. formed during experiment SFI6, SFI7, SFI8, SFI11 and SFI12 (Figure 15), in particular F.I. also formed in relatively short time during SFI8 experiment (<2 days) at T <350°C (experimental T = 350°C) i.e. at T lower than the T (400°C) of the 2 days experiment SFI4.

#### Microthermometry

Microthermometric results of F.I. formed by a micro reactor in a furnace are reported in Table 2 and Figure 16. Synthetic F.I. formed during experiment SFI6 (duration 140 hours) showed  $T_h$  from 360 to 363°C with a mean of 361°C and a standard deviation of 0.4°C,  $T_h$  of F.I. of experiment SFI7 (duration 87 hours) varies from 361 to 363°C with a mean  $T_h$  of 362°C and standard deviation of 0.1°C, F.I. of experiment SFI8 (duration 47 hours) were characterized by  $T_h$  from 336 to 341°C, with a mean value of 338°C and a standard deviation of 1°C and F.I. of experiment SFI12 (duration 56 hours) showed  $T_h$  around 372°C (Table 2, Figure 16).

$T_{m_{ice}}$  was also measured in some F.I. of SFI7 and SFI12 experiments. All F.I show  $T_{m_{ice}}$  of -6.5°C corresponding to salinity of 9.9 wt.% NaCl equiv. (Table 2). This salinity is coherent with the salinity of the F.I. formed during experiment using the externally heated pressure vessel (Table 2).

#### Temperature computation from synthetic F.I.

As the pressure within the micro-reactor varies with temperature along the H<sub>2</sub>O liquid-vapour curve or along the critical isochore the trapping T of synthetic F.I. can be computed from the intersection of F.I. isochores (i.e. isochore for H<sub>2</sub>O-NaCl fluid with 10 wt.% NaCl) and the liquid-vapor curve of H<sub>2</sub>O for  $T \leq T_c$  ( $T_c$  = critical T of water) or with the critical isochore of H<sub>2</sub>O for  $T > T_c$ . F.I. isochores have been computed with same procedure explained in paragraph 3.2.3.

Figure 17 shows that the trapping T of the of synthetic F.I. is 1-2°C above the mean  $T_h$  of F.I.. Trapping T is systematically lower than the experimental T, as expected, considering the large thermal gradient within the furnace and that the experimental T is the highest T in the furnace. The trapping T in the different experiment is always



between the experimental T (i.e. the highest T) and the lowest T in the furnace as could be expected considering that convection inside the micro-reactor would produce intermediate T.

### **3.3.4 Main results**

The main results of these experiments are: 1) synthetic F.I. forms in quartz in relatively short time even at relatively low T (48 hours at experimental T of 350°C and trapping T of 339°C; 56 hours at experimental T of 396°C and trapping T of 373°C), 2) the trapping T of synthetic F.I. coherent with the range of T given by the thermal gradient present along the micro-reactor during the different experiments within the furnace.

## **4. Experiment with the micro reactor in the KJ-35 geothermal well (Krafla, Iceland)**

### **4.1 Location and description of the test**

The principle is the same as described for the micro-reactor inserted into a furnace (paragraph 3.3). The instrument is lowered in the borehole and synthetic F.I. trapping T, computed from the intersection of the F.I. isochore with the liquid-vapor curve of H<sub>2</sub>O or with critical isochore of H<sub>2</sub>O, should allow to estimate local T.

The geothermal well of the experiments is located in the Krafla geothermal system (Iceland) (Figure 18) which is exploited by Landsvirkjun (National Power Company of Iceland). Krafla is an important geothermal area associated to the Krafla central volcano which is located within the neo-volcanic North-Iceland Rift Zone characterized by active rifting (e.g. Thordarson and Larsen, 2007).

The volcano is approximately 20 km in diameter. The Krafla geothermal field is located in an eroded, collapsed and partly filled caldera 8 × 10 km in diameter. A NNE–SSW oriented and 90 km long fissure swarm that marks the North Iceland Rift Zone bisects the caldera. Within the caldera a prominent NW–SE elongated geothermal area is present covering approximately 10 km<sup>2</sup> (Sæmundsson, 1991, 2008). The Krafla volcano is an active volcano with recurring volcanic episodes, which in the Holocene predominantly have been in the form of fissure eruptions. The volcanic activity has been centered in the eastern part of the fissure swarm during the past 3000 years occurring with a frequency of 300–1000 years (Sæmundsson, 1991). The caldera is largely filled by basaltic lavas and hyaloclastites. Rhyolites has erupted periodically in minor volumes forming subglacial rhyolitic ridges that are found mainly at or outside the margins of the caldera. Intermediate composition lavas are not abundant (Sæmundsson, 1991; Jónasson, 1994). Since 1974 extensive drilling for geothermal development have been performed in the Krafla caldera. This drilling reveals the extent of several active geothermal reservoirs and defines the subsurface geology (Kristmannsdóttir, 1978; Stefánsson, 1980, 1981; Ármannsson et al., 1987). Drilling has revealed a similar bimodal compositional distribution of the volcanic and plutonic rocks in the substrata (Guðmundsson, 1983; Ármannsson et al., 1987). The postglacial, near-surface basaltic lavas are underlain by hyaloclastite erupted during the last glacial period (Guðmundsson, 1983). A second, older sequence of hyaloclastite is overlain and underlain by interglacial lavas down to about ~1,200 m, where intrusive rocks begin to dominate. Doleritic intrusions are abundant in the deeper parts of the reservoir, but felsic intrusions have been intersected in several drill holes (Guðmundsson, 1983; Ármannsson et al., 1987). Intrusions become more abundant and coarser grained at greater depth and include gabbros.



Volcanic activity and events affect the geothermal system renewing the heat supply. However, volcanic events can also cause temporary deterioration of the fluid source with excessive volcanic gas influx, as was experienced in part of the Krafla geothermal field during the Krafla Fires 1975–1984 (Guðmundsson, 2001). The Krafla geothermal area seems closely associated with a magma chamber, which is inferred to underlie Krafla Caldera at depths of 3–7 km based on observation of attenuation of S-waves during the Krafla Fires rifting episode (Einarsson, 1978). The extent of the geothermal system in Krafla is estimated to be ~40 km<sup>2</sup> (Mortensen et al., 2009).

By 2014 a total of 46 exploration and production wells have been drilled in Krafla geothermal system (Weisenberger et al., 2015). The presence of magma at shallow depth produces acid fluids that sometimes constitute a problem to the integrity of the geothermal wells scattered across 3–4 km<sup>2</sup> and producing steam for the 60 MW power plant (e.g. Ármannsson et al., 1987).

The chosen well (made available by Landsvirkjun) is the KJ-35. This well is 2460 m deep; temperature logging carried out by ÍSOR (Iceland GeoSurvey) in 2007 showed a maximum T at about 1750 m depth, then the T decreases at higher depth (Figure 19).

The experiment with the micro-reactor was planned to be carried out at the maximum T of the well (i.e. at a depth of about 1750 m). A T (and P) logging was carried out by ÍSOR 12 days (23/06/2016) before the starting of the experiment and indicated a P of 13.5 MPa and T of 336°C at 1750 depth (Figure 19).

Two micro-reactors containing two capsules (details in Table 4) were inserted in a bigger stainless steel tube and lowered on July 5th beginning at 13:40 with a 55 m/min rate, reaching the bottom after ~30 min (Figure 20). It was pulled up from the bottom after ~69 h using the same rate. The experiment was technically successful since both capsules kept their weight after the “in situ” experiment.

## 4.2. Fluid inclusion results

Synthetic F.I. formed in all quartz chips recovered from the gold capsules of two micro-reactors (experiments SFI13 and SFI14), thus confirming the reliability of the method. All F.I. typical occur within curvilinear healed micro-fractures.

### Microthermometry

Microthermometric results of synthetic F.I. formed in one micro-reactor (experiment SF13) are reported in Table 2 and Figure 21, whereas Figure 22 shows a sequence of micro-photographs taken at different T during heating/freezing analyses. F.I. belonging to 3 distinct FIA are characterized by rather consistent  $T_h$  from 338 to 342°C with a mean of 340°C and a standard deviation of 1.4°C (Table 2, Figure 21).  $T_{m_{ice}}$  was also measured in 21 F.I.; they displayed a restricted range of  $T_{m_{ice}}$  from -6.5 to -6.6°C corresponding to salinity between 9.9 and 10.0 wt.% NaCl equiv., as data obtained in the experiment performed in the laboratory (Table 2).

### Temperature computation from synthetic F.I.

Trapping T of synthetic F.I. of SF13 experiment were computed with the same method (i.e. intersection between the isochore of synthetic F.I., for a salinity 10 wt.% NaCl, with the liquid-vapour curve of water) used for the F.I. formed in the micro-reactor placed in the furnace (paragraph 3.3). In this case, we computed the isochores corresponding to maximum and minimum  $T_h$ , the intersection of these isochores gives trapping T of 339 and 343°C (Figure 22).

## 4.3 Comparison with present-day bore-hole measured temperature



In Figure 23 the T computed from synthetic F.I. are compared with T (336°C) measured in KJ-35 well by ÍSOR with conventional method at 1750 m depth 12 days before the experiment. The difference of T is of only 3-7°C validating the proposed method.

## 5. Errors estimate of the method

Possible source of errors in the computation of T with the proposed method can be ascribed to: 1) error due to a mistake in the amount of water introduced into the reactor from synthetic F.I. , 2) error of microthermometric measurements of F.I., 3) error due to metal dilation of the micro-reactor.

We estimate the changes of trapping T due to an error of  $\pm 5\%$  in the degree of filling of the micro-reactor calculating new H<sub>2</sub>O isochore with the appropriate densities and we found that the computed T from isochore intersection differ from that of computed using the critical isochore of  $< 8^\circ\text{C}$ . For example, an error of  $\pm 5\%$  will produce a maximum error of 6°C in the temperature estimate for a fluid with a salinity of 15 wt.% NaCl trapped at 450°C.

In addition, the errors related to microthermometry are negligible. For example, error of  $\pm 2^\circ\text{C}$  in  $T_h$  measurements will produce an error of  $\pm 3^\circ\text{C}$  in the in the temperature estimate for a fluid with a salinity of 15 wt.% NaCl trapped at 450°C. Finally, errors due to volume increase within the micro-reactor due the metal dilation are minor: 3°C at 500°C.

In theory, also capsule filling can be a source of error. Care was taken in order to remain as close as possible to critical density for saline solution. This procedure is necessary to avoid capsule rupture.

However, small variations in the filling of capsules are "obliterated" by gold malleability, which allows to these capsules to follow the same isochore varying P-T conditions.

## 6. Final remarks

The method elaborated in this task can be used for T measurements in high-T geothermal wells and it is based on the production of synthetic F.I. within an apparatus that can be lowered in geothermal wells. The apparatus consists of a micro-reactor and gold capsules in which are placed: pre-fractured quartz fragment (that will trap F.I.), an alkaline-saline aqueous solution that will be trapped in the synthetic F.I. and powdered silica. The gold capsules are placed within the micro-reactor, the latter will be partially filled with an amount of distilled water such that the P-T conditions in the micro-reactor will follow the liquid-vapor curve of H<sub>2</sub>O and critical isochore of H<sub>2</sub>O (characterized by a density of 0.322 g/cm<sup>3</sup>) above the critical point of H<sub>2</sub>O.

Before a test carried out in a well of Krafla geothermal system, laboratory experiments were performed using an externally heated pressure vessel and the micro-reactor placed in a furnace. The results of such experiments indicate that synthetic F.I. form within a relatively short time (even in 48 hours) and that trapping temperatures of synthetic F.I. formed in externally heated pressure vessel give a good estimate of the experimental T, at least in the 280-400°C range.

The experiment performed in KJ-35 geothermal well at Krafla by lowering the apparatus at 1750 m depth for 69 hours produced synthetic F.I. indicating trapping T of 339-343°C that are very close to the 336°C measured at the same depth with conventional tools.



In summary, the proposed method can be used for T measurements in geothermal wells and require to hold the apparatus in the geothermal well for a relatively short time (48-72 hours).

The method can be potentially applied for temperature measurements of geothermal well temperature up to 427°C (i.e. the working temperature limit of the utilized commercial pressure vessel). This limit can be extended to higher temperature by using different pressure vessel.

### **Acknowledgements**

Daniele Borrini gave his assistance during experiments at the Experimental Mineralogy and Petrology Lab (CNR-IGG – Florence). Gylfi Páll Hersir organized the field test in Krafla. ÍSOR's employees Friðgeir Pétursson, Hörður Tryggvason and Þorsteinn Egilson measured the temperature of well KJ-35 and lowered the container in the well in Krafla. Landsvirkjun Employees and Magnus Egill Ruben, and Alain Gadalia (BRGM) at Krafla assisted with the field work, and Egill Júlíusson and Ásgrímur Guðmundsson at Landsvirkjun helped in various ways to facilitate the test in Krafla. The contribution from all these people is greatly acknowledged.

### **References**

- Anderson G. M. and Burnham, C. W. (1967). Reactions of quartz and corundum with aqueous chloride and hydroxide solutions at high temperatures and pressures. *American Journal of Science*, 265, 12-27.
- Ármannsson H., Guðmundsson Á., Steingrímsson B.S. (1987). Exploration and development of the Krafla Geothermal Area. *Jökull*, 37, 13-29.
- Ármannsson H., Fridriksson T., Guðfinnsson G.H., Ólafsson M., Óskarsson F., Thorbjörnsson D. (2014). IDDP-The chemistry of the IDDP-01 well fluids in relation to the geochemistry of the Krafla geothermal system. *Geothermics*, 49, 66-75.
- Ármannsson H., Guðmundsson Á., Steingrímsson B.S. (1987). Exploration and development of the Krafla geothermal area. *Jökull*, 37, 13-30.
- Atkinson A.B. Jr. (2002). A Model for the PTX Properties of H<sub>2</sub>O-NaCl. Unpublished MSc Thesis, Dept. of Geosciences, Virginia Tech, Blacksburg VA, 133 pp.
- Bethke P. M., Lysne P., Foley N. K., Sweetkind D. S., Landis G. P. (1990). In-situ fluid sampling by synthetic fluid inclusions, VC2B, Valles caldera, NM. *EOS* 71, 1683-1684.
- Bodnar R.J. (1993). Revised equation and table for determining the freezing point depression of H<sub>2</sub>O-NaCl solutions. *Geochimica et Cosmochimica Acta*, 57, 683-684.
- Bodnar R.J. and Vityk M.O. (1994). Interpretation of microthermometric data for H<sub>2</sub>O-NaCl fluid inclusions. In *Fluid Inclusions in Minerals, Methods and Applications*, B. De Vivo and M.L. Frezzotti. eds., pub. by Virginia Tech, Blacksburg, VA (USA), 117-130.
- Bodnar R.J. and Sterner S.M. (1987). Synthetic fluid inclusions. In: Barnes, H.L., Ulmer, G.C. (Eds.), *Hydrothermal Experimental Techniques*. Wiley, New York, 423 pp.
- Borrini D., Orlando A., Ruggieri G. (2006). Sintesi di inclusioni fluide in cristalli di quarzo: procedure sperimentali e possibili applicazioni. 85° Congresso della Società Italiana di Mineralogia e Petrologia, Fluminamaggiore, Cagliari (Italy), 27-28 september 2006, pag. 359.
- Dubessy J., Guillaume D. G., Buschaert S., Fabre C., Pironon J. (2000). Production of synthetic fluid inclusions in the H<sub>2</sub>O-CH<sub>4</sub>-NaCl system using laser-ablation in fluorite and quartz. *European Journal of Mineralogy*, 12, 1083-1091.
- Goldstein R. H. and Reynolds T. J. (1994). Systematics of fluid inclusions in diagenetic minerals: SEPM Short Course 31. Society for Sedimentary Geology, 199.
- Einarsson P. (1978). S-wave shadows in the Krafla caldera in NE-Iceland, evidence for a magma chamber in the crust. *Bulletin of Volcanology*, 41, 1-9.



- Guðmundsson Á. (1983). Jarðfræði Suðurlíða Kröflu. Hrafnáping um stöðu Kröflu Jarðhita Orkuver. 2.–3. mars 1983, Akureyri; 77–85.
- Guðmundsson Á. (2001). An expansion of the Krafla Power Plant from 30 to 60 MWe. Geothermal Considerations. Geothermal Research Council Transactions, 25, 741–746.
- Guðmundsson Á., Steingrímsson B., Ármannsson H., Sigvaldason H., Benjamínsson J., Sigurðsson Ó. (1983). Krafla, hola KJ-9. Aflsaga, efnabreytingar og endurborun. Report No. OS-83075/JHD-13, Orkustofnun.
- HiTI (2010). High Temperature Instruments for Supercritical Geothermal Reservoir Characterisation & Exploitation. Publishable summary report. [cordis.europa.eu/documents/.../122319981EN6.pdf](http://cordis.europa.eu/documents/.../122319981EN6.pdf)
- Jónasson K. (1994). Rhyolite volcanism in the Krafla central volcano, north-east Iceland. Bulletin of Volcanology, 56, 516–528.
- Knight C.L. and Bodnar R.J. (1989). Synthetic fluid inclusions. IX. Critical PVTX properties of NaCl-H<sub>2</sub>O solutions. Geochimica et Cosmochimica Acta, 53, 3-8.
- Kristmannsdóttir H. (1978). Alteration of bedrock in the Krafla geothermal system. Report no. OS/JHD-7854, Orkustofun.
- Mortensen A.K., Guðmundsson Á., Steingrímsson B., Sigmundsson F., Axelsson G., Ármannsson H., Björnsson H., Ágústsson K., Sæmundsson K., Ólafsson M., Karlsdóttir R., Halldórsdóttir S., Hauksson T. (2009). Jarðhitakerfið í Kröflu. Samantekt rannsókna á jarðhitakerfinu og endurskoðað hugmyndalíkan. In Icelandic. Iceland GeoSurvey, ÍSOR-2009/057, LV-2009/111.
- Roedder E. (1984). Fluid inclusions. Mineral Soc Am Rev Mineral, 12, 640 pp.
- Sæmundsson K. (1991). Geology of Krafla volcanic system. In: Garðarsson, A. and Einarsson Á (Eds.), Náttúra Myávatns. Hið íslenska náttúrufræðifélag, Reykjavík, 25–95.
- Sæmundsson K. (2008). Krafla. Geological map, 1:25.000. Landsvirkjun and ÍSOR.
- Sawaki T., Sasada M., Sasaki M., Tsukimura K., Hyodo M., Okabe T., Uchida T., Yag M. (1997). Synthetic fluid inclusion logging to measure temperatures and sample fluids in the Kakkonda geothermal field, Japan. Geothermics, 26, 281-303.
- Sekine K., Bignall G., Tsuchiya N. (2004). Application of synthetic fluid inclusions to simultaneous temperature-pressure logging in high-temperature (sub- to supercritical) geothermal systems. Geothermics, 33, 775-793.
- Steele-MacInnis M., Lecumberri-Sanchez P., Bodnar R.J. (2012). HOKIEFLINCS\_H2O-NACL: A Microsoft Excel spreadsheet for interpreting microthermometric data from fluid inclusions based on the PVTX properties of H<sub>2</sub>O-NaCl. Computers & Geosciences, 49, 334-337.
- Stefánsson V. (1980). Investigation on the Krafla high temperature geothermal field. Náttúrufræðingurinn, 50, 333–359.
- Stefánsson, V. (1981). The Krafla geothermal field Northeast Iceland. In: Rybach, L. and Muffler, L.J.P. (Eds.), Geothermal Systems: Principles and Case Histories, John Wiley and Sons Ltd, 273–294.
- Teinturier S. and Pironon J. (2003). Synthetic Fluid Inclusions as Recorders of Microfracture Healing and Overgrowth Formation Rates. American Mineralogist, 88, 1204–1208.
- Thordarson T. and Larsen G. (2007). Volcanism in Iceland in Historical Time: Volcano Types, Eruption Styles and Eruptive History. Journal of Geodynamics 43, 118–52.
- Weisenberger T.B., Axelsson G., Arnaldsson A., Blichke A., Óskarsson F., Ármannsson H., Blanck H., Helgadóttir H.M., Berthet J-C. C., Árnason K., Ágústsson K., Gylfadóttir S.S., Guðmundsdóttir V. (2015). Revision of the Conceptual Model of the Krafla Geothermal System. Iceland GeoSurvey, ÍSOR-2015/012; LV-2015-040, 111p.

## FIGURES

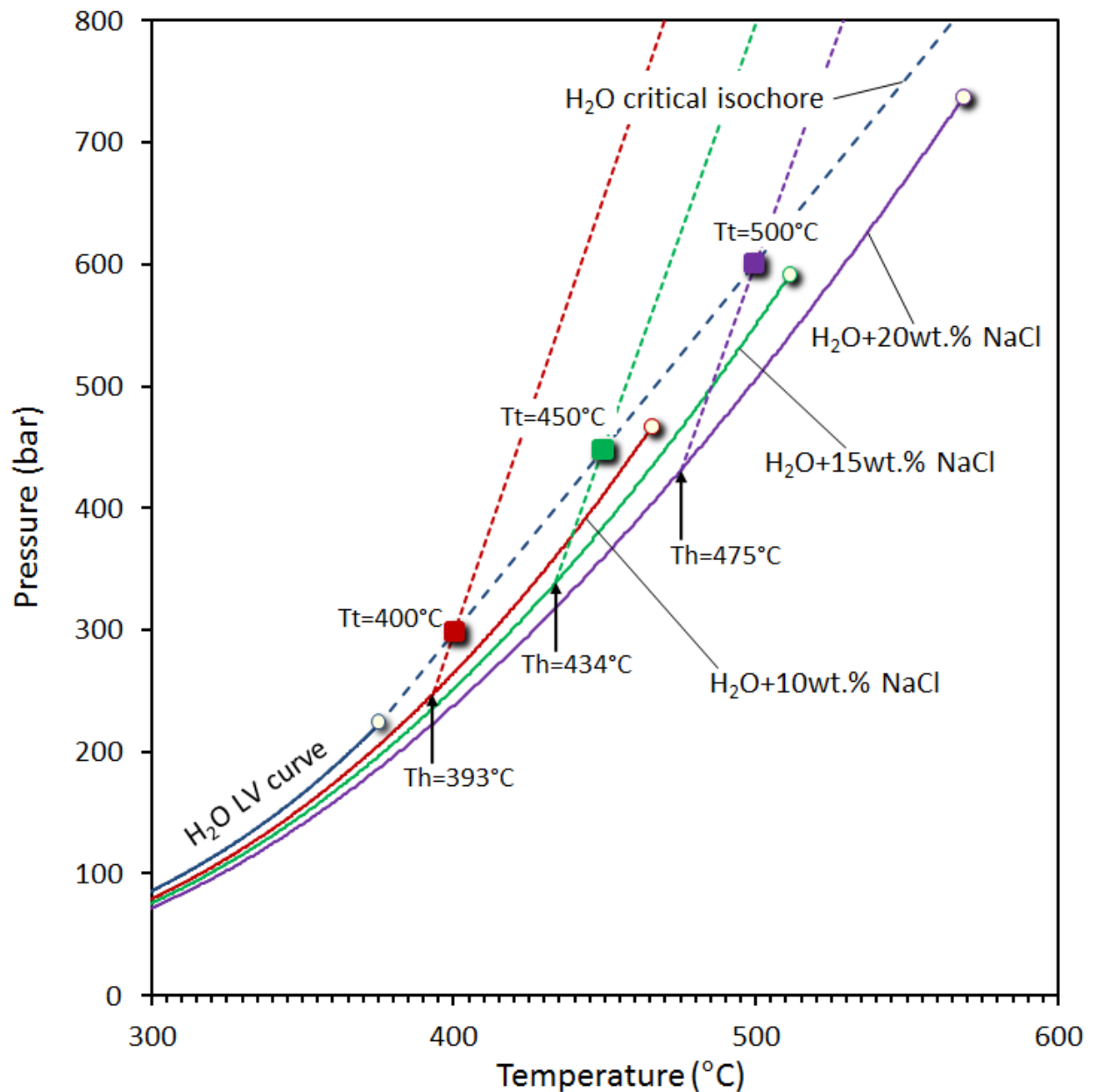


Figure 1: P-T diagram showing the method for T measurements by synthetic F.I. formed in a micro-reactor. T of trapping ( $T_t$ ) for H<sub>2</sub>O-NaCl fluid with different NaCl concentrations (10, 15 and 20 wt.%) can be obtained from the intersections of the isochores of the H<sub>2</sub>O-NaCl fluids departing from T of homogenization ( $T_h$ ) and the critical isochore of water.



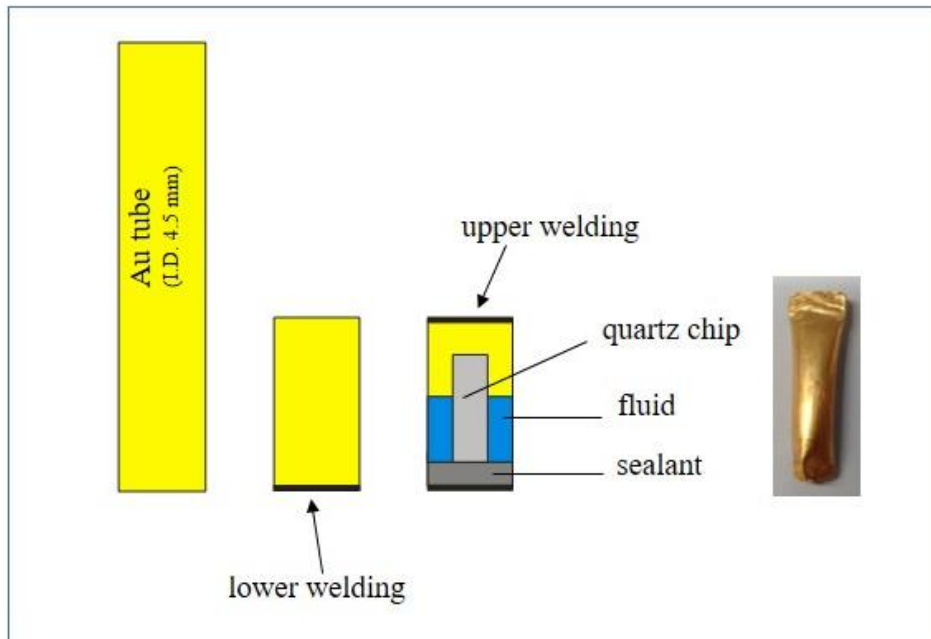


Figure 2: Sketch of a capsule preparation. A gold tube (left) is cut and welded in a part (lower welding). Quartz chip(s), solution and sealant are then inserted inside and capsule is crimped and welded in the upper part (upper welding). Imagine of a real capsule (right).

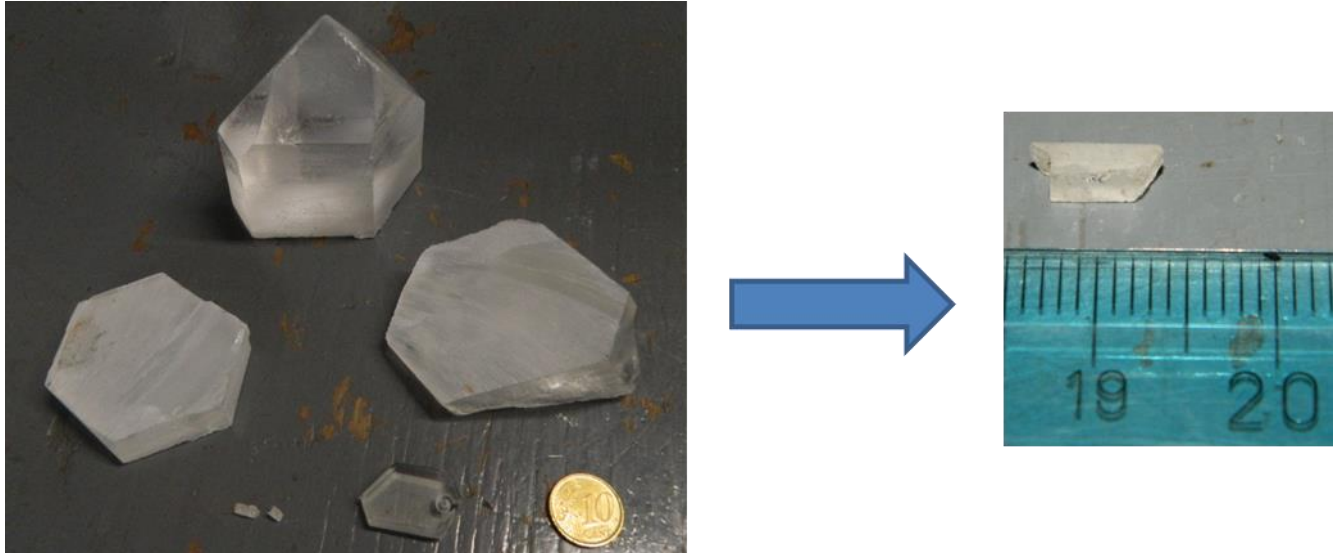


Figure 3: Brazilian quartz almost devoid of natural F.I. used for the experiment. Chips of quartz (right) have been produced with sizes compatible with sizes of the gold capsules.



Figure 4: The HR-2B-2 cold seal pressure vessel (left) and a detail showing the René 41 pressure vessel containing Au capsule(s) approaching to enter into a sliding furnace (right).

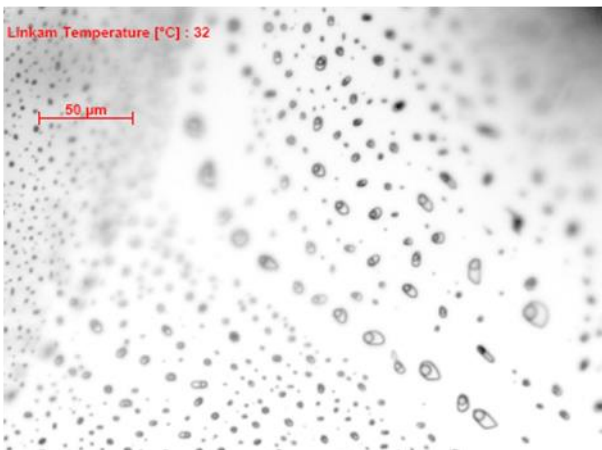
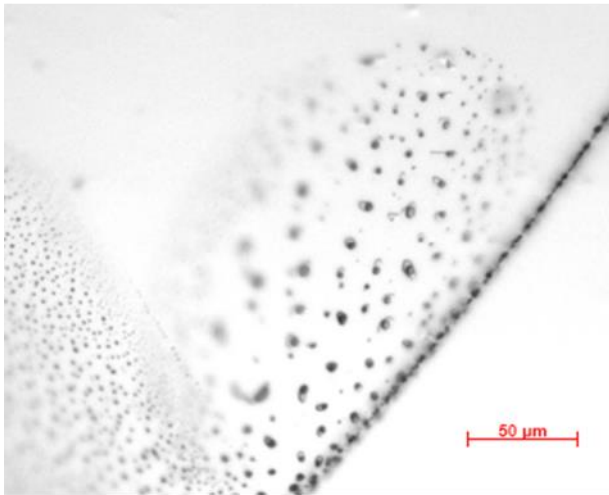
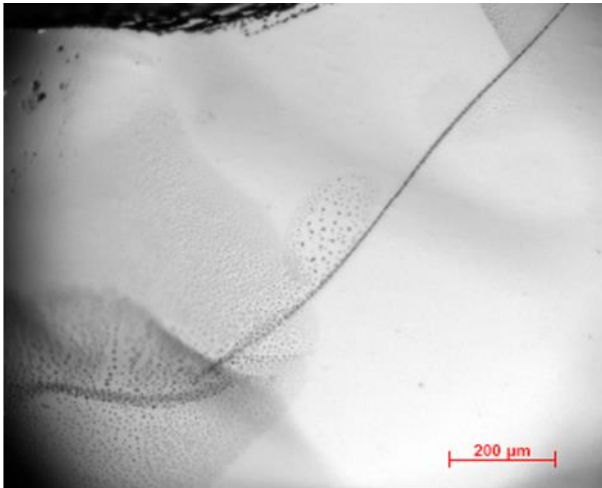


Figure 5: Micro-photographs taken at different enlargement showing the occurrence of synthetic F.I. within curvilinear healed micro-fractures in quartz.

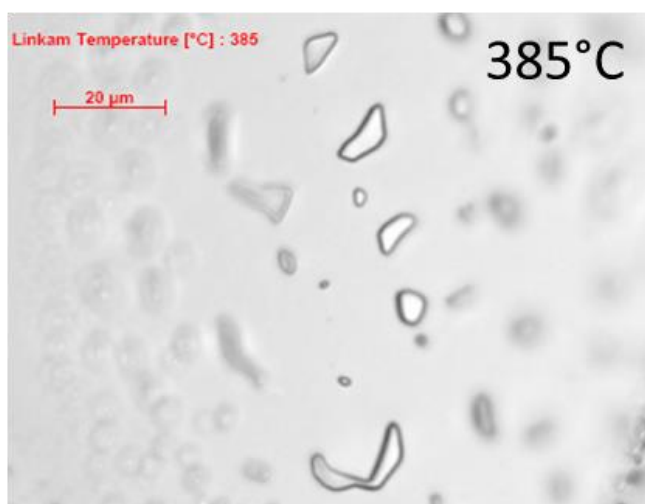
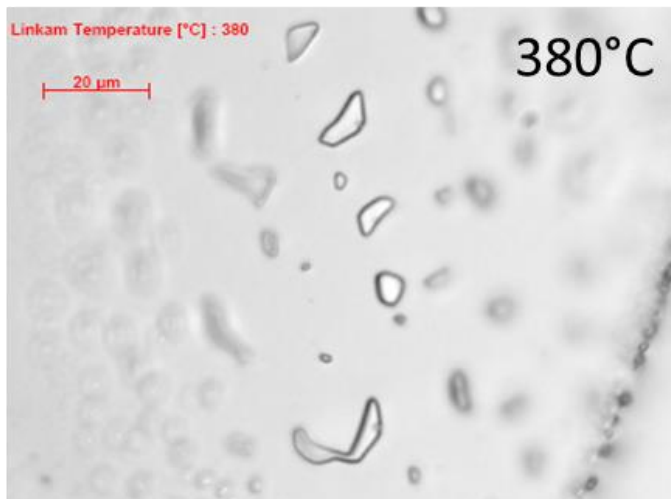
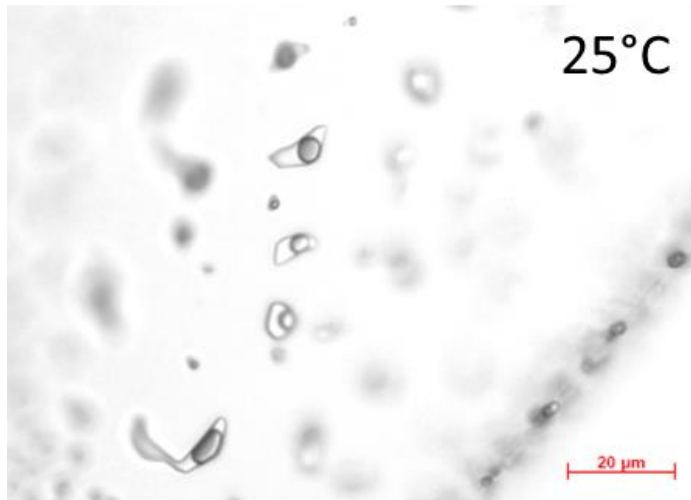


Figure 6: Sequence of micro-photograph illustrating the behaviour of F.I., formed during experiment in externally heated pressure vessel, belonging to a FIA during microthermometric analyses. Upper: at room temperature, intermediate: just before  $T_h$ , below: slight above  $T_h$ .

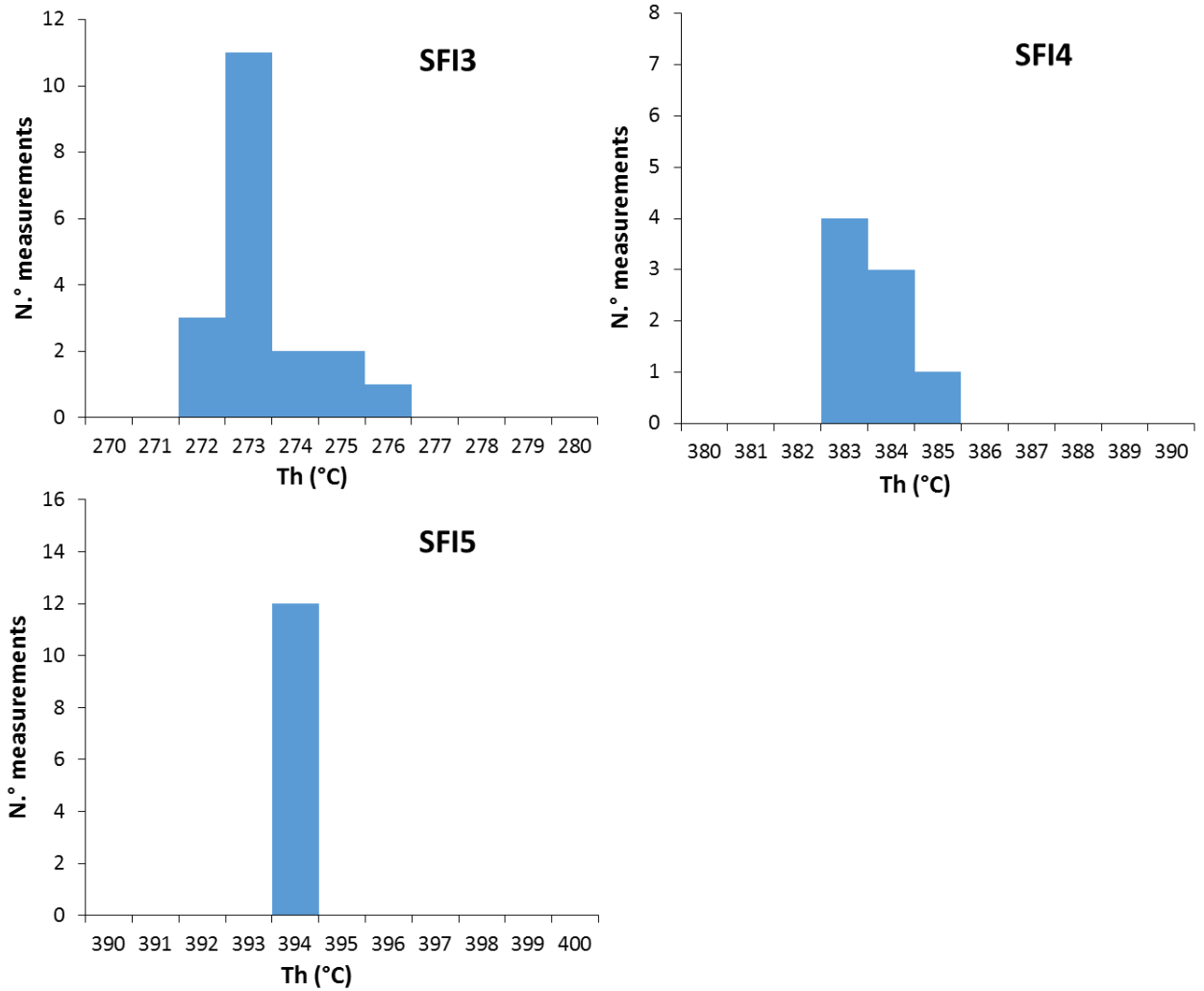


Figure 7: Frequency histograms of homogenization temperature ( $T_h$ ) of synthetic F.I. formed during the experiments in externally heated pressure vessel.

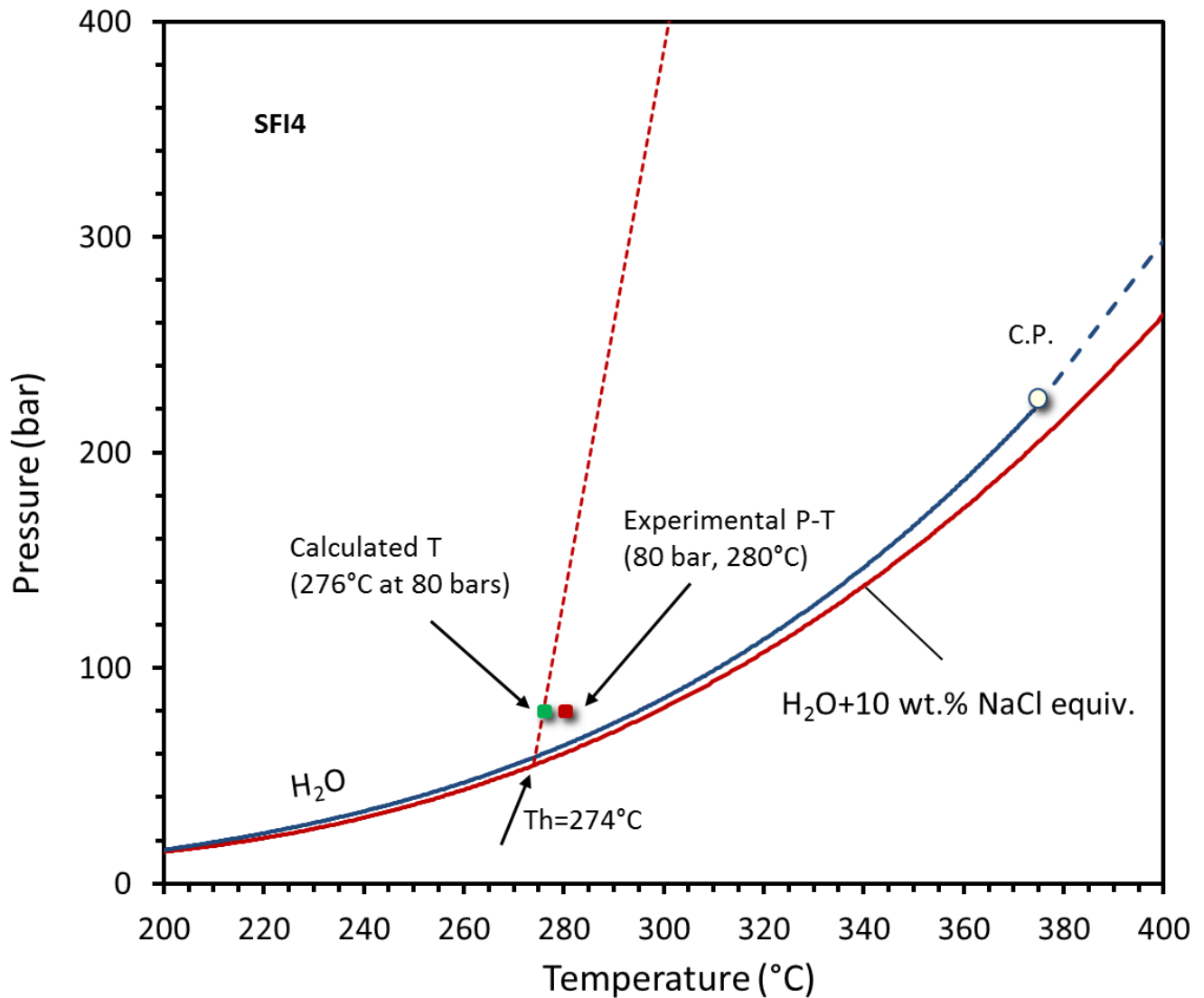


Figure 8: Comparison between experimental conditions (red square) of SFI4 experiment with conditions estimated from synthetic F.I. considering the isochore departing from  $T_h$  and assuming trapping P equal to experimental P (green square). C.P.= critical point for pure water.

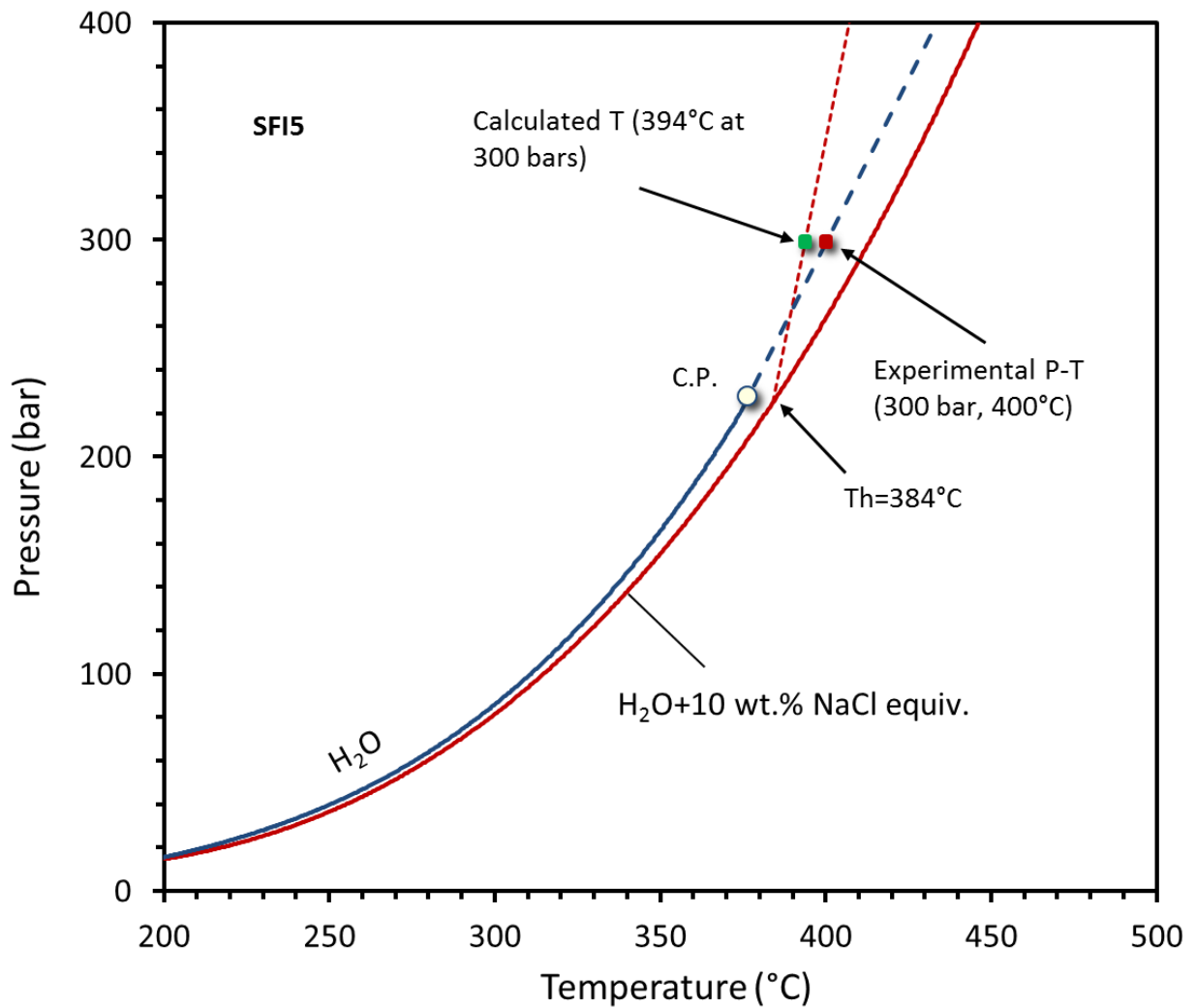


Figure 9: Comparison between experimental conditions (red square) of SF15 experiment with conditions estimated from synthetic F.I. considering the isochore departing from  $T_h$  and assuming trapping P equal to experimental P (green square).

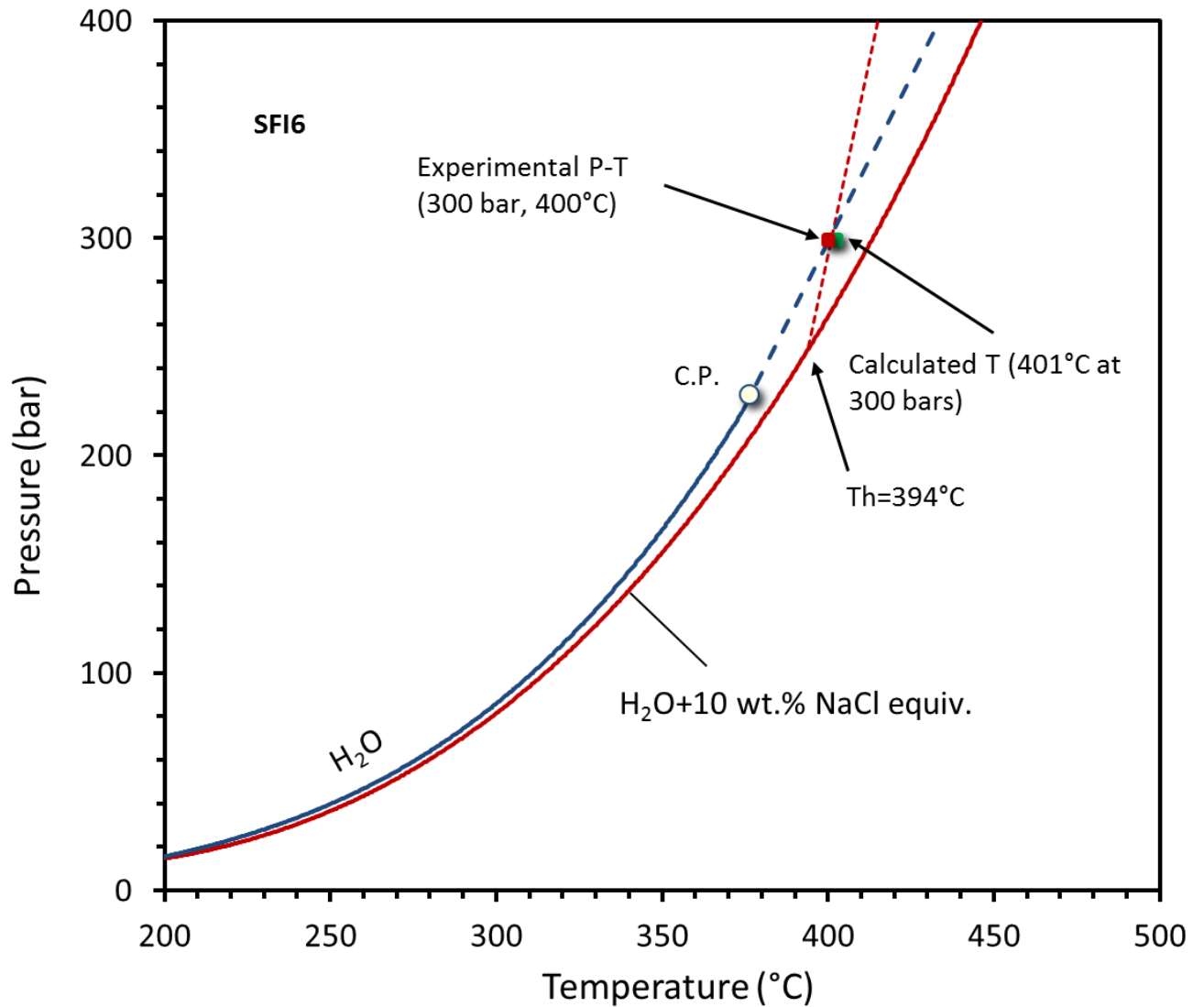


Figure 10: Comparison between experimental conditions (red square) of SF16 experiment with conditions estimated from synthetic F.I. considering the isochore departing from  $T_h$  and assuming trapping P equal to experimental P (green square).





Figure 11: Picture of micro-reactor, model MS-15 HiP (from the High Pressure Equipment Company).

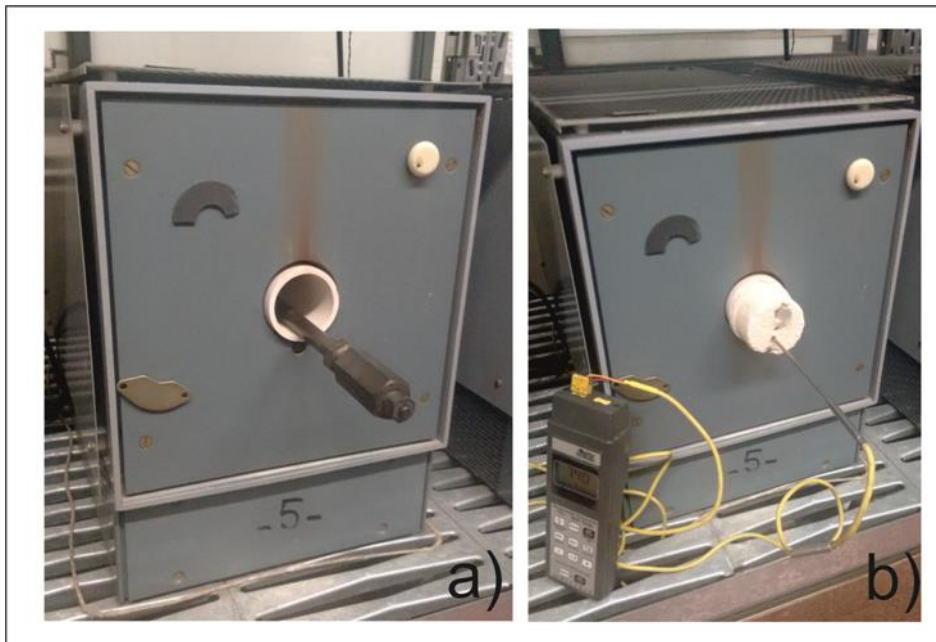


Figure 12: a) The micro-reactor entering into the furnace; b) the Micro reactor is into the furnace, the stopper is inserted and T is monitored by a K thermocouple with the junction as close as possible to capsule(s).

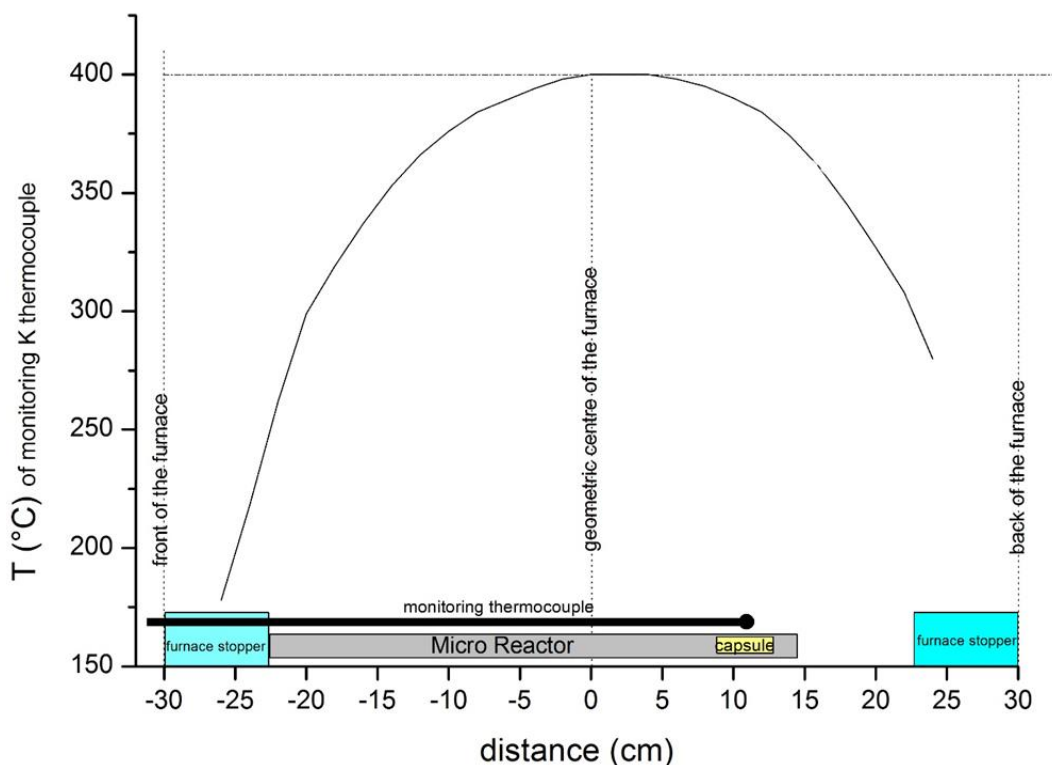


Figure 13: Graph showing calibration performed in the furnace setting control K thermocouple at  $T=400^{\circ}\text{C}$  and reading T with monitoring K thermocouple. Distance is relative to the geometric centre of the furnace. Capsule, Micro Reactor and furnace stoppers are sketched in the graph.

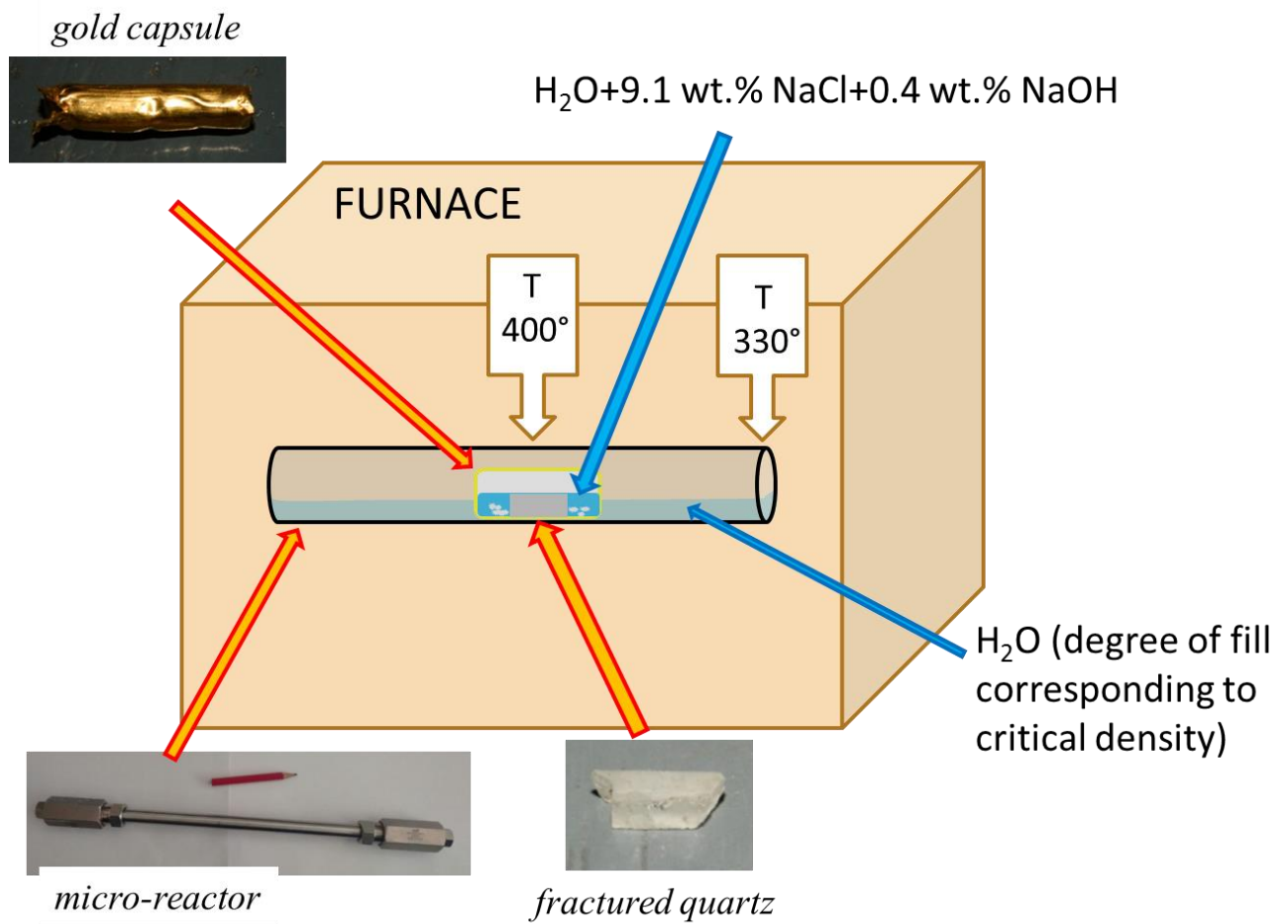


Figure 14: Simplified sketch of the experiments performed with the micro-reactor placed within the furnace. Note the large thermal gradient between the hottest part of the furnace (in this T set at 400°C) and one of the end of the micro-reactor (in this case 330°C).

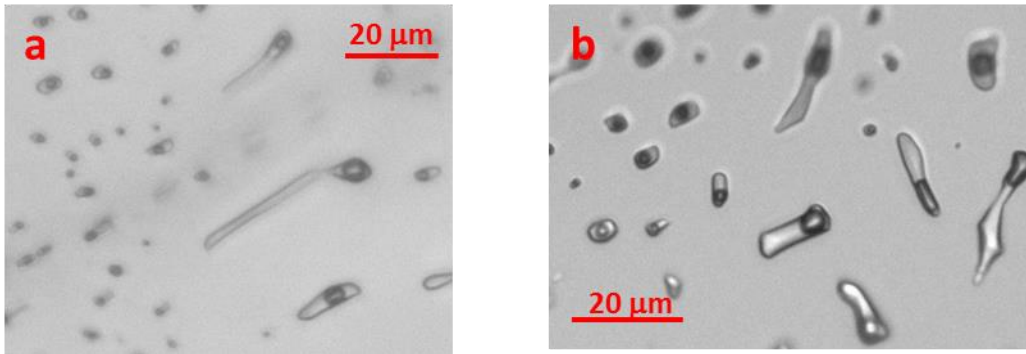


Figure 15: Synthetic F.I. during experiments SFI6 (a) and SFI7 (b) in the micro-reactor placed in the furnace

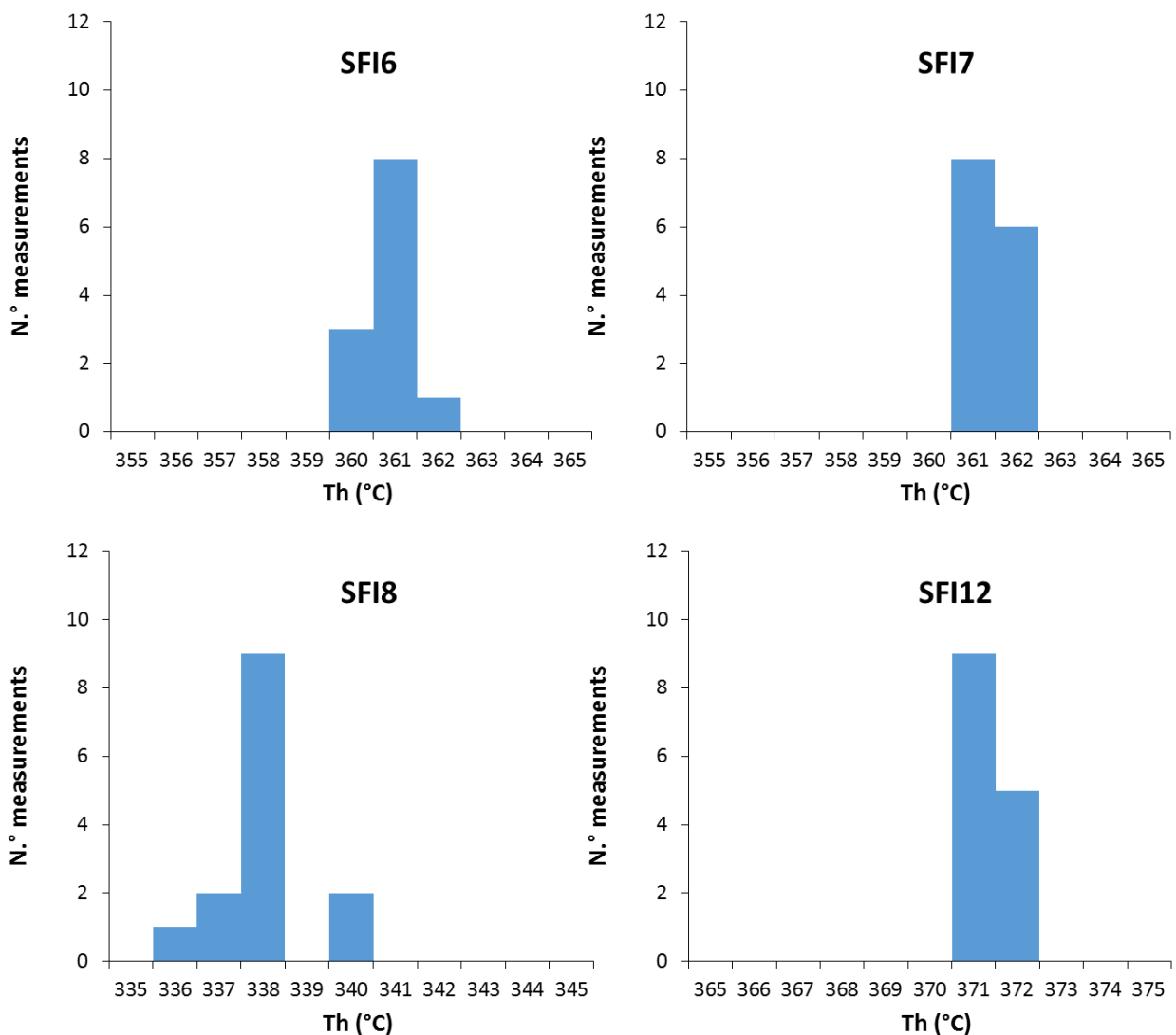


Figure 16: Frequency histograms of homogenization temperature ( $T_h$ ) of synthetic F.I. formed during the experiments run with the micro-reactor placed in the furnace.

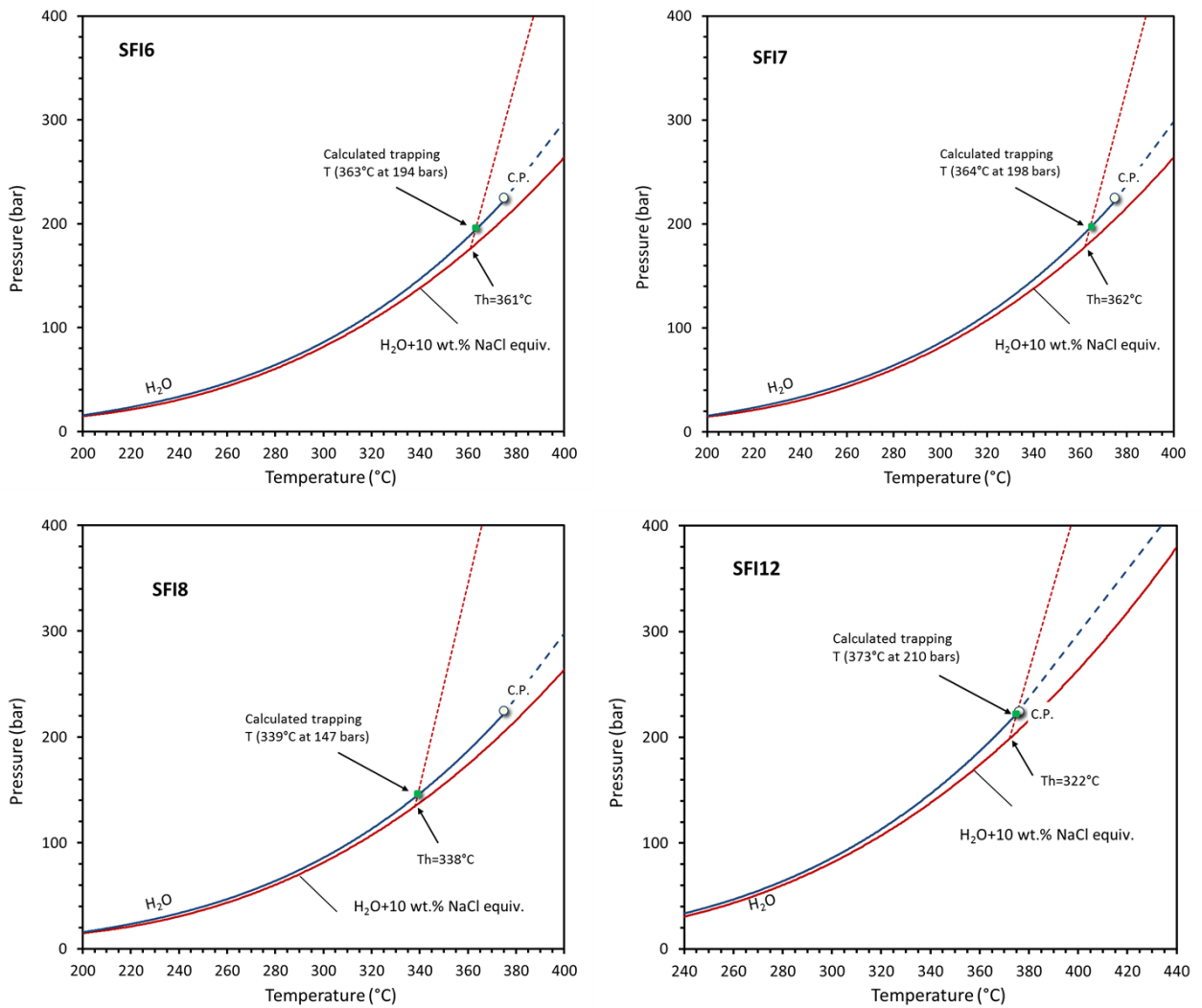


Figure 17: Trapping T of synthetic F.I. produced by placing the micro-reactor in the furnace. The trapping T is given by the intersection of F.I. isochore with the liquid-vapour curve of water.

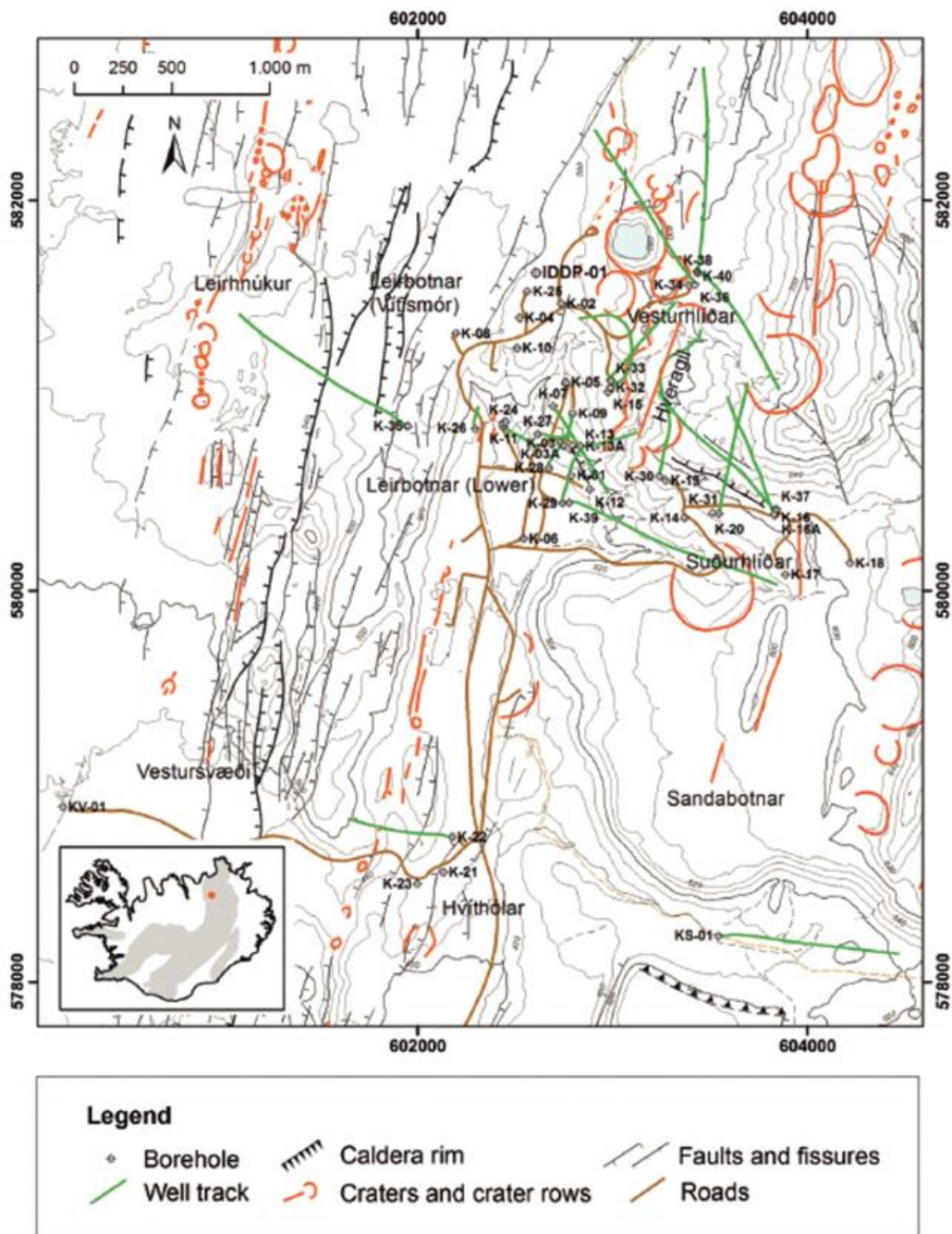


Figure 18: Map of the Krafla area showing tectonic features and wells, including that used for the experiment (K-35; from Ármannsson et al., 2014).

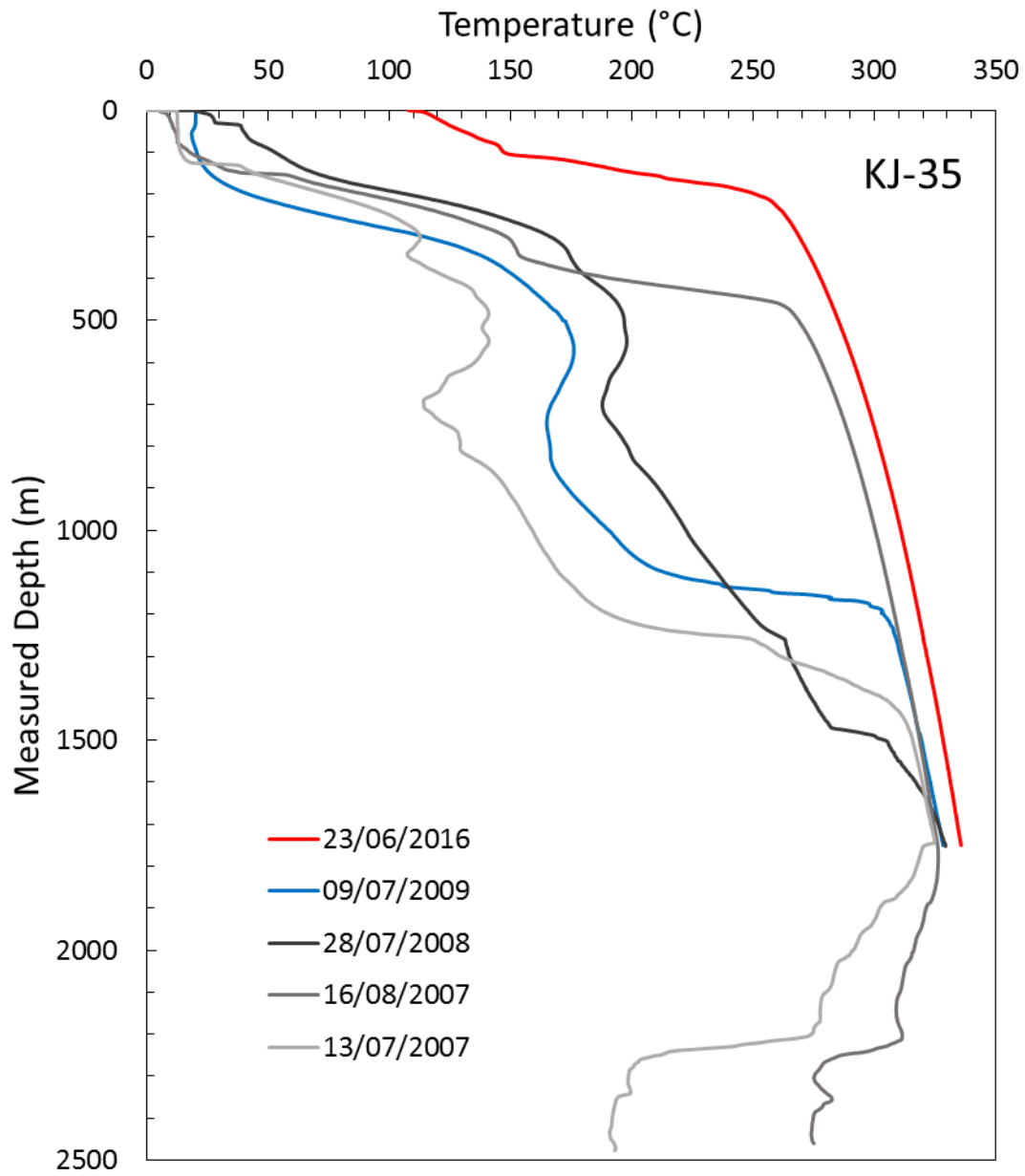


Figure 19: Thermal profiles of KJ-35 geothermal well measured at different time.

### Preparation



### Start: July 5th at 13:40



### Recover: July 8th (after 69 hours)



Figure 20: Pictures of the experiment accomplished at KJ-35 well (Krafla, Iceland). a) Tube containing micro-reactors is inserted in a bigger tube; b) the device is hosted over the well and it will be lowered through a pulley controlled by a motor hosted in a ÍSOR van; c) recover of the of the device through the pulley controlled motor; d) final recover of the tube containing the micro-reactors.



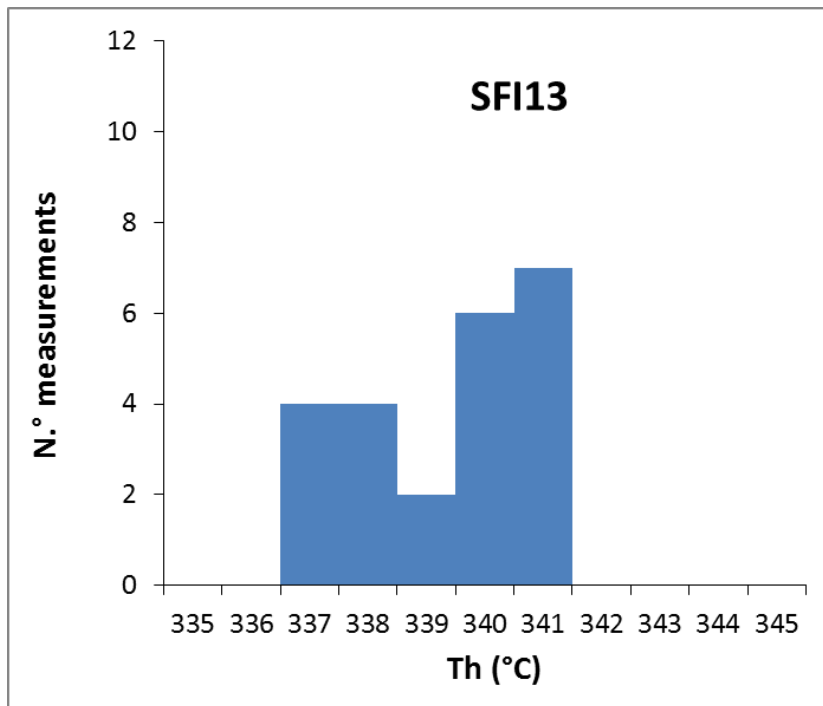


Figure 21: Frequency histograms of homogenization temperature ( $T_h$ ) of synthetic F.I. formed during the experiments in the micro-reactor placed in the KJ-35 geothermal well.

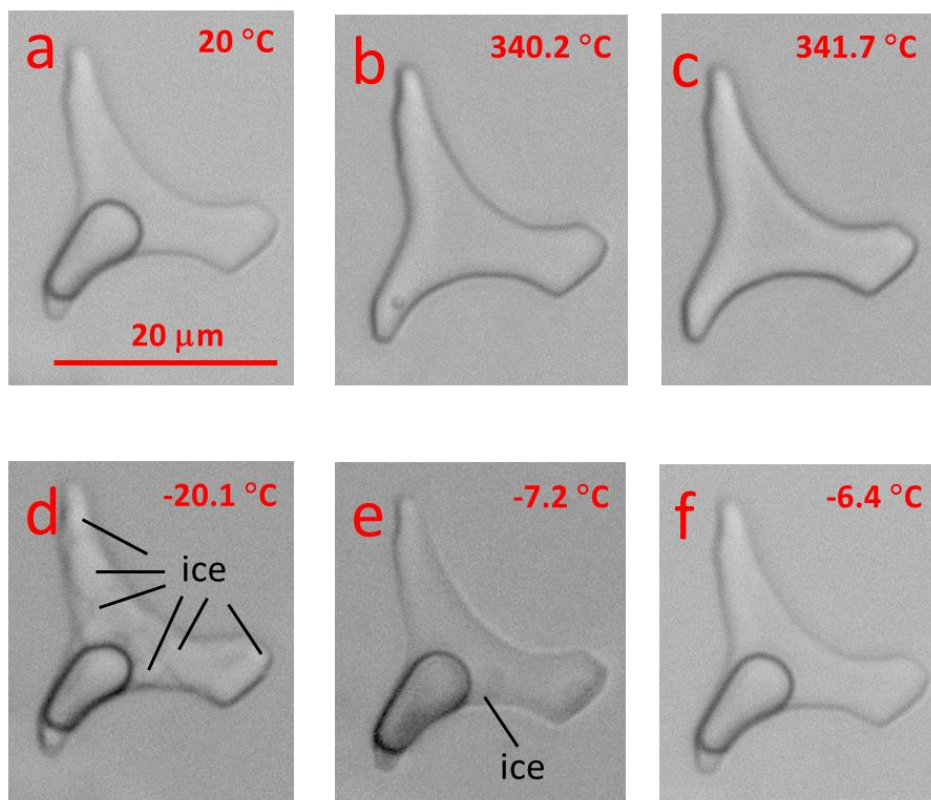


Figure 22: Sequence of micro-photographs showing the behaviour during microthermometric analyses of one synthetic F.I. produced in the KJ-35 geothermal well. a) at room  $T$ , b) just before  $T_h$ , c) F.I. just homogenized, d) after eutectic  $T$  several ice crystals are visible, e)  $0.6^\circ\text{C}$  below  $T_{m_{\text{ice}}}$  is visible only one ice crystal, f) just after  $T_{m_{\text{ice}}}$ .

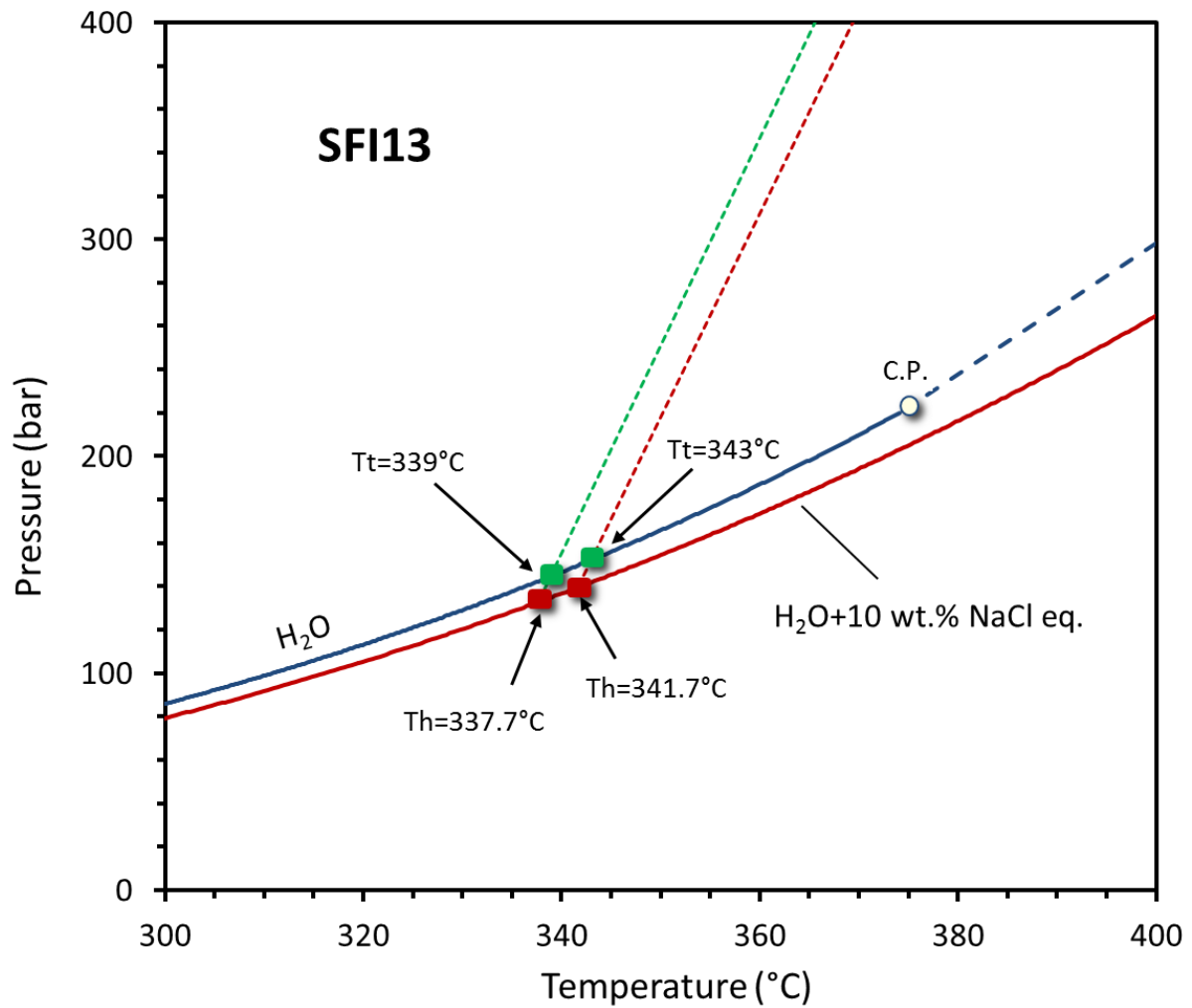


Figure 23: Trapping T of synthetic F.I. produced during the experiment in KJ-35 geothermal well. The trapping T ( $T_t$ ) are given by the intersection of F.I. isochores computed considering maximum and minimum  $T_h$  with the liquid-vapour curve of water.

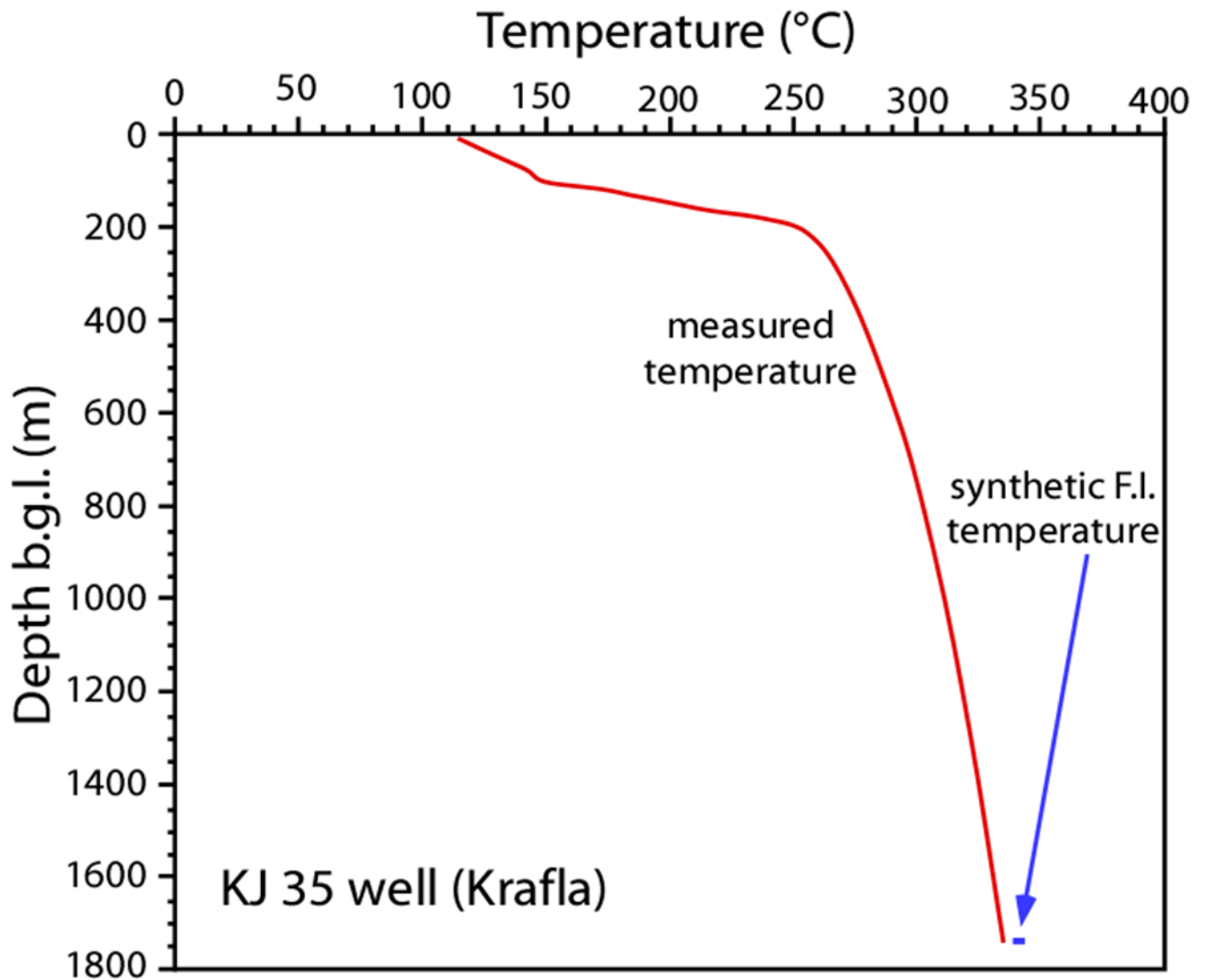


Figure 24: Temperature vs. depth profile of KJ-35 well and comparison and T of synthetic F.I. produced at a depth of 1750 m.



## TABLES

Table 1: List of experiments performed using the external heated pressure vessel. N= number of chips. Solution, 1: H<sub>2</sub>O+NaCl 9.1 wt%, 2: H<sub>2</sub>O+NaOH 0.1M+9.1 wt% NaCl (pH=13). Experiments with the same data were run together placing capsules in the same vessel. Outcome: successful (ok) and unsuccessful (no) experiments.

Experiment	SFI1	SFI2	SFI3	SFI4	SFI5
capsule (g)	0.6706	0.7139	0.772	1.0678	1.105
grinded (type)	fluorite	fluorite	silica	silica	silica
grinded (g)	0.0225	0.0259	0.0619	0.0227	0.0229
solution (type)*	1	1	2	2	2
solution (g)	0.0640	0.0573	0.1054	0.0800	0.0787
chips (type, N)	fluorite (3)	fluorite (3)	quartz (1)	quartz (1)	quartz (1)
chips (g)	0.0162	0.0252	0.0742	0.0882	0.0769
before welding (g)	0.7630	0.8102	0.9911	1.2386	1.2559
after welding (g)	0.7621	0.8104	0.9907	1.2378	1.2556
overnight at 110°C (g)	0.7625	0.8104	0.9900	1.2377	1.2556
start	04/02/2014	04/02/2014	04/02/2014	11/03/2014	11/03/2014
stop	10/02/2014	10/02/2014	10/02/2014	13/03/2014	17/03/2014
duration (h)	<b>140</b>	<b>140</b>	<b>140</b>	<b>48</b>	<b>140</b>
T (°C)	<b>280</b>	<b>280</b>	<b>280</b>	<b>400</b>	<b>400</b>
P (MPa)	<b>8</b>	<b>8</b>	<b>8</b>	<b>30</b>	<b>30</b>
<b><i>After the experiment</i></b>					
capsule (g)	0.7627	0.8102	0.9907	1.2375	1.2556
outcome	ok	ok	ok	ok	ok



Table 2: Summary of microthermometric results and calculated salinity of synthetic F.I. formed during experiment in externally heated pressure vessel (SFI3, SFI4, SFI5), in the micro-reactor placed in the furnace (SFI6, SFI7, SFI8) and in the micro-reactor placed in the KJ-35 geothermal well (SFI13).  $T_h$ : homogenization temperature,  $T_{m_{ice}}$ : final ice melting temperature. Numbers in brackets refer to number of measurements.

Experiment	$T_h$ range (°C)	$T_h$ mean (°C)	Stand. Dev. (°C)	$T_{m_{ice}}$ range (°C)	Salinity (wt.% NaCl equiv.)
SFI3	272/277 [19]	274	1	-6.5/-6.7	9.9/10.1
SFI4	383/386 [9]	384	0.5	-6.5	9.9
SFI5	394/395 [12]	394	0.1	-6.5	9.9
SFI6	360/363 [10]	361	0.4	-6.5	9.9
SFI7	361/363 [14]	362	0.1	n.m.	-
SFI8	336/341 [14]	338	1	n.m.	-
SFI12	371 [13]	371	0.3	-6.5	9.9
SFI13	338/342/ [22]	340	1.4	-6.6/-6.7	10.0/10.1



Table 3: List of experiments performed using the Micro reactor in the furnace. Legend as in Table 1. Water in the micro-reactor was placed so to approximate critical density of pure water into the apparatus. T was registered by the K monitoring thermocouple.

Experiment	SFI6	SFI7	SFI8	SFI9	SFI10	SFI11	SFI12
capsule (g)	1.1852	1.0352	1.0612	1.0307	1.0591	1.0622	1.1049
grinded (type)	silica	silica	silica	silica	silica	silica	silica
grinded (g)	0.1000	0.0853	0.0978	0.0927	0.0953	0.0966	0.0904
solution (type)	2	2	2	H <sub>2</sub> O milliQ	2	2	2
solution (g)	0.1606	0.1039	0.1254	0.0684	0.1193	0.0684	0.1324
chips (type, N)	quartz (3)	quartz (2)	quartz (2)	quartz (3)	quartz (1)	quartz (2)	quartz (1)
chips (g)	0.0847	0.0810	0.0963	0.0595	0.0405	0.0458	0.0589
before welding (g)	1.4927	1.2690	1.3621	1.2125	1.2886	1.2569	1.3596
after welding (g)	1.4927	1.2685	1.3533	1.2092	1.2883	1.2573	1.3563
overnight 110°C (g)	1.4927	1.2681	1.3533	1.2088	1.2880	1.2573	1.3561
start	09/11/2015	10/12/2015	03/02/2016	11/04/2016	11/04/2016	02/05/2016	02/05/2016
stop	16/11/2015	14/12/2015	05/05/2016	15/04/2016	15/04/2016	04/05/2016	04/05/2016
duration (h)	163	87	47	95	95	56	56
T (°C)	378	378	350	396	396	396	396
<b>After the experiment</b>							
capsule (g)	1.4926	1.2684	1.3536	1.2418	1.2237	1.2573	1.3561
outcome	ok	ok	ok	no	no	ok	ok

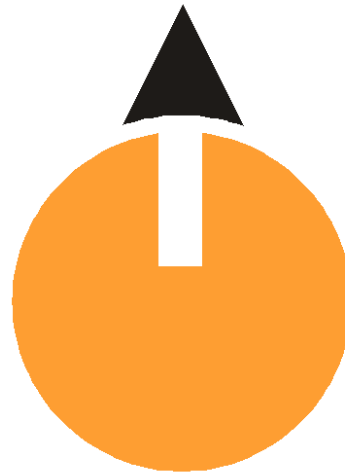


Table 4: Details of experiments performed “in situ” in the KJ-35 well (Krafla, Iceland). Legend as in Table 1.

<b>Experiment</b>	<b>SFI13</b>	<b>SFI14</b>
capsule (g)	1.1384	1.1793
grinded (type)	silica	silica
grinded (g)	0.1052	0.1123
solution (type)	2	2
solution (g)	0.1374	0.1337
chips (type, N)	quartz (2)	quartz (2)
chips (g)	0.0858	0.0906
before welding (g)	1.4312	1.4454
after welding (g)	1.4310	1.4453
overnight 110°C (g)	1.4309	1.4453
start	05/07/2016	05/07/2016
stop	08/07/2016	08/07/2016
duration (h)	69	69
T (°C) measured in KJ-35 well by logging tool	336	336
<b><i>After the experiment</i></b>		
capsule (g)	1.4315	1.4460
outcome	ok	ok

## Grant Agreement Number 608553

### **IMAGE** Integrated Methods for Advanced Geothermal Exploration



### **IMAGE-D4.3**

### **ADDENDUM to the Final report on: *High temperature (>380°C) measurement***

Responsible author	Giovanni Ruggieri (IGG-CNR)
Responsible WP-leader Responsible SP-leader	Sæunn Halldórsdóttir (ÍSOR) Gylfi Páll Hersir (ÍSOR)
Contributions by:	Andrea Orlando, Giovanni Ruggieri, Laura Chiarantini, Valentina Rimondi (IGG-CNR) Tobias Björn Weisenberger (ÍSOR)



## Introduction and summary

The method developed in task 4.3 can be used for temperature measurement in high-temperature geothermal reservoirs through the synthesis of fluid inclusions within an apparatus placed in geothermal wells. The method was successfully tested in the KJ-35 geothermal well (Krafla, North Iceland). In fact, fluid inclusion trapping temperature yielded temperature estimate in good agreement with values measured through conventional well logging methods, as reported in the final report of Task 4.3 delivered on the due date.

After this publication, ENEL Green Power (the company exploiting the Larderello geothermal field) provided a geothermal well (Lumiera 1) for an additional experiment to test the method. The test was carried out on February 2017 and synthetic fluid inclusions were examined on March 2017. Results of the trapping temperature of synthetic fluid inclusions (around 251°C) are in good accordance with temperature measured by conventional methods (249°C). This result demonstrates that the proposed method works even at lower temperatures (< 300°C).

## Experiment with the micro-reactor in the Lumiera 1 geothermal well (Larderello, Italy)

Lumiera 1 geothermal well was made available by ENEL Green Power for temperature measurements by the production of synthetic fluid inclusions. The well is located ~1.2 km SW of the country of Monterotondo Marittimo (Larderello geothermal area, Italy, Figure A1). Its depth is 920 m and 249°C and 55 bar were recorded few days before the fluid inclusion experiment by Enel Green Power at the bottom of the well. The pressure (P) - temperature (T) well profile, measured by Enel Green Power is reported in Figure A2.

Before starting the experiment, the micro-reactor was turned with a lathe in a mechanical workshop, just to reduce the outside diameter, so that it could fit in the tube which has been dropped into the well. The experiment, performed with the same procedure as in Krafla (see final report Task 4.3), started on February 17<sup>th</sup>, 2017 and ended on February 24<sup>th</sup>, 2017. After the recovery of the micro-reactor, 2 quartz chips (total weight= 0.0725 g) were extracted from the Au capsule and prepared for optical observation and microthermometric studies.

Optical observations revealed abundant fluid inclusions in quartz chips with sizes up to 20 µm (Figure A3). Their homogenization temperature ( $T_h$ ) varies from 249 to 251°C (Figure A3). Salinity of fluid inclusions was checked computing the temperature of ice melting ( $T_{m_{ice}}$ ) which is  $-6.6 \pm 0.1^\circ\text{C}$ . These values correspond to a salinity of  $10 \pm 0.1$  wt% (NaCl equivalent) in agreement with the total salinity of the aqueous solution inserted in the Au capsule.

The intersection of fluid inclusions isochore departing from liquid-vapour curve of saline fluid (10 wt% NaCl equivalent) with the liquid-vapour curve of pure water occur at ~251°C. (Figure A4). This value represents the trapping temperature of fluid inclusions and, consequently, the temperature estimate at the well bottom. The estimated temperature is only 2°C higher respect to the temperature measured by ENEL Green Power using conventional method (Figure A2).

## Conclusions

Temperature measurement through the formation of synthetic fluid inclusions was successfully achieved in a relatively low-temperature environment. In fact, synthetic fluid inclusions formed extensively within 7 days in the bottom of Lumiera 1 well. Their trapping temperature (251°C) is in good accordance with temperature measured by conventional methods (250°C). It is thus highly promising that in high-temperature geothermal wells, fluid inclusions could form in a short time, possibly in few hours. The Lumiera 1 test, together with that performed in Krafla (KJ-35 well) represent two successfully experiments, suggesting that temperature estimate in geothermal wells through synthetic fluid inclusions, with the method developed in task 4.3, could be applicable in a relatively wide range of temperature.

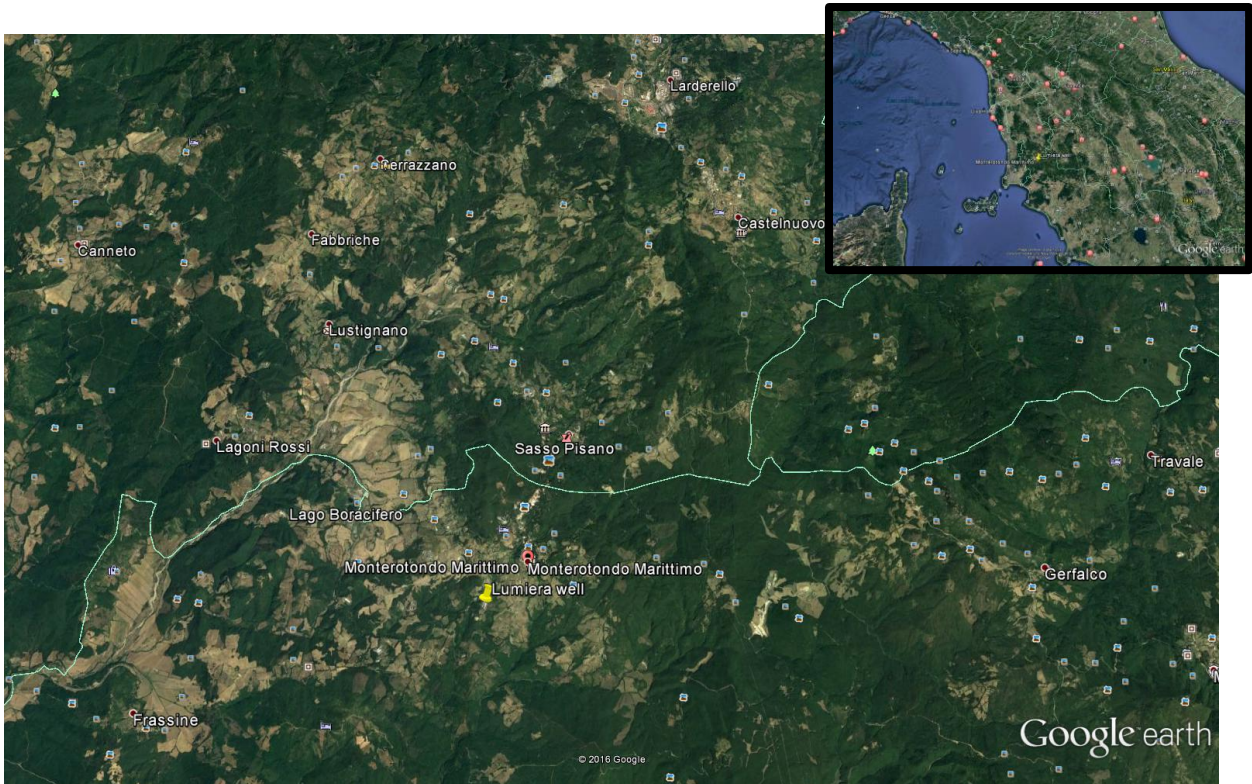


Figure A1: Lumiera1 well (yellow bookmark) is situated in SW Tuscany (see inset), close to Monterotondo Marittimo country. The main map is delineated by the red line in the inset. Picture from Google Earth.

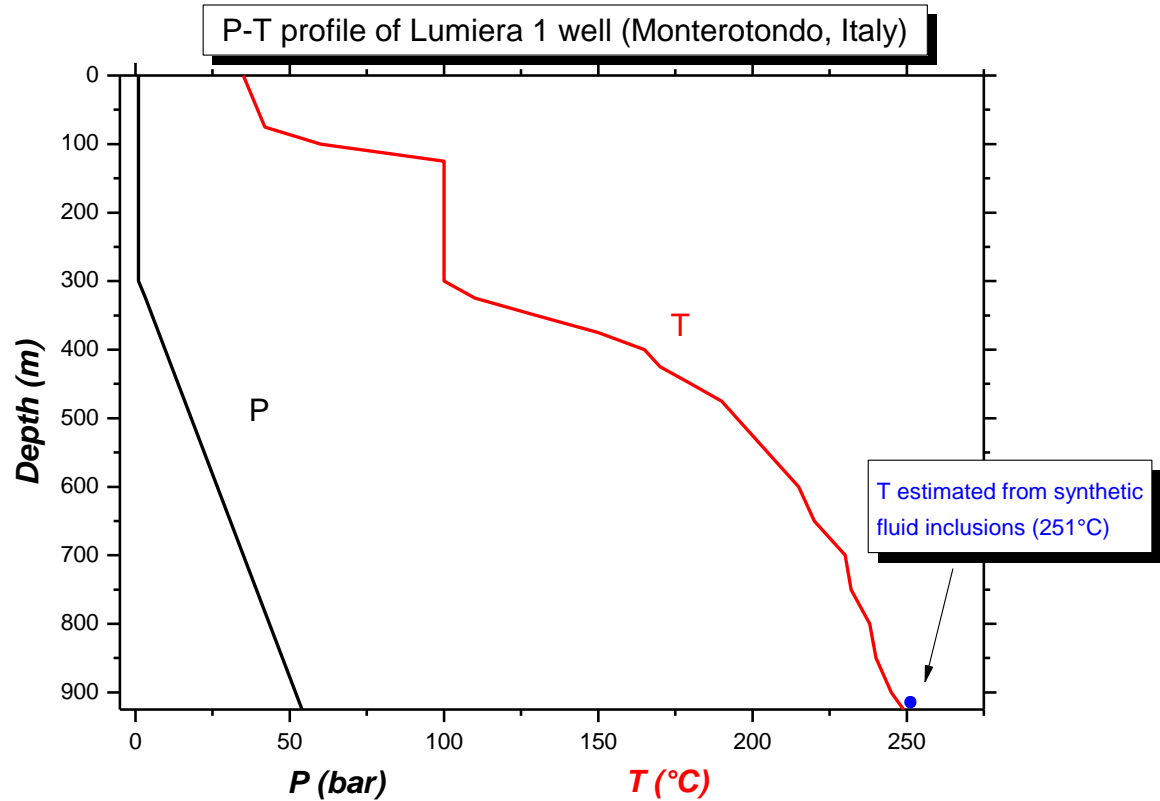


Figure A2: Pressure (P) - Temperature (T) profile of Lumiera 1 well. The blue dot represents the T estimate calculated from synthetic fluid inclusions (see text). Well P-T logging was carried with a Kuster electronic device by ENEL Green Power.

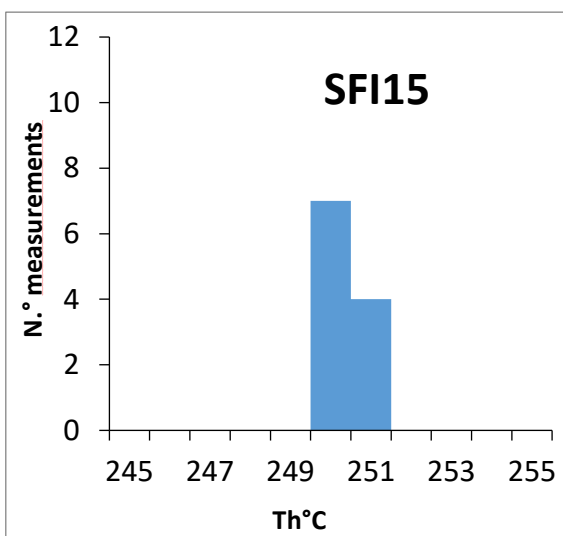
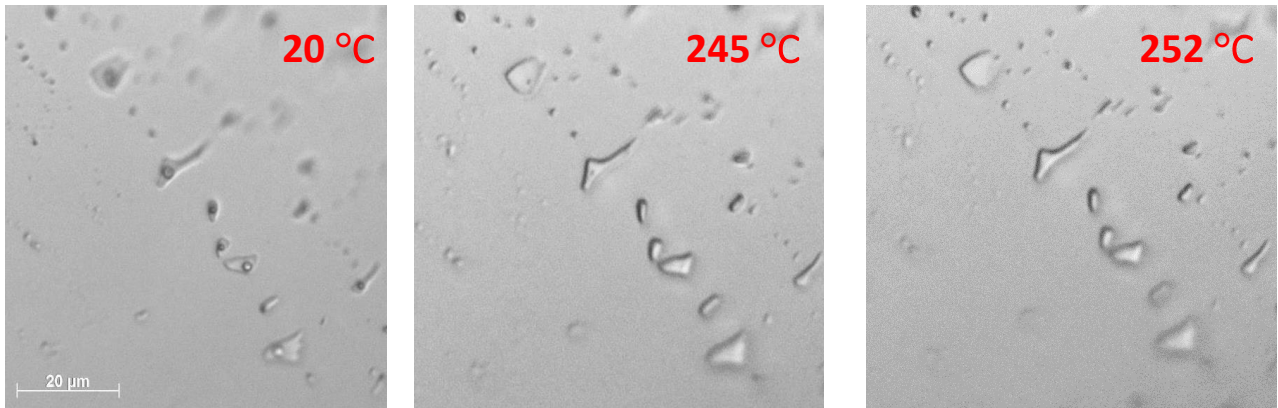


Figure A3: Microphotographs of synthetic fluid inclusions at ambient T (left) and at T just below and above homogenization T (Th). The Th measurements are visualised in the histogram.

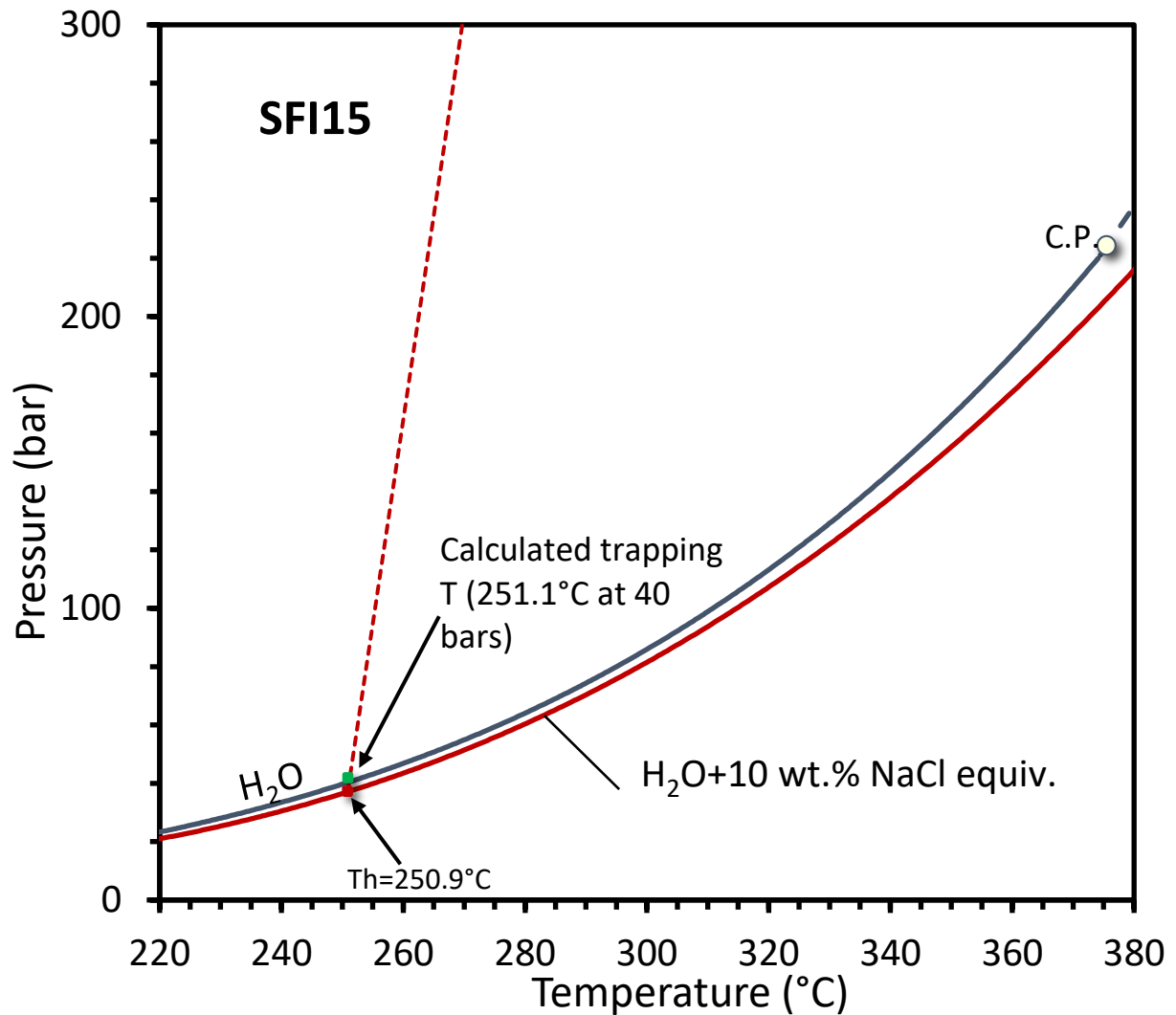


Figure A4: The liquid-vapour curves of saline fluid (10 wt% NaCl equivalent) and pure H<sub>2</sub>O are represented, together with a representative isochore (dotted red line) calculated from Th of fluid inclusions. The trapping P-T conditions of fluid inclusions are defined by the green dot.