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Restoring Halite Fluid Inclusions as an Accurate Palaeothermometer: Brillouin Thermometry Versus Microthermometry

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Halite traps inclusions of the mother fluid when precipitating. When unchanged, the density of these fluid inclusions (FIs) records the water temperature $T_f$ at the time of crystal formation. As halite is ubiquitous on Earth and geological time, its FIs possess a high potential as temperature archives. However, the use of FIs in halite as an accurate palaeothermometer has been hampered due to limitations of microthermometry, the most commonly used analytical method. Here, we show how Brillouin spectroscopy in halite FIs bypasses these limitations and allows recovering $T_f$ to within 1 °C or less. To demonstrate this, we measured samples synthesised at 24.6 ± 0.5 °C and 33 ± 1 °C, and obtained 24.8 ± 0.4 °C and 31.9 ± 0.4 °C, respectively. This novel approach thus provides an accurate palaeothermometer for lacustrine and marine environments. Moreover, Brillouin spectroscopy solves the long-standing debate on damage of halite fluid inclusions through quantifying the acceptable temperature excursion for preserving elastic behaviour: $l/(1\ \mu m)^{0.64} \times (90\ °C)$, where $l$ is the FI size. This threshold is lower for FIs close to the surface of the host crystal or to another FI. We also list ‘best practices’ for applying both microthermometry and Brillouin thermometry.

Keywords: halite fluid inclusions, palaeothermometer, Brillouin spectroscopy, microthermometry, fluid inclusion re-equilibration.

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The determination of past temperatures is a key parameter in reconstructing palaeoclimates and associated environmental conditions. Continental sedimentary deposits provide an excellent choice when searching for reliable temperature archives. As such, evaporites are of great interest. Evaporites form either from the evaporation of the water column or from saline pore water within the sediment. Although arid climates and confined environments favour the formation of evaporites, their current distribution on the Earth’s surface shows that they form in a variety of different settings (Warren 2010). They are found at most latitudes, from the tropical sabkhas of the Persian Gulf (Schreiber and El Tabakh 2000) to modern times (Piovano et al. 2002), evaporites hold a true potential in the record of past climates in arid continental to marine-related environments (Warren 2016). Halite and other evaporitic minerals have been used to infer depositional conditions such as water budget or lake level (Lowenstein and Hardie 1985, Li et al. 1996, Schreiber and El Tabakh 2000, Rigaudier et al. 2011); halite bromine content was used as a genetic criterion for evaporitic basins (Valiashko 1956, Holser 1966); and the chemistry of halite fluid inclusions (FIs) has been used to reconstruct past seawater composition (Timofeeff et al. 2001, Zimmermann 2001, Rigaudier et al. 2012, Brennan et al. 2013). A summary of some of the major proxies used on halite to reconstruct palaeo-environments was published by Blamey and Brand (2019). Twenty-five years ago, Roberts and Spencer (1995) proposed using halite primary FIs as a palaeothermometer for brines, by
measuring their homogenisation temperature ($T_h$; see Appendix A for a definition of abbreviations used in this paper). For a FI containing liquid and vapour (biphasic FI), $T_h$ is the temperature at which the vapour bubble disappears upon heating, the FI then becoming monophasic (Figure 1a). Measuring $T_h$ has long been used to obtain formation temperatures of metamorphic minerals usually containing biphasic FIs at ambient temperature, as they are trapped at elevated conditions of temperature and pressure (Sorby 1858). Conversely, most FIs in evaporites are monophasic because they form at sub-surface conditions. To circumvent the absence of a vapour bubble in halite FIs, Roberts and Spencer (1995) first cooled the halite crystals down to -20 °C in a freezer. Because the fluid is cooled at nearly constant volume, this generates negative pressure, low enough to nucleate a bubble in some FIs. Roberts and Spencer (1995) subsequently heated the FIs in a temperature-controlled microscope stage up to $T_h$. In principle, to obtain the FI entrapment temperature ($T_f$), a correction is required to account for the ambient pressure at the time of entrapment. However, as lacustrine halite FIs are generally trapped at very low pressure, this correction can be neglected, and therefore, $T_h$ is assumed to be equal to $T_f$ and, thus, to the brine temperature. Roberts and Spencer further proposed several tests to check whether the FIs followed the ‘Roedder’s Rules’ (Roedder 1984a) preserving the FIs initial mass, volume and composition. In 1999 Benison and Goldstein validated the applicability of the technique to reconstruct ancient climates, showing consistent homogenisation temperatures within individual fluid inclusions assemblages (FIAs, i.e., a group of coeval FIs in a crystal) in chevrons from Permian halites. However, Lowenstein et al. (1998) applied the same protocol on synthetic and natural modern halites, and found broad $T_h$ distributions showing unexpected results:

- A large number of FIs had a $T_h$ far below the temperature at which halite grew
- Only the maximum $T_h$ in the distribution, $T_{	ext{h, max}}$, correlated well with the highest temperature measured in the brine during the period of crystal precipitation.

Since these early experiments, several practices can be found in the literature about the most relevant temperature value to use in palaeoclimatic reconstructions: $T_{	ext{h, max}}$ (Lowenstein et al. 1999, Meng et al. 2011, Meng et al. 2013, Sun et al. 2017); $T_{	ext{h, mean}}$, (Rigaudier et al. 2011, Speranza et al. 2013); and various properties of the $T_h$ distribution (range, mean and extremes), meaning that every single $T_h$ has palaeoclimatic significance (Benison and Goldstein 1999, Losey and Benison 2000, Satterfield et al. 2005a, b,

Figure 1. Thermodynamic path followed by a FI in a NaCl-H2O phase diagram with (a) microthermometry and (b) BS. In this diagram, the horizontal (blue) curve represents the solid–liquid–vapour equilibrium (SLVE) that separates the halite + vapour domain (below) from the halite + liquid domain (above). See Bakker (2018, 2019) for details on the NaCl-H2O phase diagram. (a) Upon trapping in shallow water, FI forms as one liquid phase at vapour pressure (point ‘1’). Upon cooling (1 → 2), follows quasi-isochore (black curve) and becomes metastable: fluid occupies a larger volume than at equilibrium, and may reach negative pressures. Upon cavitation, SLVE is restored (2 → 3). Upon heating (3 → 1), FI follows SLVE, bubble shrinks and eventually disappears at $T_h$. Liquid recovers volume it occupied at trapping, and equality between $T_h$ and $T_f$ is assumed. (b) FI trapped under the same conditions (point ‘1’) is measured in monophasic state at several different temperatures (2 → 3 → 4 → 5), providing the speed of sound in the monophasic FI $w_{\text{mono}}(T)$. After forced cavitation (see text), $w_{\text{SLVE}}(T)$ is measured. $w_{\text{mono}}(T)$ intersects $w_{\text{SLVE}}(T)$ at $T_s$ equal to $T_h$. Below $T_s$, quasi-isochore is extrapolated (dashed black line). Note that with BS, FIs undergo considerably weaker stresses (approximately 4 times here) than with microthermometry. [Colour figure can be viewed at wileyonlinelibrary.com]
Kovalevych et al. 2009, Zambito and Benison 2013, Zhao et al. 2014, Zhang et al. 2015, Yang 2016, Zhang et al. 2016, Zhang et al. 2017, Xu et al. 2019). Which of them is the best practice is still an unsettled debate. Another issue, often overlooked, is the Laplace pressure difference between the vapour bubble and the liquid, which causes the bubble to collapse before \( T_b \) (Fall et al. 2009, Krüger et al. 2011). This bias can lead to underestimating \( T_b \) by several degrees Celsius.

All these uncertainties have discouraged many scientists from using the microthermometry technique. Nevertheless, FIs from sub-surface rocks hold a large potential as temperature archives, as their density is a direct physical record of palaeotemperatures. Here, we propose a new technique based on Brillouin spectroscopy (BS) to unravel the entrapment temperature information contained in halite FIs. BS as a palaeothermometer (Brillouin thermometry) was first introduced in a preliminary study by El Mekki-Azouzi et al. (2015), who validated this principle using one synthetic and three natural FIs in quartz crystals. Although the results showed good agreement, the applicability of the method remains to be proven for sub-surface soft minerals with low \( T_b \) values such as halite. BS relies on the inelastic interaction between light and spontaneous (thermal) density fluctuations in matter, causing a frequency shift (\( \Delta f \)) between incident and scattered light. In turn, \( \Delta f \) measured with BS is a function of the speed of sound (\( c \)) in the liquid. Because of this physical property, BS allows for the measurement of the entrapment temperature of any halite FI, provided it is small enough and has never experienced large thermal cycles. The speed of sound in the monophasic FI (\( c_{\text{mono}} \)) is first measured and, only then, a bubble is nucleated through deliberately stretching the FI by means of a large thermal cycle, thus allowing for the measurement of the speed of sound in the biphasic FI (\( c_{\text{bip}} \); see Figure 1b). The temperature at which the two temperature-dependent curves \( c_{\text{mono}}(T) \) and \( c_{\text{bip}}(T) \) intersect, \( T_w \), is a measurement of \( T_b \) in the case of a FI trapped at Earth surface conditions (i.e., close to atmospheric pressure and moderately low temperature). The damage caused to the FI during the bubble nucleation process does not affect the entrapment temperature information, as the latter is contained in the previously measured \( c_{\text{mono}}(T) \) curve. This is a fundamental difference with the microthermometry technique, which first requires the nucleation of a bubble by exposing the FI to a large negative pressure in the freezer before the measurement of \( T_b \). Through comparing BS and microthermometry results on laboratory-grown halite crystals, we demonstrate that BS yields \( T_b \) distributions centred on \( T_b \) while \( T_b \) distributions obtained by microthermometry show a bias towards lower temperatures. The use of the mean \( T_b \) (\( T_{b,\text{mean}} \)) thus has palaeoclimatic significance, whereas this is not the case for the mean \( T_b \) (\( T_{b,\text{mean}} \)). Conversely, we confirm the validity of the maximum \( T_b \) obtained by microthermometry (\( T_{b,\text{max}} \)) as an indicator of the maximum temperature of the brine. Furthermore, we use the speed of sound measured in fluid inclusions to investigate for the first time the mechanisms that account for the re-equilibration of FIs (i.e., the density change that causes the loss of the information on the entrapment temperature). We obtain an empirical equation predicting the maximum temperature excursion that FIs in halite can withstand before irreversibly changing volume, depending on their size. This finding solves the long-standing debate on the ability of halite FIs to record past temperatures: halite FIs prove to be good recorders of the parent brine temperature provided they are small enough to have withstood the temperature excursions the sample was subjected to during its history. Finally, based on our findings, we propose good practices to follow when using microthermometry or Brillouin thermometry on halite FIs.

Materials and methods

Set-up

The BS set-up is described in Holten et al. (2017), Pallares et al. (2016, 2014) and El Mekki-Azouzi et al. (2015). Brillouin scattering experiments were performed in backscattering geometry through the microscope objective (Wututaya PlanApo, 100x magnification). The sample was illuminated with a 54 mW beam from a single longitudinal mode laser (Coherent, Santa Clara, California, USA, Verdi V6) with wavelength \( \lambda \approx 532 \) nm. The laser beam, focused to a 1 \( \mu \)m spot, allowed the measurement of FIs a few micrometres in size without damaging them. The light backscattered from the sample was analysed with a six-pass tandem Fabry-Perot interferometer (JRS Scientific, Mettenstetten, Swiss, TFP-1), with entrance and exit pinholes 300 and 450 \( \mu \)m in diameter, respectively.

The sample was placed in a temperature-controlled stage (Linkam, Tadworth, UK, THMS600) whose temperature was calibrated with synthetic FIs of pure water and pure CO\(_2\)-H\(_2\)O hosted in quartz. The typical rate for temperature change was \( \pm 20 \) °C min\(^{-1}\). As 1 °C change in monophasic halite FIs converts to \( \sim 1 \) MPa (Figure 1), and as the elastic stiffness \( C_{11} \) of NaCl is 47.1 GPa (Szomor 1968), typical strain rates applied to FIs walls were \( 7 \times 10^{-6} \) s\(^{-1}\).

Materials

We prepared two 60 mL aqueous solutions saturated with respect to NaCl (at 20 °C, \( \sim 6.15 \) mol kg\(^{-1}\)) by
dissolving NaCl (VWR AnalR NORMAPUR, purity = 99.5%) in ultrapure water (ELGA PURELAB Flex; resistivity at 25 °C: 18.2 MΩ cm; TOC: 1 ng g⁻¹). Each solution was set to evaporate in polypropylene flat bottom beakers dipped in thermal baths at 26 and 36 °C, respectively. The room temperature was air-conditioned to 20 ± 0.5 °C. Total evaporation of the solutions required approximately 20 h. The temperature of the brines was monitored all along the evaporation process by means of a Pt100 Resistance Temperature Detector (dimensions 2 × 2 × 1 mm), calibrated with a Dostmann P795 thermometer with a Pt100 probe calibrated in four points to reach a 0.1 °C accuracy. Due to space and time-related temperature fluctuations inside the brine, the final uncertainty on crystal growth temperature was higher. The temperature measured inside the two brines was 24.6 ± 0.5 and 33 ± 1 °C, respectively. Note that the uncertainties shown here are not standard deviations but brackets due to temporal and spatial temperature fluctuations in the brines. Crystals precipitated at the surface of the solution, coalesced progressively to form floating rafts and then sank to the bottom of the beaker where they kept growing. From the salt crust remaining at the end of evaporation, we selected some of the millimetre-size flat rectangular crystals for microthermometry and BS analyses. Most of them contained numerous rectangular FIs aligned along the crystal growth bands observable under the microscope (Figure 2). Batches of halite crystals are named according to their synthesis temperature, as follows: SyntHal24.6 is the name given to the batch of crystals which grew in the brine of temperature 24.6 ± 0.5 °C, and SyntHal33 is that of crystals grown in the brine of temperature 33 ± 1 °C. In several cases, we added a subscript, such as in SyntHal33_{16}, to indicate the minimum temperature (T_{Min}) undergone by the sample (16 °C in the given example). The samples were never exposed to temperatures higher than T_f before isochore measurement (BS) or before T_h measurement (microthermometry).

Methods

In this work, the reported observation is the speed of sound w. BS measures the Brillouin frequency shift Δf. Details of Δf and its conversion to w are reported in Appendix B.

The speed of sound in a FI depends on the composition, temperature and pressure of the liquid. At solid–liquid–vapour equilibrium (SLVE), the speed of sound of the liquid as a function of temperature, w_{SLVE}(T), can be measured in a biphasic FI. Conversely, a monophasic FI does not follow the SLVE when warmed or cooled, but an isochore at density ρ (Figure 1), along which the speed of sound varies with temperature, defining the curve w_{monoph}(T), uniquely determined by ρ. The curve w_{monoph}(T) for the monophasic FI intersects w_{SLVE}(T) at T_x (Figure 3). By definition, the density along the SLVE curve equals ρ at T_x which, therefore, we identify with T_f at which the liquid with density ρ was trapped.

Strictly speaking, the thermodynamic path followed by a FI is a quasi-isochore rather than an isochore. This is due to combined effects of thermal expansion and elasticity of the crystal, and of temperature variation of the saturation concentration with respect to NaCl. Nevertheless, as T

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Figure 2. Laboratory-grown halite. SyntHal33_{16} crystal. (a) FIs are aligned along growth bands and concentrically arranged around the crystal centre (at photograph centre); some large FIs are elongated parallel to growth fronts. This alignment along growth bands is a typical arrangement of halite primary FIs, which get trapped during the course of the crystal growth. Red arrows show air bubbles pre-existing in some FIs, certainly trapped during halite formation. Region delimited by red rectangle in (a) is magnified in (b), showing several monophasic FIs. (c) Same region after heating–cooling cycle up to 130 °C and back to room temperature: almost all FIs cavitated. [Colour figure can be viewed at wileyonlinelibrary.com]
Parabolic \( w_{\text{mono}}(T) \) and \( w_{\text{SLVE}}(T) \) are fitted to \( w \) data points measured in the FI at monophasic (discs) and two-phase (circles) states, respectively (see Appendix S1 for details on the fits). Error bars: \( \sigma_w = 0.1\% \). Fitted curves intersection gives \( T_x \) (dashed-dotted line), with estimated \( \sigma_{T_x} = 1.5 \, ^\circ\text{C} \) (shaded area).

remains the only independent variable, the \( w_{\text{mono}}(T) \) curve for halite FIs crosses \( w_{\text{SLVE}}(T) \) at \( T_x \). Once all \( w_{\text{mono}}(T) \) measurements in monophasic FIs of a given sample were performed, the sample was heated to 130 °C for several minutes to stretch the inclusions. It was subsequently cooled to room temperature; this triggered cavitation of a significant number of FIs. This procedure allowed us to perform \( w_{\text{SLVE}}(T) \) measurements. Note that it is important to measure individual \( w_{\text{SLVE}}(T) \) curves rather than only one mean over several FIs, as the standard deviation on repeated measurements on one FI (0.1%) is lower than the standard deviation of the distribution of measurements (0.3%). This variation between NaCl and \( \text{H}_2\text{O} \) FIs of the same concentration partly arises because they lie at various depths within a crystal, affecting the optical path followed by the laser and causing small additional deviation in Brillouin measurements between FIs.

For each FI, we measured four and three data points along \( w_{\text{mono}}(T) \) and \( w_{\text{SLVE}}(T) \), respectively. We performed simulations of our experiments to estimate the impact of different protocols on the resulting \( T_x \) distribution. These results show that this procedure is a good compromise between measurement time and accuracy, and also that other protocols can be suitable (see Appendix S1).

The microthermometry measurements were carried out in the same temperature-controlled stage as the Brillouin measurements. In order to trigger cavitation, the samples were cooled directly on the stage and kept at -20 °C for about 30 min; such an alternative to the freezer procedure is sometimes preferred by certain authors (e.g., Speranza et al. 2013). The comparable distributions of \( T_h \), as measured in Wang et al. (2018) in halite samples cooled to -18 °C for different time spans show that the duration of the cooling step matters little. Homogenisation temperatures of biphasic FIs were measured by heating the samples with a 1 °C min\(^{-1}\) ramp. The precision of \( T_h \) measurements was ± 0.5 °C. All results reported here were further corrected for Laplace pressure (e.g., Fall et al. 2009; see Appendix S1 for details of the method applied).

In this work, all the FIs selected for measurements were initially monophasic and rectangular-shaped. We used the standard criteria to discard secondary FIs (Roedder 1962). FIs below 3 µm (Brillouin) or 7 µm (microthermometry) in size were avoided. Indeed, very small FIs require an excessively long Brillouin spectrum acquisition time and are also difficult to view and measure in microthermometry, as already noted by Krüger et al. (2011).

Halite FIs are cuboids, with different length (a), width (b) and depth (c). c corresponds to the dimension perpendicular to the field of view. Since it was not possible to measure c in this work, sizes are all expressed as a function of a and b, through the relation \( l = (ab)^{1/3} \), with \( l \) the side of a square of equivalent surface. On average in this work, \( a = 1.67 b \). c is thus unlikely to differ much from a and b, so that we expect \( l \) to be close to \( (ab)^{1/3} \).

Results

\( T_h \) and \( T_x \) values obtained on several crystals from batches SynthHal24.6 and SynthHal33 are presented in the following two sections, respectively, and in Figure 4. In the third sub-section below, the two techniques used successively on the same FIs are compared. This comparison was only possible when FIs measured with BS subsequently cavitated through cooling down to -20 °C. The statistical data of all \( T_h \) and \( T_x \) measurements are summarised in Table 1.

Comparison of microthermometry and BS on a low \( T_h \) sample

The \( T_x \) histogram obtained with BS (Figure 4a) on SynthHal24.6 crystals displays values well centred on the synthesis temperature, with \( T_{x,\text{mean}} \) lying within the \( T_h \) range (Table 1). The distribution is normal and the difference between mean and median is as low as 0.2 °C. The \( T_h \) histogram obtained with microthermometry (Figure 4d) shows a mode consistent with the synthesis temperature, along with a significant amount of \( T_h \)'s far below the synthesis temperature. Altogether, this results in a \( T_{h,\text{mean}} \sim 3 \, ^\circ\text{C} \) below \( T_h \) and a standard deviation almost three times larger.
Figure 4. Histograms of $T_x$ and $T_h$ distributions. Panels (a–d): SyntHal24.6; Panels (e–h): SyntHal33. $T_x$ distribution for all FIs (a and e), and after selection (b and f). $T_h$ distribution for all FIs (c and g), and after selection (d and h). See text for details of the selection criteria. [Colour figure can be viewed at wileyonlinelibrary.com]
than the one obtained with BS. $T_{h,max}$ corresponds to $T_h$ within ± 1 °C.

Using an ‘isolation’ criterion to discard FIs close to each other or to the crystal surface (see Discussion, first sub-section), we obtained the histograms for $T_{h,s}$ and $T_{x,s}$ shown in Figure 4b, d, respectively. This selection does not yield any significant difference, as it barely affects statistical values $T_{h/x, mean}$ and $\sigma$.

**Comparison of microthermometry and BS on a high $T_h$ sample**

$T_x$ and $T_h$ histograms (Figure 4e, g, respectively) of SynthHal33 present mean lower than $T_h$ by 4.6 and 7.3 °C, respectively. They both show a broad distribution towards low temperatures (Table 1). Distributions are non-normal, as shown by rather large $T_{h/x, median}$–$T_{h/x, mean}$ values (Table 1).

In addition to the isolation criterion (Results, first sub-section), we apply a size criterion: FIs larger than 13 µm were discarded (see Discussion, second sub-section). The corresponding $T_h$ and $T_x$ histograms are shown in Figure 4f, h, respectively. After this combined selection process, the mean $T_h$ lies within the $T_h$f range to within the standard error, and the standard deviation is reduced to a very low value of 1.5 °C. The spread of $T_{x,s}$ is also halved through applying the selection criteria, but the mean $T_x$ remains 5 °C below $T_h$. $T_{h,max}$ corresponds to $T_h$ within ± 1 °C.

**Direct comparison between $T_h$ from microthermometry and $T_x$ from BS**

Once all $w^{\text{mono}}$ measurements were made on the samples, they were cooled to -20 °C for 15–30 min. Out of the total 147 FIs previously analysed through BS, cavitation occurred in eight, on which we subsequently measured $T_{x,s}$. After that, we heated the samples up to 130 °C to stretch FIs and nucleate bubbles to finally perform $w^{\text{AVE}}$ measurements, which allowed us to obtain $T_{x,s}$.

The direct comparison of temperatures obtained by microthermometry and BS on the same FIs (Figure 5) shows that $T_x \leq T_h$ for each of the eight FIs within their error bars. The larger the FIs, and/or the milder the temperature FIs were submitted to prior to BS isochore measurements, the larger the discrepancy between $T_h$ and $T_x$. Indeed, while the two FIs submitted to $\Delta T = 33$ °C prior to BS (SynthHal33A, see Discussion (second sub-section) for more explanations on this batch) show $T_x \approx T_h$, the six FIs submitted to a narrower $\Delta T$ prior to BS, 17 °C (SynthHal33A1, and 5.6 °C (SynthHal24.6A10) show $T_x < T_h$. Among these six FIs, larger FIs show $T_x \ll T_h$ while smaller FIs show $T_x \approx T_h$.

This experiment shows that FIs may yield $T_{h/x,s}$ lower than $T_h$ both with BS and microthermometry. However, when this bias is present, $T_x$ is always lower than $T_h$ by up to 10 °C.

**Discussion**

The interpretation of FIs homogenisation temperatures in halite has long been questioned (e.g., Roedder 1984a, Lowenstein et al. 1998). When the rocks are buried several kilometres deep, inclusions may stretch due to the positive internal pressure that accumulates upon heating of the trapped solution (Roedder 1984a). Conversely, halite FIs reach significant negative pressures when brought to a typical cooling temperature of -20 °C (Figure 1; for more details about liquids at negative pressure, that is. under tension, see Caupin and Heibert (2006) and Caupin et al.

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**Table 1. Statistics of the $T_{h/x}$ distributions**

<table>
<thead>
<tr>
<th></th>
<th>$N$</th>
<th>$T_h$ (°C)</th>
<th>$T_{h/x, mean}$ (°C)</th>
<th>$T_{h/x, median} - T_h/x_{mean}$ (°C)</th>
<th>$T_{h/x, max}$ (°C)</th>
<th>$T_{h/x, min}$ (°C)</th>
<th>$\sigma$ (°C)</th>
<th>SE (°C)</th>
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</thead>
<tbody>
<tr>
<td>SynthHal24.6C19 (BS)</td>
<td>51</td>
<td>24.6 ± 0.5</td>
<td>24.7</td>
<td>0.2</td>
<td>29</td>
<td>21.1</td>
<td>1.9</td>
<td>0.27</td>
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<tr>
<td>SynthHal24.6C19 selected (BS)</td>
<td>33</td>
<td>24.6 ± 0.5</td>
<td>24.8</td>
<td>0.2</td>
<td>29</td>
<td>21.1</td>
<td>2</td>
<td>0.36</td>
</tr>
<tr>
<td>SynthHal24.6-20 (Microthermometry)</td>
<td>30</td>
<td>24.6 ± 0.5</td>
<td>21.8</td>
<td>2.7</td>
<td>25.8</td>
<td>10.2</td>
<td>5.2</td>
<td>0.98</td>
</tr>
<tr>
<td>SynthHal24.6-20 selected (Microthermometry)</td>
<td>24</td>
<td>24.6 ± 0.5</td>
<td>20.9</td>
<td>3.3</td>
<td>25.8</td>
<td>10.2</td>
<td>5.5</td>
<td>1.18</td>
</tr>
<tr>
<td>SynthHal33-16 (BS)</td>
<td>51</td>
<td>33 ± 1</td>
<td>28.4</td>
<td>0.3</td>
<td>34.9</td>
<td>29.3</td>
<td>1.7</td>
<td>0.63</td>
</tr>
<tr>
<td>SynthHal33-16 selected (BS)</td>
<td>19</td>
<td>33 ± 1</td>
<td>31.9</td>
<td>0.3</td>
<td>34.9</td>
<td>29.3</td>
<td>1.7</td>
<td>0.41</td>
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<tr>
<td>SynthHal33-30 (Microthermometry)</td>
<td>26</td>
<td>33 ± 1</td>
<td>25.7</td>
<td>2</td>
<td>32.8</td>
<td>12</td>
<td>6</td>
<td>1.23</td>
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<tr>
<td>SynthHal33-30 selected (Microthermometry)</td>
<td>13</td>
<td>33 ± 1</td>
<td>28.1</td>
<td>0.2</td>
<td>32.7</td>
<td>21.4</td>
<td>3</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Each set of measured data was analysed as a whole and after selection, following the criteria described in the text. Error bars associated with $T_h$ values are the intervals of synthesis temperature. $\sigma$ is one standard deviation. SE, the standard error, is the uncertainty on the mean within a 68.27% confidence interval (1σ) with respect to Student’s $t$-distribution.
Absolute negative pressures constitute a critical factor to consider in understanding the re-equilibration of FIs during microthermometry experiments. As halite is prone to plastic deformation, negative pressures exceeding halite yield stress should lead to the plastic deformation of the FI walls and thus lead to irreversible shrinkage. Both our microthermometry and BS experiments are consistent with the occurrence of a non-reversible collapse of inclusions walls upon cooling, resulting in the lowering of the $T_{x/y}$ yielded by FIs. As a matter of fact, it appears that with both techniques some FIs resist collapsing while others do not. The following section addresses the causes that can potentially account for these observations.

### The ‘vicinity’ of FIs as a mechanical softener

A FI applies a stress on its host as soon as it undergoes a temperature different from $T_f$. If spherical, the FI is surrounded by a stress field which is maximal at the inclusion rim and diminishes asymptotically to 0 MPa away from the inclusion. Zhang (1998) addressed the case of the elastic equilibrium and plastic deformation of a host/inclusion system. For a simplified system consisting in a spherical inclusion centred inside a spherical host, he determined the internal pressure at which the host interface with the inclusion begins to yield. At atmospheric external pressure, this can be written as follows:

$$P_{FI,\text{lim}} = \frac{2}{3} Y_S \left(1 - \frac{R_{FI}^3}{(R_{FI} + d_{host})^3}\right)$$

$P_{FI,\text{lim}}$ is the FI internal pressure that triggers plastic deformation at the FI rim, $R_{FI}$ the radius of the FI, $d_{host}$ the distance between the host surface and FI rim, and $Y_S$ the yield stress of the host. This relation highlights the importance of the ratio between the FI size and its depth in the host and shows that a very weak internal pressure is sufficient to trigger plastic deformation when this ratio approaches 1. In other words, big FIs close to the surface are more prone to plastic deformation (Figure 6). Nevertheless, $P_{FI,\text{lim}}$ tends to a constant $2/3(Y_S)$ when $R_{FI}/(R_{FI} + d_{host}) \approx 0$. For $R_{FI}/(R_{FI} + d_{host}) < 0.5$ and $< 0.2$, the effect has an impact lower than 13% and 1%, respectively. This weakening effect due to host surface proximity should be generalisable to any surface proximity, such as a neighbouring FI. In a finite element model, Burnley and Schmidt (2006) tested the effect of proximity between two FIs on their volume change and noticed that from a distance smaller than one FI size, FIs started ‘detecting each other’.

Based on these two studies, we define a concept of isolation that considers both host surface and neighbouring FIs following the equation:

$$\text{Iso}_{FIa} = \max \left[ \frac{R_{Fla}}{R_{Fla} + d_{host}}, \frac{R_{Fla}}{R_{Fla} + d}, \frac{R_{Flb}}{R_{Flb} + d_{host}} \right]^{-1}$$

$\text{Iso}_{FIa}$ is the isolation of an inclusion FIa, $R_{Fla}$ and $R_{Flb}$ the respective radii of FIa and FIb, $d$ the distance between FIa and FIb rims, and $d_{host}$ the distance between host surface and FIa rim. By construction, $\text{Iso}_{FI} > 0$. This approach is admittedly an oversimplification, as it does not consider the influence of FI shape, the host anisotropy or the interaction between stress fields of neighbouring FIs. Consequently, this criterion should be considered only as a semi-quantitative one. In this work, the ‘isolation’ criterion (see Results, first and second sub-sections) consists in discarding FIs with $\text{Iso}_{FI} \leq 1$.

Our experiments reveal the role of isolation in FI re-equilibration (Figure 7a, c, e). Many FIs with a low $\text{Iso}_{FI}$...
exhibit a $T_x$ lower than that of more isolated FIs of comparable size. This is particularly obvious for small FIs ($< 13 \mu m$) in SyntHal3316 (Figure 7c). Conversely, we observe little to no isolation-dependent trend in crystals from batches SyntHal330 (Figure 7e) and SyntHal24.619 (Figure 7a). We explain these observations as follows:

- in SyntHal24.619 FIs, the internal negative pressure was too weak to induce re-equilibration, even in the case of low $Iso_0$ FIs;
- in SyntHal330 FIs, the internal negative pressure was strong enough to induce the re-equilibration of all FIs, hence the difficulty to observe a clear difference between high and low $Iso_0$ FIs;
- in SyntHal3316, the internal negative pressure was not strong enough to generate the irreversible deformation of small isolated FIs ($< 13 \mu m$; see Discussion, second subsection) while it was in the case of low $Iso_0$ FIs of the same sizes, hence the visible lower $T_x$ obtained on the latter.

$T_{Min}$ and FI size-decisive drivers of re-equilibration

The $T_x$-size relation for SyntHal24.619 and SyntHal3316 is shown in Figure 7a, c, respectively. In addition, in order to test the effect of a very large $\Delta T$ on the $T_x$-size trend, we performed BS on a third sample, SyntHal330 (Figure 7e). $T_x$ can strongly depend on the FI size, and this dependence is all the stronger as samples underwent $T_{Min}$, $\ll T_i$ before thermometry measurement. Indeed, while SyntHal24.619 shows no systematic variation of $T_x$ with size, SyntHal3316 and SyntHal330 show a strong and very strong variation, respectively. This can be explained by the growing values of $\Delta T$: 5.6, 17 and 33 °C, respectively. In order to define a potential size threshold, we plot the cumulative $T_{x,mean}$ from the smallest to the largest isolated FI for each of the cases (Figure 7a). Displaying the data this way, it is possible to visualise the size threshold above which $T_{x,mean}$ no longer corresponds to $T_i$ within the error bars (i.e., within the standard error on the mean). Three situations were observed, depending on $\Delta T$:

- With a small $\Delta T$ (SyntHal24.619), the cumulative $T_{x,mean}$ was constant and equal to $T_i$ whatever the size. No FI underwent discernible re-equilibration.
- With a moderate $\Delta T$ (SyntHal3316), the cumulative $T_{x,mean}$ was constant and equal to $T_i$ up to a size threshold $\sim 13 \mu m$ and then decreased. The tension built inside FIs was enough to induce plastic deformation of the wall of FIs larger than $\sim 13 \mu m$.
- With a high $\Delta T$ (SyntHal330), no threshold was observed, $T_{x,mean}$ decreasing steadily with larger FIs. Virtually no FI could withstand the strong tension. Fitting a power law curve to $T_x$ as a function of size, pinpointing the intersection with $T_i$ we identified a potential threshold size of 4.1 µm.

When testing the influence of FI size on $T_x$ obtained with microthermometry a lower correlation is found (Figure 7g, i). The cumulative $T_{x,mean}$, as a function of size (Figure 7h, j)

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Figure 6. ‘Bad’ and ‘good’ fluid inclusions when performing thermometry on halite. (a) 2-radii circles drawn around FIs illustrate violations of isolation criteria used in this work. Stress field of FI A, selected for $T_{h/x}$ measurement, encompasses two surfaces: that of the host crystal and of FI B. It contributes to lowering the FI A elasticity limit and leads to plastic deformation of its walls. Similarly, FI A lies in the region of FI B strong stress field, which also contributes to plastic deformation of its walls. Moreover, its large size and the large thermal range to which it was subject also exposes it to plastic deformation. (b) FI is is distant enough from any other FI and the surface, it is small, and thermal extremes undergone are mild. [Colour figure can be viewed at wileyonlinelibrary.com]
to four values from SyntHal24.6.19, SyntHal33.16, SyntHal33.10, SyntHal24.6.20 and SyntHal33.20. Points are coloured according to their ISO$_{h}$ value (see Discussion, first sub-section). Right column: cumulative $T_{h/x,mean}$ for SyntHal24.6.19 (b), SyntHal33.16 (d), SyntHal33.10 (f), SyntHal24.6.20 (h) and SyntHal33.20 (j); the mean was calculated over successive data subsets, adding one by one FIs ordered by ascending size. Insets show the standard error on the cumulative $T_{h/x,mean}$ (°C) as a function of size (μm). Only isolated FIs (ISO$_{h}$ > 1) were used for these cumulative $T_{h/x,mean}$ plots. Break of slope around 13 μm in panel d is used to determine threshold size under which FIs are undamaged (black solid vertical line). The size at which the power law curve fitted to the re-equilibrated FIs (red line in panel e; weakly isolated FIs are given a weaker weight in the fit) reaches $T_h$, the values before Laplace pressure correction. (Colour figure can be viewed at wileyonlinelibrary.com)

To better constrain the process of halite FI re-equilibration, we measured $w$ at several $T$ through complete thermal cycles from $T_h$ down to 0 °C and back to $T_h$ in six FIs from SyntHal24.6. In other words, we used BS to measure $P_{f,lim}$. When a FI is heated or cooled, starting from $T_h$, $w^{mono}(T)$ follows a linear quasi-isochore. Under this regime, the FI walls respond elastically to the stress that accumulates as the temperature departs from $T_h$ and $w^{mono}(T)$ remains unchanged. However, once $\Delta T > \Delta T_{lim}$ and $P_{f,lim}$ is reached, the FI changes shape in an irreversible way. Beyond this limit, the walls deform in a plastic mode, and $w^{mono}(T)$ follows a parabolic trend. The temperature at which $P_{f,lim}$ is reached is notably underlined by $w^{mono}(T)$ deviating from the elastic straight line. Thus, a FI that has not re-equilibrated during the thermal cycle should present $w^{mono}(T)$ matching the linear theoretical speed of sound of a FI deforming elastically, and yield $T_h$, before and after cycle both close to $T_h$.

The results, presented in Figure 8, first confirm the size-related resistance to collapse. On the one hand, in small FIs, $w^{mono}(T)$ follows an elastic trend and yield $T_h$s before and after cycle close to each other and close to $T_h$ (Figure 8a, b). On the other hand, in large FIs, $w^{mono}(T)$ deviates from the elastic path through cooling down and $T_h$ is lower after thermal cycle (Figure 8c, d). We also investigated the mechanical behaviour of two very close FIs of different size (Figure 8e). This last case clearly shows that the vicinity of FIs triggers and enhances plasticity, as both FIs, whatever their size, show a trend strongly deviating from the elastic path, and yield a $T_h$ much lower than $T_h$ after cycle.

After converting $\Delta T$ into pressure and applying a factor of $3/2$ to the measured $P_{f,lim}$ to get the host yield stress (this factor arises from Equation (1)), in the case of a perfectly isolated FI, we plot the yield stresses versus size determined in this work along with published data (Figure 9). In particular, we use the data of Zou and Spolenak (2013), who performed uniaxial compression experiments on monocrystalline NaCl micro-pillars of sizes ranging from 0.25 to 4 μm. We fit a power law to their data:
Figure 8. Re-equilibration limit of various FIs revealed by BS. Samples from SyntHal24.6. 4 FIs of increasing size (a–d) and two neighbouring FIs (e). $w^{\text{mono}}(T)$ measured during cooling to 0 °C (left-pointing black arrows fitted by black dashed parabola) and then during heating from 0 °C (right-pointing grey arrows fitted by grey dashed parabola). In (e), data for FI2 during cooling and heating shown with left-pointing red and right-pointing orange arrows fitted by short-dash black and grey parabolas, respectively. After cavitation, we measured $w^{\text{SLVE}}(T)$ (orange diamonds fitted with orange solid parabolas). Dot-dashed purple line: expected $w^{\text{mono}}(T)$ if deformation is elastic. Slope and error envelope of this line obtained by taking mean and standard deviation of the slopes of all the measured non-re-equilibrated and isolated FIs from SyntHal24.6 and SyntHal331.6. Vertical orange shaded area: yield zone. Uncertainty on each measurement slightly smaller than symbols. Note: for better accuracy, SLVE values were fitted with $w(T)$ equation of pure water saturated with NaCl (Millero et al. 1987), rescaled by a factor. [Colour figure can be viewed at wileyonlinelibrary.com]
where $Y_s$ the yield stress of NaCl (MPa) and $d$ the dimension of the surface on which the pressure is applied (i.e., the diameter for a circular section and the side for a square section). We observe that all the halite yield stresses calculated in our study for different sizes of FIs fall on this power law curve (Figure 9). This is a strong evidence that Equation (3) applies to halite fluid inclusions. Additionally, the fact that the yield stress measured by several authors on plurimillimetric samples is also consistent with Equation (3) validates the applicability of the fit up to FIs of millimetric size. Dividing $Y_s$ by the aforementioned factor (3/2), we get:

$$P_{FI,lim} = (90 \text{ MPa})[d/(1 \mu m)]^{0.64} \quad (4)$$

where $l$ is the side of the square FI. Considering a gradient 1 MPa °C$^{-1}$ inside FIs, typical for NaCl-H$_2$O FIs (see Appendix S1), we get:

$$\Delta T_{lim} = (90 \text{ °C})[l/(1 \mu m)]^{0.64} \quad (5)$$

with $\Delta T_{lim}$ the amount of overheating/overcooling from $T_i$ that can be applied before reaching $P_{FI,lim}$.

Note that the data from Zou and Spolenak (2013) is the yield flow at 5% strain, which is very similar to the yield stress since the stress–strain curve in their experiments is very flat once yield stress is reached (i.e., samples in their experiments undergo little strain hardening).

**Proposed ‘best practice’ for thermometry on halite**

Based on our findings and those of previous workers, we suggest the following practices and cautions when performing thermometry on halite FIs (see also Figure 6):

1. **Avoiding large $\Delta T$.** For samples kept at atmospheric pressure (i.e., close to 0 MPa), an excessive internal pressure inside FIs is responsible for re-equilibration. Thus, when working on halite FIs, it should be assured that the crystals experience the narrowest temperature range as possible, from sampling to measurement. Drilling campaigns during peak summer or winter should be avoided, and samples should be stored in an air-conditioned room. The thermal history from deposit to sampling (e.g., burial temperature) should also be constrained as much as possible.

2. **Selection of small inclusions.** Through implementing Equation (5) with an estimate of $\Delta T$, it is possible to estimate the FI size below which re-equilibration is unlikely to have happened. Note that Equation (5) applies to NaCl-H$_2$O FIs, with gradient 1 MPa °C$^{-1}$. It is possible that gradients are different in FIs with different composition, and should be the subject of another study. Plotting the $T_{hi,x}$ as a function of FIs size (µm)

![Figure 9. Pure NaCl single crystal yield stress as a function of size. Data from Zou and Spolenak (2013) are shown by black crosses and fitted with a power law (solid black line). Extrapolation of this power law (black dashed line) matches well yield stress values obtained through compressive (Skrotzki and Haasen 1981), bending (Rothwell and Greenler 1964) and tensile (Narita et al. 2002) mechanical tests on millimetric [100]-oriented NaCl crystals. Note that when the data provided by authors are the critical resolved shear stress (CRSS), we multiplied it by 2, according to Schmid’s law. [Colour figure can be viewed at wileyonlinelibrary.com]]
size is a necessary (but not sufficient) step to check FIs are not re-equilibrated.

(3) Selection of isolated inclusions. The concept of isolation is presented in the Discussion (first subsection) and illustrated in Figures 7c and 8e. A FI close to any other surface is more prone to plastic deformation. As regards our results and Equation (1), the limit $h_{\text{min}} \geq 1$ is appropriate.

(4) Gaussian $T_{h/x}$ distribution in each FIA. If the number of $T_{h/x}$s is statistically high enough, the normal distribution of $T_{h/x}$s in one FIA should be checked, as non-Gaussian distributions are very likely to indicate re-equilibration (Vyk and Bodnar 1998). The closeness of $T_{h/x,\text{mean}}$ and $T_{h/x,\text{median}}$ can be used to check if $T_{h/x}$s distributions are normal, as shown in Table 1.

(5) Narrow $T_{h/x}$ distribution in each FIA. The contemporaneity in a FIA implies all FIs should yield close $T_{h/x}$s. In order to ascertain FIs had not re-equilibrated since their entrapment, Goldstein (2001) proposed to check that 90% of the $T_{h/x}$s from one FIA do not deviate more than 10–15 °C, which corresponds to $\sigma_{T_h} \sim 3$ and 4.6 °C, respectively. This statement, based on observations in FIs from different minerals and various $P_{f}, T_{f}$ conditions, is often used in the literature to rule out re-equilibration issues. However, we believe this cannot apply entirely to low $T_h$ halite FIs. Fall and Bodnar (2018) reviewed a large amount of studies and showed that highly saline FIs trapped in the monophasic state typically show a range in $T_h$ lower than 5 °C. Similarly, from 222 $T_{h/x}$s in 58 FIs in Benison and Goldstein (1999), we calculate a mean $\sigma_{T_h} \sim 1.3$ °C. It converts into a 4.3 °C range within a 90% confidence interval. We conclude that a $T_h$ range significantly higher than 5 °C in a FIA either highlights re-equilibration processes or shows a great variability in temperature conditions during entrapment. In the case of $T_{h/x}$s obtained with BS, one expects a larger spread as the instrumental error adds up to the ‘natural’ error. Typically, 1.5 < $\sigma_{T_h}$ < 2 °C in synthetic NaCl-H$_2$O FIs, but the distribution may be different for other chemistries. Analogously to $T_h$, distributions, $T_r$ distributions presenting $\sigma_{T_r}$ significantly larger than expected may be due to re-equilibration or temperature variability of the parent brine.

In addition to these five criteria applicable to both techniques, we add some other points that are specific to microthermometry.

(6) $T_{h/x,\text{max}}$ as high as possible. As explained before, the colder the temperature, the higher the tension inside the monophasic FI and the higher the risk of FI re-equilibration. However, the higher $T_{h/x,\text{max}}$, the lower the probability to cavitate. Consequently, in order to apply the mildest cooling temperature sufficient to make FIs cavitate, we propose to slowly cool down the sample in the microscope stage until first cavitations occur, and keep the sample at this threshold temperature for as long as necessary in the stage or in the freezer. For instance, in the case of our synthetic halites, -12 to -15 °C seems a good choice; out of thirty-eight FIs whose cavitation temperature was checked, none cavitated above -12 °C, then nine cavitated between -12 and -15 °C during the -5 °C min$^{-1}$ cooling ramp, and eight others subsequently cavitated while stored for 2 days at -15 °C in the freezer. We do not expect all samples to show similar rates of cavitation, as this process is controlled by multiple parameters. The fluid surface tension is one of them and depends on salinity (Weissenborn and Pugh 1996) and pH (Allen et al. 2009).

(7) Correction of the Laplace pressure. Because of the pressure differential between the vapour and the liquid (Young 1805), FIs homogenise at $T_h < T_f$. This effect becomes more pronounced for small FIs; for pure water inclusions at $T_f = 150^\circ$C, Fall et al. (2009) calculate a $T_h$ lower than $T_f$ by 1 °C for 1000 mm$^{-3}$ inclusions, by 3 °C for 10 mm$^{-3}$ inclusions and by 5 °C for 1 mm$^{-3}$ inclusions. We calculate a weaker effect for NaCl-saturated aqueous FIs, with a correction of 0.3 °C for 1000 mm$^{-3}$ inclusions, 0.9 °C for 10 mm$^{-3}$ inclusions and 1.7 °C for 1 mm$^{-3}$ inclusions. The effect can be quantitatively observed on our microthermometry results in Figure 7. See Appendix S1 and Krüger et al. (2011) for more information on the correction of this effect.

(8) The exclusive use of $T_{h/x,\text{max}}$ unless the absence of re-equilibration is demonstrated. Our work confirms the observations of Lowenstein et al. (1998): in a sample cooled in the stage or in the freezer, only the highest $T_h$ values match the brine temperature. All the other values indicate that FIs underwent shrinkage during the cooling process. Thus, unless the $T_h$ distribution in each FIA is Gaussian, narrow and uncorrelated with FIs size as stated above, the use of the mean and standard deviation has no meaning and we thus strongly recommend only keeping $T_{h/x,\text{max}}$ for convincing palaeotemperature reconstructions. One could argue that broad $T_h$ distributions do not necessarily underline re-equilibration but might rather be due to a short time variability of the brine temperature at the time of FIs entrapment, as stated in paragraph (5) of this section. However, unless authors have quantitative information about temperature variability in the parent
brine, the dilemma is impossible to untangle. In the case of the selection of \(T_{h,x}\) as the only relevant \(T_r\), one gets the maximum temperature of the brine during the FIA formation. For instance, in the case of a FIA trapped within 1 day/1 year in a shallow water body, \(T_{h,x}\) provides information on the temperature around midday/summer, respectively. We see here how important it is to have a constraint on the timing of halite precipitation, in order to be able to give a temporal meaning to temperature information. Note that selecting \(T_{h,x}\) implies a sufficient amount of \(T_{h}\) per FIA, namely several dozens.

**Brillouin spectroscopy – A precise and accurate thermometer**

All the Brillouin thermometry measurements were performed on halite crystals with very well constrained synthesis temperatures within \(±1\) or \(±0.5\, ^°C\) (SynthHal33 and SynthHal24.6, respectively), which improves upon previous halite thermometry studies (Roberts and Spencer 1995, Lowenstein et al. 1998). Thence, it is possible to compare precisely our results with \(T_{r}\). Once restricted to small and isolated FIs, the Brillouin thermometry \(T_{h}\) shows a normal distribution. As populations show \(1.5 \cdot \sigma_{x} < 2\, ^°C\), the ensuing uncertainty on each individual \(T_{r}\) as a proxy for \(T_{r}\) is \(1.5\)–\(2\, ^°C\) (1-sigma confidence interval). Nonetheless, the mean value converges towards \(T_{r}\) with a growing \(T_{x}\) population, and our experiments show that \(T_{x}\) brackets to within \(±0.5\, ^°C\) standard error (1-sigma). It implies \(T_{x}\) can be considered as a single accurate and precise \(T_{r}\) for any FIA from geological samples, provided the FIs in a same assemblage were all trapped at the same temperature.

The main source of uncertainty in Brillouin thermometry is the instrumental error, which gives \(0.1\% \cdot \sigma_{w} < 0.15\%\). It results in a temperature uncertainty \(1.5\, ^°C \cdot \sigma_{x} < 2\, ^°C\) (See Appendix S1 for more information on experimental uncertainty and estimated time needed to reach \(±0.5\, ^°C\) uncertainty on \(T_{r}\)). Note that this conversion from \(\sigma_{w}\) to \(\sigma_{x}\) is valid for NaCl-H\(_2\)O compositions. Indeed, the composition controls the intersection angle between \(w_{\text{macro}}(T)\) and \(w_{\text{SLVE}}(T)\), which in turn governs the conversion ratio from \(w\) to \(T_{r}\) uncertainties. Thus, \(\sigma_{x}\) can be higher or lower depending on the FIs composition.

We conclude that there are three major advantages using Brillouin thermometry instead of microthermometry:

1. It is a way to avoid too large a \(\Delta T\) and ensure \(T_{x}\) measurements from non-re-equilibrated FIs. Indeed, BS first measures the quasi-isochoric speed of sound curve \(w_{\text{macro}}(T)\) in the monophasic FI, and only afterwards, it requires a large thermal excursion to nucleate a bubble and measure the SLVE speed of sound curve \(w_{\text{SLVE}}(T)\). As the entrapment temperature information is contained in \(w_{\text{macro}}(T)\), BS thus avoids any risk of damaging the FIs during analysis. With Equation (5), we calculate for a typical natural sample of \(T_{r} < 25\, ^°C\) that has undergone \(\Delta T \approx 20\, ^°C\) a size threshold \(\approx 10–11\, \mu m\). Using microthermometry with \(T_{h,x} < -20\, ^°C\), this threshold would decrease down to \(3\, \mu m\).

2. It rehabilitates the use of \(T_{h,x} < 0\, ^°C\) instead of \(T_{h,x} > 0\, ^°C\). Selecting extrema in a histogram is always a delicate process, as one cannot be certain that the selected minimum or maximum is not an outlier, or if additional measurements would increase the maximum value (J. Mavrogenes, in Interactive Discussion of Spadini et al. (2015) available at https://www.clim-past-discuss.net/10/C2187/2015/cpd-10-C2187-2015.pdf).

3. As it is based on the analysis of monophasic FIs and consequently does not rely on nucleation statistics, it makes the measurement of whichever FI possible, which is particularly convenient when it comes to analyse a FIA that only contains a few FIs.

**Conclusions**

In this study, we performed Brillouin spectroscopy and microthermometry to investigate the potential of halite fluid inclusions as temperature archives, and evaluate the ability of each of the two methods to reconstruct consistent palaeotemperatures. These measurements were performed on lab-grown halite crystals synthesised at \(24.6 < 0.5\) and \(33 < 1\, ^°C\).

Our Brillouin thermometry measurements, along with Brillouin mechanical tests, enable us to highlight the \(T_{r}\)-size relation. We deduce re-equilibration pressure thresholds \(p_l\) dependent on \(T_{r}\) size and plot them along with yield stress values of NaCl crystals found in solid mechanics literature. The power law we fit matches both the results of this study as well as published data, and allows us to propose an empirical equation linking \(p_l\) to the size threshold above which FIs stretch/shrink in a plastic mode: \(p_{l} \approx (l/1\, \mu m)^{0.64} \times (90\, \text{MPa})\). In the case of a NaCl-H\(_2\)O FI where the quasi-isochore P-T slope is \(1\, \text{MPa} \cdot ^°C^{-1}\), we can thus link the threshold amount of overheating/overcooling to the FI size through: \(\Delta T_{l} \approx (l/1\, \mu m)^{0.64} \times (90\, ^°C)\). We also demonstrate that FIs close to other FIs or to
the host surface by less than two radii have a lower yield stress.

Our microthermometry measurements yield broad $T_h$ distributions, with only $T_{h,\text{max}}$ matching the brine temperature. After selection based on FIs size and isolation, the mean $T_h$ is 3.7 and 4.9 °C below $T_T$ respectively. The body of arguments we get through converging our data and those previously published, along with thorough considerations on the physical processes at stake when FIs undergo a cooling cycle, lead us to prompt authors to check the $T_h$ distribution in each fluid inclusion assemblage, ensuring that the range of $T_h$ values does not exceed 5 °C and that no $T_h$-size correlation exists. If not, some FIs are potentially damaged, and the use of a mean value becomes improper. In this case, we recommend using $T_{h,\text{max}}$ as a relevant palaeoclimate indicator. We also recommend to slowly cool the sample in the stage to the temperature at which the first bubbles nucleate, and use this temperature as $T_{h,\text{mean}}$ for as long as necessary to nucleate a sufficient amount of bubbles, in a freezer or in the stage.

The Brillouin thermometry on halite FIs circumvents the biases and drawbacks of microthermometry, namely the Laplace pressure and, above all, the re-equilibration of FIs due to overcooling. Our protocol consists in measuring the isochore of monophasic FIs, subsequently nucleating a bubble by means of a large thermal excursion to measure the solid-liquid-vapour speed of sound in the biphasic FIs, and deducing their $T_h$ at the intersection of the isochore and solid-liquid-vapour curves. Because the entrapment temperature information is contained in the initially measured isochore, this method avoids any strong temperature excursion affecting the palaeotemperature record, which is a major advantage compared with microthermometry. After the selection of FIs based on their size and isolation, the mean $T_h$ for the two batches studied was 0.2 above and 1.1 °C below $T_T$ respectively, and the $T_h$ distribution was Gaussian and narrow, with a standard deviation $\sigma_{T_h} \leq 2$ °C. If the error was purely statistical, the standard error on the mean would be $\sigma_{T_h}/\sqrt{N} = 0.4$ °C in the present case. While the errors on $T_h$ make it difficult to use for palaeoclimate interpretations, the accuracy and precision of BS shown in this work make it a powerful method for halite FIs-based palaeotemperatures reconstructions.

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Conflict of interest

The authors have no conflict of interest to declare.

Data availability statement

The data that support the findings of this study are available from the corresponding authors upon request. Most of the research data used in this work can be found in the online supporting information (see Appendix S2).

References

Al Ghafri S., Maitland G.C. and Trusler J.P.M. (2012) Densities of aqueous MgCl2 (aq), CaCl2 (aq), KI (aq), NaCl (aq), KCl (aq), AlCl3 (aq), and (0.964 NaCl + 0.136 KCl) (aq) at temperatures between (283 and 472) K, pressures up to 68.5 MPa, and molalities up to 6 mol·kg·1. Journal of Chemical and Engineering Data, 57, 1288–1304.


references


Bodnar R.J. and Bethke P.M. (1984)


Caupin F. and Herbert E. (2006)


Bragg (100) powder diffraction of fluid inclusions proposed as a paleothermometer for subsurface rocks. Scientific Reports, 5, 13168.

Fall A. and Bodnar R.J. (2018)
How precisely can the temperature of a fluid event be constrained using fluid inclusions? Economic Geology, 113, 1817–1843.

Fall A., Rimstidt J.D. and Bodnar R.J. (2009)


Goldstein R.H. (2001)


Holser W.T. (1966)


Fluid inclusions in halite from the Roet (Lower Triassic) salt deposit in Central Germany. Evidence for seawater chemistry and conditions of salt deposition and recrystallization. Carbonates and Evaporites, 24, 45–57.


Electrodynamics of continuous media. Pergamon Press (Moscow, Russia), 460pp.


references


references

Paleoclimatic information recorded in fluid inclusions in halites from Lop Nur, Western China. Scientific Reports, 7, 16411.

Szmor P.O. (1968)
Elastic constants and tensile strength of NaCl-type alkali halides. Physica Status Solidi (B), 28, 529–537.


Voliashko M.G. (1956)
Geochemistry of bromide in the processes of salt deposition and the use of the bromide content as a genetic and prospecting tool. Geochemistry USSR, 6, 570–587.

Vityk M.O. and Bodnar R.J. (1998)
Statistical microthermometry of synthetic fluid inclusions in quartz during decompression re-equilibration. Contributions to Mineralogy and Petrology, 132, 149–162.


Warren J.K. (2016)

Surface tension of aqueous solutions of electrolytes: Relationship with ion hydration, oxygen solubility, and bubble coalescence. Journal of Colloid and Interface Science, 184, 550–563.


Yang C. (2016)

Young T. (1805)

Extremely high temperatures and paleoclimate trends recorded in Permian ephemeral lake halite. Geology, 41, 587–590.


Late Eocene to early Oligocene quantitative paleotemperature record: Evidence from continental halite fluid inclusions. Scientific Reports, 4, 5776.

Zimmermann H. (2001)

Zou Y. and Spolenak R. (2013)

Supporting information

The following supporting information may be found in the online version of this article:

Appendix S1. Supplementary material.

Appendix S2. Research data.

This material is available from: http://onlinelibrary.wiley.com/doi/10.1111/ggr.12312/abstract (This link will take you to the article abstract).
Appendix A

List of abbreviations and definitions

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>FI</td>
<td>Fluid inclusion</td>
</tr>
<tr>
<td>FIA</td>
<td>Fluid inclusion assemblage, that is the most finely discriminated, petrographically associated group of coeval inclusions</td>
</tr>
<tr>
<td>( T_f )</td>
<td>Formation temperature of the FI (°C)</td>
</tr>
<tr>
<td>( T_{min} )</td>
<td>Minimum temperature undergone by a FI since its entrapment (°C). For fluid inclusions measured with microthermometry, it corresponds to the cooling temperature used in the stage to nucleate a bubble (°C)</td>
</tr>
<tr>
<td>( T_{max} )</td>
<td>Maximum temperature undergone by a FI since its entrapment (°C)</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Maximum value between the amplitude of cooling below ( T_f ), ( T_f - T_{min} ) and the amplitude of heating above ( T_f ), ( T_{max} - T_f )</td>
</tr>
<tr>
<td>( \Delta T_{lim} )</td>
<td>Maximum ( \Delta T ) a FI can bear without irreversible volume change</td>
</tr>
<tr>
<td>( P_{FI,lim} )</td>
<td>Maximum internal negative or positive pressure a FI can bear without irreversible shrinkage or stretching, respectively</td>
</tr>
<tr>
<td>( T_{cav} )</td>
<td>Temperature at which cavitation (i.e., bubble nucleation) occurs in a FI</td>
</tr>
<tr>
<td>( T_h )</td>
<td>Temperature of homogenisation (bubble disappearance) obtained with microthermometry (°C)</td>
</tr>
<tr>
<td>( T_x )</td>
<td>Crossing temperature obtained with Brillouin thermometry (°C)</td>
</tr>
<tr>
<td>( T_{h,x} )</td>
<td>( T_h ) or ( T_x )</td>
</tr>
<tr>
<td>( T_{h,x,mean} )</td>
<td>Mean ( T_{h,x} ) in a group of FIs (°C)</td>
</tr>
<tr>
<td>( T_{h,x,min} )</td>
<td>Minimum ( T_{h,x} ) in a group of FIs (°C)</td>
</tr>
<tr>
<td>( T_{h,x,max} )</td>
<td>Maximum ( T_{h,x} ) in a group of FIs (°C)</td>
</tr>
<tr>
<td>BS</td>
<td>Brillouin spectroscopy</td>
</tr>
<tr>
<td>( v )</td>
<td>Speed of sound in a FI (ms(^{-1}))</td>
</tr>
<tr>
<td>( v_{mono} )</td>
<td>Speed of sound in a monophasic FI (ms(^{-1}))</td>
</tr>
<tr>
<td>( v_{s-lv} )</td>
<td>Speed of sound at solid-liquid-vapour equilibrium in a biphasic FI (ms(^{-1}))</td>
</tr>
<tr>
<td>( \sigma_v )</td>
<td>1-sigma uncertainty on the speed of sound</td>
</tr>
<tr>
<td>( \sigma_{T_h} )</td>
<td>Standard deviation of a ( T_h ) distribution</td>
</tr>
<tr>
<td>( \sigma_{T_x} )</td>
<td>Standard deviation of a ( T_x ) distribution</td>
</tr>
<tr>
<td>( \Delta f_b )</td>
<td>Brillouin frequency shift in a FI (GHz)</td>
</tr>
<tr>
<td>( \Delta f_{b,SLVE} )</td>
<td>Brillouin frequency shift at solid-liquid-vapour equilibrium in a biphasic FI (GHz)</td>
</tr>
</tbody>
</table>

Appendix B

Brillouin frequency shift and the speed of sound of liquids

All liquids are subjected to thermal density fluctuations (acoustic waves). Brillouin scattering from a liquid results from the inelastic interaction of light with these fluctuations (Landau et al. 1984). The spectrum of the backscattered light (Figure B1) shows two inelastic peaks, to the left and to the right of the excitation frequency. In a first approximation, the Brillouin shift \( \Delta f_b \) that is the frequency shift between the inelastic peaks and the excitation frequency, is proportional to the speed of sound \( v \):

\[
\Delta f_b = \frac{2nw}{\lambda}
\]  

(B1)

where \( \lambda = 532 \text{ nm} \) is the wavelength of light, and \( n \) is the refractive index of the liquid. This neglects sound dispersion, that is, the frequency dependence of the speed of sound. Because the Brillouin shift is large, around 9.3 GHz in our experiments, this effect cannot always be neglected. Indeed, if the liquid exhibits relaxation on a timescale of the order of the inverse frequency (around 100 ps), dispersion is expected.

\[\Delta f_b (\text{GHz})\]

\[\text{Count}\]

Figure B1. Typical Brillouin spectrum. The spectrum shown was recorded at 25 °C in a FI from batch SyntHal24.6. The counts of scattered photons are plotted as a function of the light frequency shift. Vertical bars correspond to the shot noise (square root of the counts). The curve, fitted as explained in Pallares et al. (2014), provides the speed of sound in the fluid.

In the work of El Mekki-Azouzi et al. (2015), performed with a smaller Brillouin shift and at high temperature where the relaxation time is very short, dispersion is negligible.
In other works of our group dealing with pure water at low temperature (Pallares et al. 2014, Holten et al. 2017), dispersion effects were corrected using the viscoelastic formalism in the memory function approach. We refer the reader to Pallares et al. (2014) for a detailed explanation with the relevant equations. In the present work, with saturated salt solutions at low temperature, which are even more, slowly relaxing than pure water, the same correction is needed. The Brillouin spectrum can then be fitted with a formula having three free parameters (the peak amplitude, the relaxation time and the speed of sound at zero temperature) and two input parameters: the speed of sound at infinite frequency \(c_\infty\) and the refractive index \(n\). For pure water, \(c_\infty = 3000\, \text{m s}^{-1}\), as determined from X-ray measurements (Bencivenga et al. 2009). As we are not aware of a corresponding value for saturated salt solutions, we use the same value as for pure water. For the refractive index \(n\), we used the following procedure. We assumed the validity of the Gladstone-Dale relation between the density \(\rho\) and the refractive index \(n\) at \(\lambda = 532\, \text{nm}\) of a NaCl solution of molality \(m\) at temperature \(T\) and pressure \(P\):

\[
 n(T, P, m) = 1 + K(m)\rho(T, P, m) \tag{B2}
\]

where \(K\) is a function of molality only. We measured \(n\) at \(T = 25\, ^\circ\text{C}, P = 0.1\, \text{MPa}\) and for a series of NaCl molarities using a Schmidt-Haensch ATR-L refractometer. This yields

\[
 K(m) = 0.3352254 \times 10^{-3} - 3.113319 \times 10^{-6} + 7.013441 \times 10^{-9}\, \text{m}^2 \tag{B3}
\]

with \(m\) in mol kg\(^{-1}\). Then, to determine the density \(\rho\) in a FI, we used the parameterisation from Al Ghafri et al. (2012) for \(\rho(T, P, m)\), which was established for \(T\) from 298 to 472 K, \(P\) from 0.1 to 68.5 MPa and \(m\) from 0 to 6.0 molal. We extrapolate it to slightly higher \(m\) to cover saturated solutions. For a biphasic FI, we approximate the vapour pressure by a constant 0.1 MPa (this causes a negligible error) and assume that the molality \(m\) is the saturation value \(m_{\text{sat}}(0.1\, \text{MPa})\) at the temperature of interest; this is justified by considering the short time needed for precipitation/dissolution in comparison with the experimental times. For \(m_{\text{sat}}(0.1\, \text{MPa})\), we used the empirical fit by Farelo et al. (1993) based on data from 293 to 360 K at ambient pressure. Comparison with an empirical fit by Sawamura et al. (2007) based on data from 273 to 313 K and from 0.1 to 300 MPa shows that the extrapolation of the fit by Farelo et al. (1993) is valid down to 273 K (deviation less than 0.2%). For a biphasic FI, the refractive index is thus calculated as:

\[
 n(T) = 1 + K[m_{\text{sat}}(T, 0.1\, \text{MPa})]. 
\]

\[
 \rho(T, 0.1\, \text{MPa}, m_{\text{sat}}(T, 0.1\, \text{MPa})) \tag{B4}
\]

For a monophasic FI, we use the same expression as for a biphasic FI. This introduces a small error that increases with the departure from \(T_w\), because the density and saturated concentration in the monophasic FI are different from those in the biphasic FI. For a pure isochore, using extrapolations of relevant data, we estimate the error on \(n\) and on \(\rho\) to a few tenths of per cent. For a real sample, it will be less, as the changes in the host matrix (see Appendix S1) will bring the density of the monophasic FI closer to that of the biphasic FI at the same temperature. Furthermore, it is important to note that at \(T_w\), when the Brillouin spectra in monophasic and biphasic FI become identical, the error vanishes and our results are unaffected.

In this work, we divided all the measured \(\omega(T, \text{time})\) values by the \(\omega_{\text{rel}}(25\, ^\circ\text{C}, \text{time})\) value of a reference pure H\(_2\)O biphasic FI in a synthetic quartz crystal, which is regularly measured all along the day of experiments. Note that for the clarity of the paper, all \(\omega(T, \text{time})\) values divided by the \(\omega_{\text{rel}}(25\, ^\circ\text{C}, \text{time})\) were then multiplied by a constant, \(\omega_{\text{rel mean}}(25\, ^\circ\text{C}) = 1471.7\, \text{m s}^{-1}\), obtained through averaging 1284 values of the reference inclusion measured throughout dozens of days of experiments. Measurements relative to a reference avoid the need for a correction factor. Moreover, it allows us to remove the spectroscope drift observed in the course of the day. Indeed, as shown in Figure B2, the speed of sound measured in one FI may vary up to 1% along the course of the day and from one day to another. As the drift is the same for all measured FIs, it confirms the instrumental origin of the drift, presumably due to thermal expansion of the spectrometer setup. Thus, measuring the value of a reference FI throughout the day of experiments enabled us to estimate the drift and correct all measurements for it. The results in Figure B2 show a very good repeatability of the speed of sound measured in the halite FI once corrected for the drift, to within almost 0.02%. However, as the standard error on each cluster is on average 0.05%, we cannot claim repeatability better than 0.05%. Anyway, this is much lower than our estimate of the short-term instrumental error, 0.1% (that is, the standard deviation on measurements repeated one after the other on the same FI during several tens of minutes). Therefore, these experiments lead us to regard the uncertainty on the drift correction as negligible and to estimate the overall uncertainty as 0.1%. However, the machine can reveal less stable some days, involving a larger uncertainty on the drift...
correction. Hence, all in all, the overall uncertainty lies somewhere between 0.1% and 0.15%. This is further discussed in Appendix S1. In previous works using the same setup but without correction for the drift (Pallares et al. 2014, 2016, El Mekki-Azouzi et al. 2015), the error was estimated as 0.3%.

Figure B2. Daily drift of the spectroscope revealed by measurements on one halite FI and the reference pure water FI. The three top panels show repeated measurements at 25 °C of the speed of sound as a function of time in the reference pure water FI ($w_{\text{SLVE}}^{\text{ref}}$ (25 °C, time); hollow diamond symbols) and one halite FI (red hollow rectangles). Black dashed lines are parabolas fitted to $w_{\text{SLVE}}^{\text{ref}}$ (25 °C, time). All values are divided by a constant: $w_{\text{SLVE}}^{\text{ref}}$ (25 °C, time) values are divided by $w_{\text{SLVE}}^{\text{ref,mean}}$ (25 °C) (see text), while the halite FI values are divided by its average speed of sound 1782.2 ms$^{-1}$ (mean from dozens of measurements taken over several days). The bottom panel shows the mean speed of sound for each of the five clusters plotted above divided by the parabolic fits of $w_{\text{SLVE}}^{\text{ref}}$ (25 °C, time). Bars represent the standard error on the mean for each cluster. The horizontal band represents the mean of the five mean values; its thickness accounts for the standard deviation of the five mean values.