

Analytical techniques applied to fluid inclusion studies: basics and applications

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Introduction¹

Fluid inclusions are small amounts of fluid trapped inside minerals. This fluid is "custodian" of the physicochemical properties of the mother fluid and, therefore, it can be seen that this fluid "bottled" inside the crystal is a relic which preserves a faithful record of the physical and chemical conditions of the fluid that was in the environment at the time of the fluid inclusion's formation. Unlike other geothermometric/geobarometric methods, that require indirect calculations (for example, phase equilibriums between minerals, etc.), the study of fluid inclusions allows direct estimates of the original fluid's characteristics to be made, in such a way that characterization of the physical-chemical properties of fluids trapped in the fluid inclusions shows us the characteristics of the mineralizing fluids, in terms of temperature, pressure, composition, density, etc.

Fluid inclusions can be found in any mineral that was formed from a fluid. Because in practice most minerals are formed from processes involving fluids, the study of these tiny remnants of fluid, trapped in the minerals, could be applied to almost any field of geology. Therefore, although in practice fluid inclusions are used mainly in studies related to the metallogeny of mineral deposits due to its applied character, this type of study is becoming increasingly frequent in different areas of geology and in some related

¹ This text is only a summary of the talk that will be given at this workshop. The text does not aim to be a review of the state of the art or a new text about the world of fluid inclusions. For this purpose readers can consult a wide-ranging, interesting bibliography that covers these topics (i.e., Barnes, 1979; Hollister and Crawford, 1981; Roedder, 1984; Shepherd et al., 1985; de Vivo and Frezzotti, 1994; Goldstein and Reynolds 1994; Samson et al., 2003; etc.).

sciences. Solely by way of an example, we can say that these studies have been implemented in:

- * ore deposits
- * hydrothermal environments
- * sedimentary environment and diagenetic processes
- * metamorphic terranes with different metamorphic grades
- * volcanic areas
- * mantle environments
- * petroleum exploration
- * tectonic history of deformed areas
- * gemology
- * paleoclimatology
- * paleohydrogeology
- * extraterrestrial environments
- * weathering of historical monuments
- * analysis of air-inclusions in ice cores
- * ambar
- * etc.!

The reasons why studies of fluid inclusions are becoming increasingly common must be sought at the confluence of a number of factors:

* Microthermometry is a cheap technique: for the price of a small quantity of nitrogen, a high number of results can be obtained (though it is a very subjective estimation, we calculate that with 5-10 euro of liquid nitrogen, determinations corresponding to 10-20 fluid inclusions can be carried out).

* The equipment is relatively cheap in comparison with other analytical techniques: a heating and freezing stage should not cost more than about €30,000 (aprox.). This means that the majority of geology departments at research centres (and many companies) have a fluid inclusion laboratory.

* Sample preparation laboratories do not require special equipment: any laboratory in a university geology department or company that deals with the preparation of common

thin sections can prepare the doubly polished thin sections that are required for the study of fluid inclusions.

* The interpretation of results is done with relative “ease”.

* Any determination "only" requires an observer (... with plenty of patience!).

These factors explain why fluid inclusion studies are currently being applied in an ever more routine fashion in numerous studies related to Mineralogy and other Earth Sciences. As a sign of this boom, the indicators can be analyzed:

(1) At present there are three conferences dedicated specifically to the world of fluid inclusions: PANCROFI (“Pan-American Current Research on Fluid Inclusions Conference”), which held its 9th edition in June 2008; ECROFI (“European Current Research on Fluid Inclusions”), which will be celebrating its 20th edition in 2009, and ACROFI (“Asian Current Research on Fluid Inclusions”) that celebrates its 2nd edition in November, 2008. Likewise, numerous international congresses dedicate monographic sessions to presenting the most recent advances related to geofluids and the world of fluid inclusions.

(2) An abundance of literature is generated in this regard. Not only are there many monographic books devoted to study of fluid inclusion, but the majority of recent textbooks include detailed chapters on fluid inclusions and their application in different fields of science. Likewise, the majority of the scientific magazines on geosciences include numerous papers featuring fluid inclusions. In the same sense, Internet also provides numerous websites on the subject (see examples in Table 1) and there is even a fluid inclusion listserver (fluid-inclusions@lists.wisc.edu, see <http://www.geology.wisc.edu/flincs/fi.html> for details) with more than 350 users dedicated to this subject matter.

(3) There are an enormous number of research groups worldwide, dedicated to the study of fluid inclusions.

(4) Most geology departments offer courses that, to one degree or another, include matters related with fluid inclusions.

Description	Website Address
Fluid inclusion database project	http://www.ga.gov.au/minerals/research/methodology/geofluids/flincs_about.jsp
Fluid inclusion laboratory Leoben	http://fluids.unileoben.ac.at/Home.html
Fluid inclusion laboratory Leoben	http://institute.unileoben.ac.at/mineralogie/Fluid_Inc_Lab/Flinc_Lab.html
Fluid inclusion research at National University of Ireland	http://www.nuigalway.ie/nanoscale/fluid_inclusion.html
Fluid inclusion section of the Duan Group	http://www.geochem-model.org/research/fluidinc/
Geowissenschaftliches Zentrum (Prof. Van den Kerkhof)	http://www.uni-goettingen.de/en/11113.html
Links for mineralogist (fluid inclusions)	http://www.mineralogie.uni-wuerzburg.de/links/petrology/fluid.html
Personal web site Ronald J. Bakker	http://institute.unileoben.ac.at/mineralogie/Bakker/Ronald.html
Petroleum & aqueous inclusion research	http://www.petroleuminclusion.uhp-nancy.fr/
Siena geofluids lab home page	http://www.dst.unisi.it/geofluids-lab/
The world of fluid inclusions	http://www.geology.wisc.edu/flincs/fi.html
University of Bern (Fluid Inclusion group)	http://www.geo.unibe.ch/diamond/diamond.php
Virginia Tech Geosciences/ Fluids Research Group	http://www.geochem.geos.vt.edu/fluids/
Working group on inclusions in minerals (WGIM)	http://www.ima-mineralogy.org//com-wg/WGIM/WGIM.html

TABLE 1. Description and addresses of some websites related to fluid inclusions.

General topics on fluid inclusions²

Fluid inclusions are small cavities inside crystals. These cavities capture remains of fluid from which minerals are formed, or fluids that have circulated through the same

² Many topics of this chapter are summarized from general books on fluid inclusions (see references at footnote 1).

ones after its formation. They are typically smaller than 30-50 microns and can contain different combinations of liquid, solid or gaseous phases. The *liquid phase* is usually constituted by water with different ions in solution (Ca(II), Na(I), K(I), Mg(II), etc.), mostly as chlorides. The *gaseous phase* is constituted by water vapour and, occasionally, varying amounts of CO₂ and, to a lesser extent, N₂, CH₄ or H₂S. The *solid phase* can be divided into two types: phases formed by saturation of salts in the liquid phase (halite, sylvite...) or trapped phases from the environment at the time of formation of fluid inclusions that remain in equilibrium with the phases present in the cavities (generally oxides, sulphides or silicates).

Fluid inclusions are expected in all those minerals which are formed in environments that involve fluids, i.e. they are expected in a large number of minerals formed in nature. The problem for this study is its observation. To this end, we use minerals with sufficient transparency for internal observation. Among transparent minerals, quartz, calcite, dolomite, fluorite and sphalerite are the most common. In the case of opaque minerals, fluid inclusions are also present but their observation is practically impossible, at least in a routine manner. Occasionally, in areas of weakness (fractures, foliations...) of some opaque crystals or in areas of slimmed edges, it is possible to see the presence of fluid inclusions intuitively. In the case of opaque ores, some attempts have been made with infrared microscopy (see details below), although positive results are limited to a few cases.

The criteria used to classify fluid inclusions are very varied (morphology, number of phases at room temperature, chronology with respect to host mineral...).

The first one of them classifies fluid inclusions according to their shape (polyhedral, irregular, oblate...) and does not contribute a lot of genetic information.

Classification based on the number of phases (one-phase, two-phase, three-phase, multiphase) gives rise to a more informative classification about the genesis of fluid inclusions. In a first approximation, single-phase fluid inclusions could be indicative of low temperature processes, coexistence of fluid inclusions with varying degrees of filling (filling degree = ratio of liquid volume vs. gas volume in the cavity) could suggest boiling processes or presence of immiscible fluids, while the abundance of three-phase inclusions including precipitated minerals (halite, sylvite...) indicates saturation in salts, etc.

As for chronological classification, this classifies fluid inclusions as primary (trapped at the same time as the formation of host mineral), secondary (trapped after the formation of the host crystal) and pseudosecondary (fluid inclusions caught in intermediate situations between the primary and secondary ones).

In practice, such rigid classifications are not always useful for daily work in the laboratory. They really impose the criterion of *population*, which groups fluid inclusions of the same characteristics according to a combination of the above criteria (size, shape, number of phases and proportions between them, "age" with regard to host crystals...). Populations must be related with regard to geological context and inside the paragenetic sequence (in terms of mineralization stages, fracturation or folding events, etc.), so that they are representative of the geological process, object of study.

Petrographic study of fluid inclusions

Any study of fluid inclusions must begin with careful petrographic study of the different populations of fluid inclusions, in such way that the fluid inclusions analyzed truly represent the characteristic fluid of the process that we want to characterize. It is frequent that a mineral has been formed in a specific environment (and, as a consequence, caught part of the fluid from which it is formed) and, subsequently, being subjected to various processes, not only traps fluids from these later processes, but even fluid trapped originally can be affected and modified with regard to the conditions of trapping (for example, Roedder, 1984; Shepherd et al., 1985; Goldstein and Reynolds, 1994). This means that the fluid inclusions that can be observed in a crystal can be the result of different fluids with which the crystal has interacted throughout its history. Therefore, to ensure the representativeness of the study in question, we must conduct a proper petrographic study that selects the representative inclusions and avoids the temptation of focusing solely on the more aesthetically beautiful, best-formed or larger fluid inclusions.

The petrographic study usually takes place with a petrographic microscope that, according to the case in question, can be equipped with a camera for microphotographs or a video recorder that allows an adequate documentation of the results of the study. Nevertheless, the use of the cathodoluminescence (see for example Van den Kerkhof and Hein, 2001) equipment is becoming ever more frequent (mounted on optical

microscopes or placed in scanning electron microscopes), which "reveal" the internal structure of crystals, a structure that is not always appreciated with the polarized light microscope. Cathodoluminescence is an effect that occurs as result of electron bombardment on a solid. Amongst other effects, this can produce the emission of light in the focused area. This effect can be determined by chemical factors or as consequence of aspects related with the structure of the mineral. In transparent minerals, this effect can be used to study their internal structure. Specifically in terms of the petrography of fluid inclusions' host crystals, this technique may be useful to reveal zoned growths, dissolution/recrystallization processes, interruptions or discontinuities in the growth of the crystal, etc. The use of cathodoluminescence has, amongst other advantages, low cost, ease of use, use of the same slides used for optical petrography, the possibility of studying with the same microscope used for the polarized light study, and the chance to change the mode of observation without moving the same motive in the same sample (allows instantaneous correlation of the image of transmitted light with the image of cathodoluminescence).

Certain minerals that behave as opaque in observation using transmitted light microscopy become transparent once observed by means of a microscope equipped with an infrared emission source. In accordance with Wilkinson (2001) and references therein, with infrared microscopy and in favourable circumstances it is possible to observe the internal structure (zoning, maclas, etc.) of the host mineral, or it can even be possible to carry out the microthermometric study of fluid inclusions hosted in some opaque minerals (for example, wolframite, stibnite, molybdenite, hematite, pyrrargyrite, cinnabar, chalcocite, enargite, tetrahedrite-tennantite, pyrite, etc.).

As a result of the petrographic study of fluid inclusions using these different techniques, the petrographic study must provide information about populations of fluid inclusions (number, types, relative chronology -between them, with regard to geological events-, etc.). In short, the importance of the petrographic study is that it should be the basis for proper decision-making about the type of fluid inclusions on which the later job is done.

Analytical techniques applied to the study of fluid inclusions

The purpose of fluid inclusion studies is the characterization of the physicochemical properties of fluids trapped in the cavities under study. This characterization usually tries to discover the conditions of temperature, pressure and composition of the original fluids (the latter can involve different aspects: total salinity of the inclusion, proportion among major cations, kind of volatiles –if present-, presence of organic liquids, etc.).

In any case, to obtain this information it is necessary to use a combination of techniques, which can vary from simple petrographic observation to the use of more complex and sophisticated analytical techniques. However, given the small size of fluid inclusions (usually smaller than 30-50 microns), the most common technique is microthermometry. The information obtained from the microthermometric characterization of fluid inclusions is usually the basis for deciding to utilize, where appropriate, other more sophisticated analytical techniques.

Microthermometry^{3,4}

The microthermometric study of fluid inclusions is done using a heating and cooling stage, a device that allows us to increase or diminish temperature over a wide range, between -200°C and $+600^{\circ}\text{C}$ approximately. This stage is placed on a microscope, so that the phase changes occurring can be observed as well as the temperature at which these changes take place. For this purpose, thin sections used in fluid inclusions studies are polished on both sides and are thicker ($\approx 100\text{-}200$ microns) than the thin sections used in conventional petrographic studies (≈ 30 microns).

As a normal working protocol, the fluid inclusions are cooled to the lowest temperature that the stage can achieve and, subsequently, the phase changes taking place are observed while the temperature rises towards room temperature again. The first change of phase that should be observed in the liquid phase is the appearance of the first

³ This technique is very common and is widely described in any of the general books that are included in the section of bibliographical references (for example, Roedder, 1984; Shepherd et al. 1985; De Vivo & Frezzotti, 1994; Goldstein & Reynolds, 1994, etc.). To avoid being repetitive, this section is only a brief summary and readers interested in more information are submitted to any of the above mentioned books.

⁴ See also exercise included in appendix 1 about microthermometric data treatment, especially useful for beginners.

liquid in the cavity (eutectic temperature). This temperature is characteristic of each system and, therefore, allows us to associate the composition of the fluid inclusion with a chemical system. Table 2 summarizes some of the most common chemical systems found in natural fluids as well as their eutectic temperatures. In regard to the gaseous phase, the first change that should be observed during heating is the melting of CO₂ -or other gases that could be present in the cavity-. Table 3 includes some microthermometric characteristics of the most frequently occurring volatiles in nature. Later, other phase transitions may be observed in the liquid phase, in the vapour phase or at the interphase region (melting of the last crystal of ice, melting of hydrohalite or other salt hydrates, melting of clathrates, homogenization of CO₂, etc.). Using the temperatures observed for these phase transitions, and with adequate diagrams, we can estimate the salinity, types and contents of the volatiles, etc.

Later, the inclusions are heated from room temperature to the temperature at which homogenization of the cavities occurs. This temperature is known as the homogenization temperature and represents the minimum trapping temperature for the fluid inclusion. To determine the P-T trapping conditions, it is necessary to calculate the isochore corresponding to the fluid inclusion. In a space P-T, this isochore determines a straight line, for which it can be said that: (1) its slope is a function of the density of the fluid inclusion; (2) the homogenization temperature is the minimum value of the aforementioned straight line; (3) the line contains the trapping P-T, although with unknown coordinates until the present time. To determine the trapping P-T, it is necessary to use an independent geothermometer/geobarometer or any of the procedures described in the relevant literature (see for example chapter 7.6 of Shepherd et al., 1985).

Using different data input (microthermometric data, micro raman data, cation ratios, volume fraction estimations, etc.), several computer packages make extensive calculations related with fluid inclusions (isochores, bulk density, molar volume, salinity, composition of fluid inclusion, etc.). In this sense, the most popular could be FLINCOR (Brown, 1989), MacFlinCor (Brown & Hagemann, 1994), CLATHRATES (Bakker, 1997) or FLUIDS (Bakker, 2003). See also Bakker & Brown (2003) for more details about these software packages, and the website <http://institute.unileoben.ac.at/mineralogie/Bakker/Programs/Computer.html> for latest updates.

Chemical system	Eutectic temperature
H ₂ O-NaCl-CaCl ₂	-52.0°C
H ₂ O-CaCl ₂	-49.5°C
H ₂ O-NaCl-FeCl ₂	-37.0°C
H ₂ O-FeCl ₂	-35.0°C
H ₂ O-NaCl-MgCl ₂	-35.0°C
H ₂ O-MgCl ₂	-33.6°C
H ₂ O-NaCl-KCl	-22.9°C
H ₂ O-NaCl	-20.8°C
H ₂ O-KCl	-10.6°C

TABLE 2. Eutectic temperature for the most frequent naturally occurring salt system (simplified from Shepherd et al., 1985).

Species	T _{triple} (°C)	T _{critical} (°C)	Raman frequency (cm ⁻¹)
N ₂	-210.0	-147.0	2331
CO ₂	-56.6	31.1	1285
CO ₂	-56.6	31.1	1388
CH ₄	-182.5	-82.1	2917
H ₂ S	-85.5	100.4	2580 (liquid)
H ₂ S	-85.5	100.4	2590 (in water)
H ₂ S	-85.5	100.4	2611

TABLE 3. Temperature of the triple point, critical temperature and Raman frequency for common volatiles in fluid inclusions (summarized from Shepherd et al., 1985; Burke, 2001 and Diamond, 2003).

Use of other study techniques

In the majority of fluid inclusion studies, a microthermometric characterization is sufficient to identify the fluids that could have intervened in the genesis of the fluid inclusions and to characterize their conditions of formation, which is the usual aim of this type of studies.

Based on the results from microthermometric analysis, the decision to use other study techniques will be conditioned by several factors. The most important thing is to decide whether additional information about the characteristics of certain phases is needed (characterization of volatile, solute contents, etc.). Depending on economic availability, technical means or instruments available and, above all, depending on the interest in carrying out additional characterization of certain phases, we can use different analytical techniques. In this sense, any analytical technique might be appropriate. However, we must bear in mind that the main limitation of any chemical study of fluid inclusions is the small size of the cavities to analyze. The list of techniques that have been used for this purpose is very large, although some of them have only been used occasionally or with little success. Table 4 summarizes some of these techniques. Later are described some of them.

Raman microprobe

According to Burke (2001) and Burruss (2003), the Raman scattering is a consequence of inelastic collisions of a beam of light with vibrating polyatomic molecules or molecular groups (for example, fluid in an inclusion). These collisions cause energy changes to specific energy states of the molecule, which, in turn, correspond to the mode of vibration of each type of bond in a molecule. Selection rules explain whether a vibrational mode is infrared and/or Raman active (Raman and infrared adsorption spectroscopy are complementary analytical techniques ideal for the study of molecular species in fluid inclusions). Raman scattering is a weak effect (only about 10^{-8} of the incident photons). Thus, an intense light source is needed to illuminate the sample. A monochromatic laser beam is normally used. Using a monochromator and adequate filters to separate and measure the Raman scatter from the elastically scattered light, we can obtain a Raman spectrum. With this spectrum we can study the position and the intensity corresponding to the energies of the vibrational modes of the different species in the sample.

In the case of fluid inclusions, Raman analysis can be quantitative or qualitative. Identification of the phases is based on the position of the peaks of the spectra obtained by the Raman microprobe and quantification is done according to their relative intensity.

Study of fluid inclusions with a Raman microprobe is carried out with three main purposes:

(1) Study of the gaseous phases present in the gas bubble. Of the gaseous phases, the most common are the presence of carbon dioxide, nitrogen, methane or dihydrogen sulphide, with typical bands ($\Delta\nu$ in cm^{-1}) at 1285 and 1388 $-\text{CO}_2-$; 2331 $-\text{N}_2-$; 2917 $-\text{CH}_4-$ and 2580 and 2611 $-\text{H}_2\text{S}-$ (Burke, 2001). From the peak areas it is possible to establish the relative proportion between the volatile phases. If the equipment is properly calibrated, from this information the corresponding molar fractions of every gas can be calculated.

(2) Identification of the solid phases that are trapped as minerals or precipitated minerals. Among them the most frequent are sulphates and carbonates, and less frequent, silicate, native sulphur, or hematite. They are usually identified using databases with spectra of reference. Nevertheless, the databases are not fully developed for a range of reasons (Burke, 2001): (A) Many minerals (e.g., NaCl and KCl, very important for fluid inclusions) have only weak Raman spectra, or no spectra at all – due to type of bonds. (B) The laser beam causes important differences in the spectra (in peak intensities - and also position) and with the orientation of the crystal. (C) In solid solutions, the peak position depends on the chemical composition of the mineral.

(3) On occasions, using cryogenic equipment attached to a Raman microprobe, it is also possible to use Raman for analyzing the solid phase that originates on freezing the liquid phase of the fluid inclusion. In this case, the aim is usually to identify salt hydrates that are formed by subjecting the fluid inclusions to freezing. The Raman microprobe is a powerful tool for identifying the stoichiometric hydrates that crystallize upon cooling, being able to obtain Raman spectra for hydrates of geological interest (for example, $\text{NaCl}\cdot 2\text{H}_2\text{O}$; $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$; $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$;

NONDESTRUCTIVE ANALYSIS*Qualitative and semiquantitative*

- | | |
|----------------------------------------------------------------------------------|----|
| - Visible light microscopy | |
| - Cathodoluminescence microscopy | CL |
| - Ultraviolet microscopy (Ultraviolet fluorescence microscopy) | UV |
| - Infrared microscopy | IR |
| - IR absorption spectrometry (Fourier transform IR microspectrometry) FTIR/FTIRM | |
| - Microthermometry (sometime, with infra-red microthermometry) | |

Semiquantitative and quantitative

- | | |
|---------------------------------------------------------------------------|---------|
| - Laser Raman microprobe (or Laser Raman spectroscopy) | LRM/LRS |
| - Electron probes: | |
| Scanning electron microscopy and energy dispersive spectrometer | SEM-EDS |
| Electron microprobe | EPMA |
| Transmission electron microscopy | TEM |
| - Nuclear/ionic probes: | |
| Proton-induced X-ray emission (+/-Rutherford backscattering spectrometry) | |
| PIXE (RBS) | |
| Proton-induced gamma rays | PIGE |
| Elastic recoil detection analysis | ERDA |
| - X-ray probes: | |
| Synchrotron X-ray fluorescence | SXRF |
| Extended X-ray absorption fine structure | EXAFS |
| - Nuclear magnetic resonance/Proton magnetic resonance | NMR/PMR |

TABLE 4. Different techniques used for analysis of fluid inclusions (from Roedder, 1990, and modified with data from Samsom et al. 2003 and from this summary).

DESTRUCTIVE ANALYSIS

Analysis of the gas phase

- Gas chromatography (sometime, combined with mass spectrometry) GC (or GC-MS)
- Laser microprobe mass analyzer or laser induced mass analyzer LAMMA/LIMA
- Mass spectrometry (Quadrupole mass spectrometry) MS (QMS)

Analysis of the solutes in the liquid phase

- Atomic absorption spectrometry AAS
 - Flame-atomic emission spectroscopy FAES
 - Ion chromatography IC
 - Atomic-emission spectroscopy AES
 - (Laser ablation) inductively-coupled plasma mass spectrometry (LA-)ICP-MS
 - (Laser ablation) inductively-coupled plasma optical emission spectroscopy (LA-)ICP-OES
 - Instrumental neutron activation analysis INAA or NAA
 - SEM and cryogenic SEM (with energy dispersive analysis) (Cryo) SEM-EDS
 - Ion probe (secondary ion mass spectrometry) SIMS
- Also reported: thin-film anodic stripping voltammetry, coulometry, radiometry, emission spectroscopy, spectrophotometry, potentiometry -with ion-specific electrodes-, fluorimetry ...

Analysis of inclusion solids

- Scanning electron microscopy and energy-dispersive spectrometry SEM-EDS
- Electron diffraction ED
- X-ray diffraction (+/- using the Gandolfi camera technique) XRD

TABLE 4 (cont.). Different techniques used for analysis of fluid inclusions (from Roedder, 1990, and modified with data from Samsom et al. 2003 and from this summary).

MgCl₂·12H₂O; FeCl₃·6H₂O; KCl·MgCl₂·6H₂O) with sufficient quality in order to determine them in natural fluid inclusions (Dubessy et al., 1982). The salt hydrates can be used to determine the salinity of the solutions. Ni et al. (2006) demonstrates that hydrohalite has a positive correlation to salinity (i.e. the mass of hydrohalite increases with increasing salinities and decreasing mass of ice), being another effective way to

obtain the salinity of fluid inclusions. Thus, both the height and area ratios of hydrohalite 3423 cm^{-1} and 3405 cm^{-1} peaks against the ice 3098 cm^{-1} peak, and the total area ratios of hydrohalite peaks against ice 3098 cm^{-1} peak can be used to estimate the salinity of fluid inclusions.

Analysis of individual fluid inclusions

As has been shown above, fluid inclusions could contain fluids that have been trapped at different moments in the "life" of the host crystal. This gives rise to the existence of different populations of fluid inclusions. It is very common for a crystal not to contain a unique type of fluid. Instead it will reflect, to varying degrees, the different fluids characterizing the various processes that the fluid inclusion host crystal has undergone, from its formation up to the moment of observation. In addition, fluid inclusions may have suffered processes of re-equilibration during the evolution after their trapping. As a consequence, it becomes more and more frequent that, depending on the precision level decided according to the aims of the study proposed, characterization of the composition of fluid inclusions to bulk sample scale is not sufficient and the properties of individual fluid inclusions must be determined.

For this proposal, a number of specific techniques, capable of analyzing individual fluid inclusions in a "point" form, can be found in specialized literature. Among these techniques, we can nowadays emphasize the laser ablation (LA) group (destructive techniques), and the microprobes group (non-destructive techniques).

In relation to the first group, Fabre et al. (1999) explain that LA can be based on ICP-MS (inductively coupled plasma mass spectrometry) or on optical emission spectroscopy (OES). Both techniques are coupled with LA at microscopic scale to extract the liquid to be analyzed within the fluid inclusions. According to the same authors, LA-ICP-MS could be more adequate for determination of trace elements and LA-ICP-OES gives better detection limits results for major elements, especially Na and Ca. The limitations of LA-ICP-AES⁵ arise from the lack of sensitivity of AES for some elements and the difficulty in determining absolute concentrations of components in the fluid inclusions

⁵ LA-ICP-AES and LA-ICP-OES (AES: atomic emission spectroscopy; OES: optical emission spectroscopy) could be considered the same technique.

(Wilkinson et al. 1994). Also, detection limits (Günter et al., 1998) are higher for LA-ICP-AES (in the $\mu\text{g g}^{-1}$ to mg g^{-1} range) than for LA-ICP-MS (in the ng g^{-1} to $\mu\text{g g}^{-1}$ range). As a consequence, LA-ICP-MS is more frequently used today.

Gagnon et al. (2003) indicate different advantages for LA-ICP-MS techniques: low capital cost, ease of use, ability to obtain data from depth fluid inclusions, etc. In addition, these authors point out the minimal sample preparation, the possibility of obtaining quantitative analysis of individual fluid inclusions, the high spatial resolution (down to $2\mu\text{m}$), the high sensitivity (less than $\mu\text{g/g}$), moderate/high precision (5-30%), and the possibility of obtaining rapid multielement analysis over wide mass (6-240 amu) and dynamic (up to 11 order of magnitude) ranges, etc. In contrast, Gagnon et al (2003) indicate some weaknesses to overcome in the future: internal standardization, correction of host mineral contribution to the fluid inclusion signal, elimination of spectral interferences, etc.

Günter et al. (1998) explained a stepwise opening procedure for a controlled ablation (a small hole is drilled for the partial release of liquid and vapour, followed by complete drilling using a pit covering the entire inclusion) in order to avoid the explosion and splashing of material, with the consequent loss of solid internal precipitates. Gagnon et al. (2003) propose an alternative strategy for ablation, consisting in a traversed opening. The method consists of traversing the sample surface until the laser beam is over the top of the fluid inclusion and then allowing the laser beam to drill into the inclusion. In practice, the most adequate procedure for ablation depends on each sample and some preliminary essays must be done prior to analyzing fluid inclusions.

Günter et al. (1998) also explained the procedure for quantification of element concentrations. Element ratios calculated from integrated intensity are calculated from the elements ratios via an internal standard element, whose concentration was determined prior to ablation (in this case, concentration of Na determined using microthermometric measures). A complete description for quantification of element concentration can be found at Gagnon et al. (2003). These authors analyze several alternatives for calibration standard (including NIST and USGS synthetic glasses, synthetic fluid inclusions, desolvated solution standards, microcapillaries, microwells or fluid inclusion analogues) and for measurement of internal standards.

Gagnon et al. (2003) also include an example in which concentration units are obtained from raw data using readily available commercial spreadsheets and spectral analysis software.

Regarding the microprobes group, Anderson & Mayanovic (2003) made an extended review of electron, nuclear and X-ray microprobes. In this review, the techniques using an electron microbeam for analysis of fluid inclusions are divided into three types:

(1) Scanning electron microscopy: used for identification or semiquantitative analysis of daughter minerals (in combination with energy dispersive analysis), for analysis of decrepitated mounds, or for analysis of frozen fluid inclusions (in combination with a cryogenic stage).

(2) Electron microprobe: used for semiquantitative analysis of unopened fluid inclusions, limited by the electron beam's shallow level of penetration.

(3) Transmission electron microscopy: used mainly for morphological studies.

According to Ryan (1999), nuclear microprobe techniques can be divided into PIXE (Particle-Induced X-ray Emission), PIGE (Proton-Induced Gamma-ray Emission) and ERDA (Elastic Recoil Detection Analysis) for the purpose of analyzing fluid inclusions. PIXE provides detection limits around 40 ppm for different elements and is useful for elements ranging from Cl to U (with the exception of rare earth elements). PIGE is particularly used for lighter elements (Li, B, F, Na, Mg and Al) and ERDA for H analysis. In addition, RBS (Rutherford Backscattering Spectrometry) coupled with PIXE provides the geometrical information needed for quantitative elemental analysis (Strivay et al., 2008).

With respect to x-ray probes, synchrotron X-ray fluorescence (SXRF) and x-ray absorption fine structure (XAFS) have been used to analyse fluid inclusions (for example, Anderson & Mayanovic, 2003; Cauzid et al. 2006) providing minimum detection limits of a few ppm for many metals.

As Anderson & Mayanovic (2003) indicate, electron microprobe analyses are semiquantitative but these techniques are accessible to many researchers. In contrast, nuclear and X-ray microprobe analyses are quantitative, but laboratories equipped with these techniques and suitable for fluid inclusion analyses are very limited at present.

Conclusions

The study of fluid inclusions is a highly useful tool for analysing the physicochemical properties of the fluids involved, not only in mineralising processes but also in many geological processes involving fluids. Their detailed study requires an approximation to the problems using different analytical techniques, but this is often sufficient only with a suitable microthermometric characterization. For other investigations with more ambitious objectives, the portfolio of analytical techniques that are available nowadays is quite extensive, ranging from simple techniques commonly used within the majority of research laboratories to complex techniques that are difficult to access. Likewise, advances in the development of new analytical techniques and their application to the study of fluid inclusions, especially in the quantitative study of individual fluid inclusions, is taking place at a frantic pace, so that "barriers" are quickly broken and "borders" take less and less time to be crossed. The use of these techniques depends, therefore, on both the requirements of each specific study and on the economic resources or the facilities for access to instrumentation available to each researcher. However, the future is coming: what will it have to offer us?.

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Appendix 1⁶

This exercise (based on Morales, 1995) is focused on beginners working with the microthermometry of fluid inclusions. The aim is to familiarize them with the management and treatment of acquired data and its interpretation. In Table A, the results of a hypothetical microthermometric study of fluid inclusions are summarized. It can be supposed that the petrographic characteristics of these fluid inclusions suggest that all fluid inclusions belong to a unique population (primary two-phase fluid inclusions with a very similar degree of fill throughout). The following questions are proposed:

1. Which chemical composition can be assumed for the studied fluid? From which of the parameters studied can this be deduced?
2. Make a histogram of frequencies for the values of temperature for: (A) melting of the last crystal of ice, (B) melting of hydrohalite, and (C) homogenization.
3. Represent fluid inclusions from Table A on a diagram of Borisenko (1977, -in Shepherd et al. 1985-), and calculate the salinity and the Na/Ca relationship for each inclusion using the aforementioned diagram.
4. Make new salinity calculations using formulae proposed by Potter et al. (1978) and Bodnar (1993). What conclusions do you reach by comparing the results obtained by the three methods?
5. Represent data on a T_H vs. salinity diagram, using different symbols according to the Na/Ca relationship of each inclusion. Which conclusions can be reached from this diagram?
6. From the histograms obtained in paragraph 2 and the graphs obtained in paragraphs 3 and 5, can we say that the number of measures is sufficient, or is it necessary to continue the process of data acquisition? What geological interpretation can be “invented” from these graphs?
7. Choose a fluid inclusion that is considered to be representative and calculate the isochore using the formula proposed by Zhang and Frantz (1987). If a formation temperature of 450°C is assumed for the host mineral of fluid inclusion, at what pressure could fluid be trapped?

⁶ Answer to these questions and more information for interested persons to go more deeply into this kind of exercises will be sent if you write an e-mail to smorales@ugr.es

Table A. Microthermometric values obtained from a hypothetical study of fluid inclusions.

Ref.	T _{FM}	T _M	T _{MH}	T _H	Ref.	T _{FM}	T _M	T _{MH}	T _H
1	-52.0	-16.5	-35.0	402	16	-49.8	-11.1	-29.1	381
2	-53.0	-12.5	-33.0	385	17	-50.0	-10.9	-28.1	378
3	-50.2	-13.5	-32.0	391	18		-9.7	-29.1	373
4	-49.7	-13.0	-30.0	384	19		-8.8	-29.9	370
5	-52.1	-16.0	-31.5	396	20	-49.5	-10.1	-27.2	377
6	-50.4	-11.5	-32.4	385	21	-48.8	-8.8	-25.9	366
7	-49.7	-14.6	-30.4	392	22	-47.6	-8.1	-28.2	362
8	-47.8	-11.3	-32.6	381	23		-7.5	-28.1	363
9	-48.7	-14.7	-33.9	397	24		-8.1	-25.5	361
10	-52.1	-12.2	-29.1	381	25		-7.5	-25.4	358
11	-51.5	-11.2	-30.3	383	26	-48.9	-2.0	-24.1	301
12	-50.4	-15.4	-32.6	398	27	-46.9	-9.2	-32.2	371
13	-49.9	-12.6	-31.1	387	28	-48.9	-7.2	-26.1	358
14	-48.8	-10.4	-30.3	380	29		-6.4	-25.2	344
15	-47.9	-9.6	-30.7	377	30		-6.0	-25.0	348

Calculation for salinity

$$\text{Salinity (\% wt.)} = 1.76958T_m - 4.2384 \cdot 10^{-2}T_m^2 + 5.2778 \cdot 10^{-4}T_m^3 \quad (\text{Potter et al., 1978})$$

$$\text{Salinity (\% wt.)} = 1.78T_m - 0.0442T_m^2 + 0.000557T_m^3 \quad (\text{Bodnar, 1993})$$

Calculation for isochores (Zhang and Frantz, 1987)

$$P = A_1 + A_2T$$

$$A_1 = 6.100 \cdot 10^{-3} + (2.385 \cdot 10^{-1} - a_1)T_h - (2.855 \cdot 10^{-3} + a_2)T_h^2 - (a_3T_h + a_4T_h^2)m$$

$$A_2 = a_1 + a_2T_h + 9.888 \cdot 10^{-6}T_h^2 + (a_3 + a_4T_h)m$$

ABBREVIATIONS

T_{FM}: Eutectic temperature
T_M: Temperature of melting of last crystal of ice
T_{MH}: Temperature of melting of hydrohalite
T_H: Homogenization temperature
m: Molality
a₁, a₂, a₃, a₄ → Constants

	a ₁	a ₂	a ₃	a ₄
H ₂ O	2.857*10 ⁻¹	-6.509*10 ⁻²		
CaCl ₂	2.848*10 ⁻¹	-6.445*10 ⁻²	-4.159*10 ⁻¹	7.438*10 ⁻³
KCl	2.846*10 ⁻¹	-6.403*10 ⁻²	-2.306*10 ⁻¹	3.166*10 ⁻³
NaCl	2.873*10 ⁻¹	-6.477*10 ⁻²	-2.009*10 ⁻¹	3.186*10 ⁻³