

Low temperature behaviour of natural saline fluid inclusions in saddle dolomite (Paleozoic, NW Spain)

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ABSTRACT

The origin of many dolomites is still a matter of debate because of many possible chemical and hydrological conditions of formation. Fluid inclusion studies have been applied in order to improve knowledge about paleofluids responsible for the precipitation of dolomite, and used to define temperatures and salinities. The combination of Raman Spectroscopy and microthermometry is tested here to improve the analytical method to identify the main ion species present in individual inclusions. Natural samples of saddle dolomite from the Cambrian Láncara Fm., Cantabrian Mountains (NW Spain), contain zoned crystals with two-phase aqueous fluid inclusions (liquid-rich). The most stable phase assemblage in these inclusions at $-150\text{ }^{\circ}\text{C}$ consists of ice, hydrohalite and an unknown salt hydrate. The latter melts between -47 and $-41\text{ }^{\circ}\text{C}$, probably representing a eutectic temperature. Subsequently, ice melts in the range of -32.5 to $-29\text{ }^{\circ}\text{C}$ and, finally,

hydrohalite melts between -9 and $-3.5\text{ }^{\circ}\text{C}$. Salinities can be calculated in the fluid system $\text{H}_2\text{O}-\text{NaCl}$ with addition of another salt, either CaCl_2 or MgCl_2 , and result in 7.5–10.6 eq. mass% NaCl and 17.0–21.0 eq. mass% CaCl_2 . Dependent on the rate of cooling runs, three different types of metastability may occur, i.e. the absence of hydrohalite, the unknown salt-hydrate is not formed, and the nucleation of only ice. Salinity calculations from those melting temperatures differ substantially from equilibrium behaviour values. The unknown salt-hydrate needs to be further specified by comparison to standard solutions. The method gives an opportunity to characterize the major compounds in complex fluid systems active during dolomitization, thus contributing to a better understanding of the 'dolomite problem'.

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Introduction

One of the essential problems in understanding dolomite origin is the chemical composition of the fluids from which the dolomite precipitated. Two types of dolomite formation processes are common in diagenetic environments: cementation and replacement of carbonates. Dolomite cementation in pore space and vugs can occur directly from aqueous solutions of variable salinities in different diagenetic environments. Fluid inclusions provide the only direct evidence of the fluid responsible for dolomitization. To characterize the properties of this fluid, microthermometry has been applied as a routine method in some studies concerning dolomite formation (see also Morrow *et al.*, 1986; Coniglio *et al.*, 1994; Qing and Mountjoy, 1994; Zeeh *et al.*, 1995; Boni *et al.*, 2000). Major element composition and salinity can be estimated from the eutectic temperature

and the final melting temperature of ice respectively. Limitations of the optical microscope make the identification of these phase changes sometimes impossible. Furthermore, it is generally difficult to be confident that all the phase assemblages, observed during the heating of a frozen inclusion represent an equilibrium phase configuration (see also Bakker, 2004). Anomalous behaviour of fluid inclusions during freezing has been observed in calcium-rich inclusion solutions in pegmatite hydrothermal systems (Kozlowsky, 1984).

The crush-leach method (e.g. Roeder, 1984; Banks and Yardley, 1992) provides additional information about the major and minor elemental solute composition of the aqueous phase in fluid inclusions. Disadvantages of this bulk analytical method, however, are the inevitable analysis of all fluid inclusion generations present in the samples, and quantitative salinity calculations still depend on microthermometric data.

The combination of Raman spectroscopy with microthermometry represents a powerful method to estimate better the major-ion composition of individual fluid inclusions (Dubessy *et al.*, 1982; Bakker, 2004). Most salt-

hydrates that nucleate at low temperature in fluid inclusions (i.e. $\text{NaCl}\cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$) can be identified with Raman spectroscopy.

In this study, this method has been tested on natural inclusions in dolomite from the Láncara Fm., Cantabrian Zone, NW Spain (Fig. 1). Eutectic and other phase change temperatures are established, in addition to the identification of metastable phase assemblages that can lead to erroneous interpretation of the salinity of the fluids.

Geological setting and dolomite occurrences

The Cantabrian Zone (Lotze, 1945) is the foreland fold-and-thrust belt of the Variscan orogen in NW Iberia (Julivert, 1971). The succession was deformed during Late Carboniferous by thin-skinned tectonics. A dolomitization event post-dates the emplacement of the main Variscan structures. Two main carbonate intervals of the Paleozoic sedimentary succession, i.e. Láncara Fm. (Cambrian) and Barcaliente and Valdeteja Fms. (Carboniferous, see Gasparrini, 2003) were affected by dolomitization. The dolostones in the

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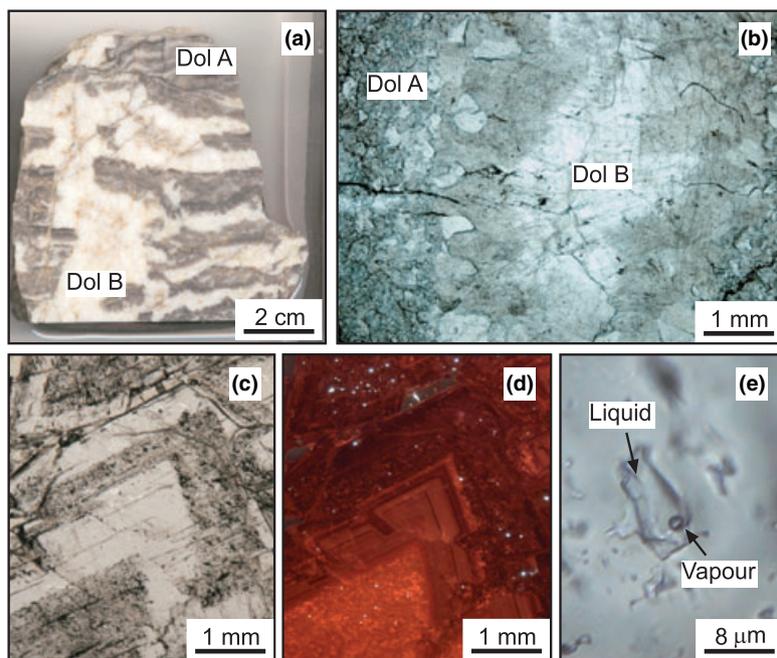


Fig. 1 (a) Hand specimen of the dolomitized Lánçara limestone. (b) Photomicrograph of the dolomite, showing the gradual transition between the two generations of dolomites (Dol A and Dol B). (c,d) Cathodoluminescence and normal photomicrograph of Dol B generation. Dol B show a complex pattern, with a first inclusion-rich red luminescent zone, then a second inclusion-free finely zoned red-dull to non-luminescent zone, followed by third non-luminescent inclusion-rich zone and finally inclusion-free finely zoned red-dull to non-luminescent part. (e) Two phase liquid-rich aqueous fluid inclusions in Dol B generation.

Lánçara Fm. is of burial origin, as demonstrated by the coarse crystallinity, non-planar textures, zebra structures and fluid inclusions total homogenization temperature between 80 to 110 °C (Laponi *et al.*, 2004). The dolomitization front is well defined in the field and crosscuts the bedding planes, without a transitional interval between dolomitized and undolomitized lithologies. Two different generations of dolomite can be petrographically distinguished: a replacive generation, rarely saddle dolomite (*Dol A*), and a coarser void-filling generation, always saddle dolomite (*Dol B*) (Fig. 1a,b). The transition between these two phases occurs in an approximately 1-mm thin zone, without sharp boundaries. *Dol A* is not zoned and shows uniform red colour under the cathodoluminescence microscope whereas *Dol B* has a complex zonation pattern (Fig. 1c,d). This pattern is partly defined by a variable abundance of fluid inclusions.

Analytical methods

The fluid inclusion study was conducted on doubly polished 100–120 μm thick sections prepared with a cold polishing technique, reaching the maximal temperature of 35 °C in order to prevent re-equilibration and/or decrepitation of the inclusions by preparation heat. Microthermometric measurements were carried out in a Linkam MDS 600 heating-freezing stage (University of Heidelberg, Germany). Calibration was performed by means of synthetic fluid inclusions at –56.6 and 0.0 °C, i.e. triple point of CO₂ and triple point of H₂O respectively. Liquid and gas phases in the fluid inclusions were analysed by a LABRAM confocal-Raman spectrometer (University of Leoben, Austria) using a 100 mW frequency-doubled Nd-YAG laser. A 532.2-nm wavelength (green laser) was used for radiation. The laser beam was focused within the inclusions through an Olympus BX 40 micro-

scope, equipped with a 40 and 100× lenses, combined with a confocal optical arrangement. A Linkam TMS 93 stage, attached to the Raman microprobe, enabled spectroscopic analysis at controlled temperatures. Raman spectra were measured in a time span of 20 s at selected temperatures. The spectra were analysed for the peak positions and compared with already compiled tables for the most common substances (Dubessy *et al.*, 1982; Samson and Walker, 2000; Bakker, 2002, 2004).

The Raman measurements were performed on fluid inclusions near the sample surface to reduce the high background signal of the host. Twelve inclusions were selected from more than 100 inclusions where microthermometric data are available. At very low temperatures, around –190 °C, Raman spectra of ice and salt-hydrates consist of well defined peaks with narrow half-width. At higher temperature, the position and shape of the same molecular vibration changes, becoming less pronounced with a larger half-width and, therefore, more difficult to distinguish (see also Bakker, 2004). Two different types of heating/cooling experiments were carried out for comparison, to recognize stable and metastable assemblages: (i) normal heating–cooling procedure, including fast cooling down to –190 °C and then reheating up to the temperature of melting a specific phase; and (ii) composite heating–cooling procedure, during which reheating reached –50 °C, followed by cooling down again to –190 °C. The composite procedure enhanced nucleation and generated stable phase configurations at selected temperatures. Exact melting temperatures were obtained from the analysis of Raman spectra at low temperatures, following rapid cooling after a supposed observed melting event. This method uses the absence of phases to identify melting temperatures: once the melting temperature of a solid phase has been reached, the melting fluid persists metastably during following cooling, with consequent disappearance in the Raman spectrum of the peaks related to the solid phase.

Salinity is calculated in the ternary H₂O–NaCl–CaCl₂ (Nader 1996) by means of the Computer package Fluid (Bakker, 2003). Salinity is expressed in

eq. mass % (see justification in Bakker, 2004), and is obtained from final ice and hydrohalite melting temperatures. It should be noted that the use eq. mass% of certain salt species does not give any information about those salt species that are actually dissolved in the water but do not nucleate any solid phase.

Results

The fluid inclusion study was mainly carried out on the generation *Dol B* saddle dolomite cements. The crystals have inclusion-rich cores and growth zones of alternating abundances of fluid inclusions parallel to zoning characterized by different cathodoluminescence (Fig. 1c,d). The inclusions contain a vapour and a liquid phase with a volume fraction ranging from

0.78 to 0.97 (Fig. 1e) at room temperature. Larger inclusions (up to 12 μm in length) occur preferentially in the outer part of the crystal cores and along crystal growth zones.

In a normal heating–cooling procedure, the inclusions show a metastable behaviour. During fast cooling to $-150\text{ }^\circ\text{C}$, many inclusions do not reveal nucleation of any crystalline phase, but form an amorphous solid ('glass') with a Raman spectrum similar to water (Fig. 2a,b). The vapour bubble increases continuously its volume fraction during cooling down to $-150\text{ }^\circ\text{C}$ and remains perfectly spherical. During reheating, the 'glass' slowly recrystallizes, which is noticeable by the contraction of the bubble and the development of a microcrystalline mixture with a granular texture and a brownish colour between -80

and $-70\text{ }^\circ\text{C}$. The temperature of appearance of the granular texture can be easily mistaken for the eutectic point of the fluid system by using only optical microscopy. Ice and the amorphous solid liquid can be detected by Raman spectroscopy at $-80\text{ }^\circ\text{C}$ (Fig. 2c). After further cooling, ice and hydrohalite are identified by Raman spectroscopy within this mixture (Fig. 2d).

In a composite heating–cooling procedure, stable phase assemblages were cultivated in fluid inclusions at low temperatures, which differ substantially from the previously obtained assemblages. Probably, the most stable phase assemblage at $-150\text{ }^\circ\text{C}$ consists of ice, hydrohalite and an unknown salt-hydrate (Fig. 3), which may include CaCl_2 , MgCl_2 , or a mixture of the two. The Raman spectrum of the unknown salt-hydrate at $-150\text{ }^\circ\text{C}$ consists of the peak-wave-numbers 3200, 3366, 3396, 3425, 3454 and 3510 cm^{-1} , with variable intensities. This salt-hydrate melts between -47 and $-41\text{ }^\circ\text{C}$ (with an error of $\pm 1\text{ }^\circ\text{C}$, because of the difficulties in observing the melting behaviour) and may correspond to the eutectic temperature of the fluid system. However, this relatively large range in melting temperatures may represent peritectic melting. A lower eutectic temperature is suspected, but could not be identified by the combined method of Raman spectroscopy and microthermometry. Subsequently, ice melts in the range of -32.5 to $-29\text{ }^\circ\text{C}$. Hydrohalite is the last solid phase that melts during a heating run, between -9 and $-3.5\text{ }^\circ\text{C}$. The presence of NaCl in solution was identified by Raman spectroscopy. The obtained spectra of hydrates do not have similarities with standard spectra of CaCl_2 and MgCl_2 hydrates (Samson and Walker, 2000; Bakker, 2004). Other major salt types need to be compared with standard solutions that are not yet available. Calculated salinities vary between 7.5–10.6 eq. mass% NaCl and 17.0–21.0 eq. mass% CaCl_2 .

Three different types of metastable phase assemblages and melting at low temperature were identified: (i) hydrohalite is absent, ice is the last melting solid phase (-39 to $-33\text{ }^\circ\text{C}$) and the unknown salt hydrate melts between -41.5 and $-39\text{ }^\circ\text{C}$; (ii) the unknown

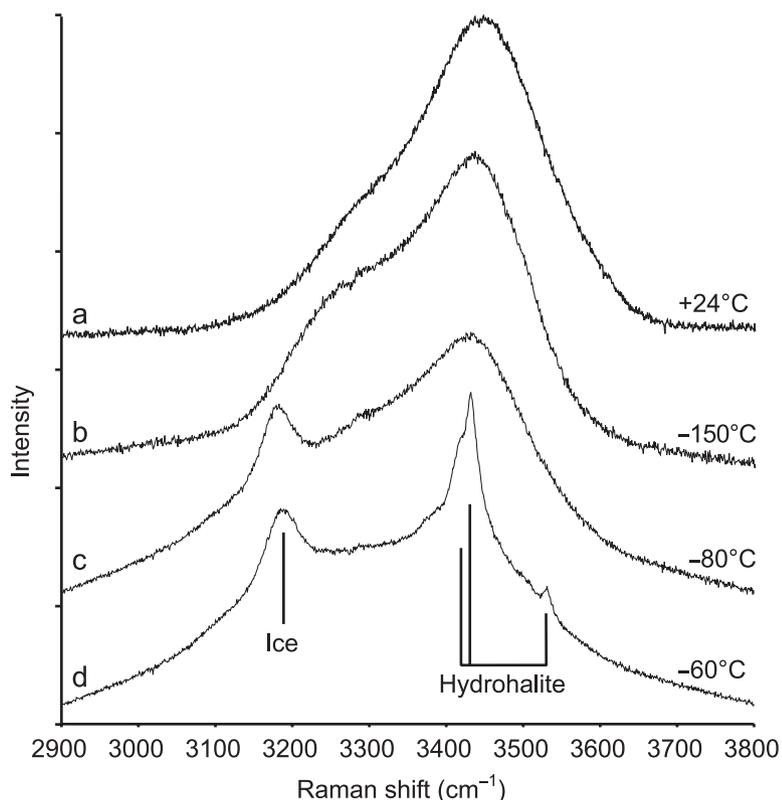


Fig. 2 Raman spectra measured at four different temperatures during normal heating–cooling procedure. At $-150\text{ }^\circ\text{C}$, the inclusion does not nucleate any recognizable crystalline phase, forming an amorphous solid with a Raman spectrum similar to the one of liquid H_2O (a,b). At about $-80\text{ }^\circ\text{C}$, the glass transforms into a randomly orientated microcrystalline mixture with a granular texture and a brownish colour: appearance in the Raman spectrum of the peak of ice, with part of the inclusion persisting as amorphous solid (c). At $-60\text{ }^\circ\text{C}$ (d), the only recognizable salt-hydrate phases recognizable are ice and hydrohalite; no nucleation of hydro-X phase is observed.

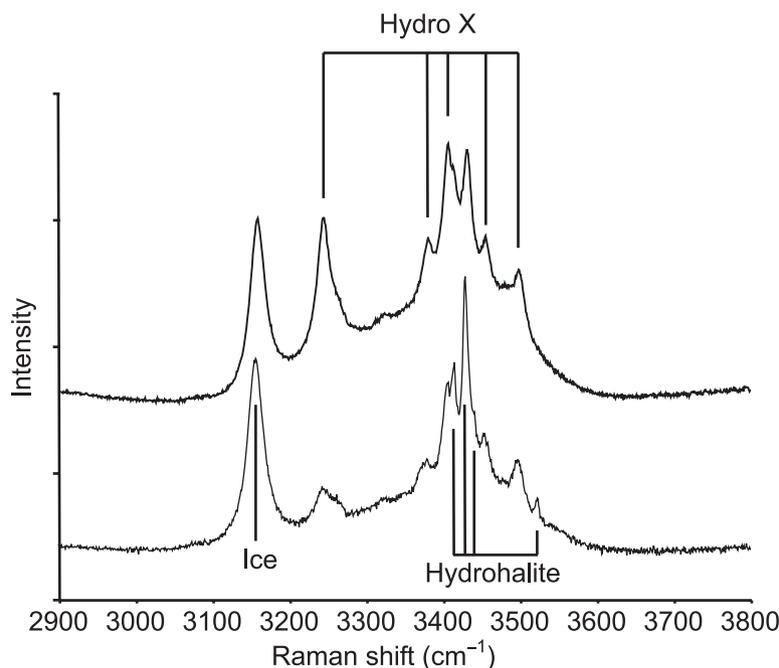


Fig. 3 Raman spectra in the fluid inclusions at $-150\text{ }^{\circ}\text{C}$ after composite heating–cooling procedure. Three different solid phases are recognizable: ice, hydrohalite and a third unknown salt-hydrate phase (hydro-X).

salt-hydrate is not formed, this type of behaviour occurs with the normal heating–freezing procedure (i.e. fast cooling); and (iii) only ice is formed at low temperatures and remains in the presence of the brine and the vapour bubble, even down to $-190\text{ }^{\circ}\text{C}$. Metastable melting can also be deduced from unusual phase changes, such as simultaneous melting of ice and the unknown salt hydrate, or simultaneous melting of ice and reappearance of a vapour bubble. Salinity calculations (in equivalent mass%) from these measurements lead to erroneous values.

Discussions and conclusions

The rate of temperature changes in heating/cooling procedures (i.e. heating and cooling rates) used during the measurement of the fluid inclusions plays a crucial role in the nucleation of stable phase assemblages. Raman spectroscopy revealed that different heating/cooling experiments produced different phase assemblage at low temperatures. Consequently, the fluid inclusions displayed different melting behaviours, which could lead to spurious salinity calculations. The fluid trapped in the *Dol B* generation

in the Cambrian Láncara Fm. can be characterized in a water–salt system. NaCl in the aqueous solution was identified as a dissolved salt species from Raman spectra of hydrohalite in frozen inclusions. Another salt-hydrate spectrum was identified, which is similar to that measured by Gasparrini (2003) from fluid inclusions in dolomite from the Carboniferous Barcaliente and Valdetaja Fms. Further experimental studies are required to obtain the identity of this hydrate, which most probably consists of CaCl_2 and MgCl_2 . Nevertheless, similar fluids caused dolomitization in both Cambrian and Carboniferous carbonates in the southern Cantabrian Zone.

It can be assumed that a local fluid source is mainly defined by the adjacent host rock; consequently, different dolomitized rock formations would reveal different fluid systems. The similarity between dolomitizing fluids affecting the Cambrian limestones and the Carboniferous limestones favours an external fluid source, which flooded both rock types presumably in a late stage of the Variscan orogeny.

The Raman-peak patterns are compared with the one obtained from

experimental data on synthetic fluid inclusions, in the CaCl_2 –NaCl (Samson and Walker, 2000) and NaCl– MgCl_2 fluid systems (Bakker, 2004). No clear similarity is observed between the observed peak configurations and the published data. To identify the unknown salt-hydrate, it has to be taken into account that the peak positions of specific salt hydrates may be shifted by several wavenumbers because of the presence of a mixture of salt-hydrates within the inclusions. Furthermore, the presence of more than one unknown cation cannot be excluded yet, and this would add another factor of complexity in the interpretation of the Raman spectra.

The most stable phase assemblage at low temperatures in frozen inclusions consists of vapour, ice, hydrohalite and an unknown salt-hydrate. The unknown hydrate melts between -47 and $-41\text{ }^{\circ}\text{C}$, near the eutectic temperature of the fluid system. Ice melting and hydrohalite melting is used to calculate the salinity: 7.5–10.6 eq mass% NaCl and 17.0–21.0 eq. mass% CaCl_2 . Melting of ice in a metastable assemblage occurred at lower temperatures, leading to erroneous salinity calculations.

In conclusion, low temperature Raman spectroscopy is a powerful method of investigation for complex salt solutions, capable of minimizing approximation in the calculation of the salinities of fluid inclusions. It revealed the care that has to be taken when studying complex fluid systems. It may give a crucial contribution to a better understanding of the ‘dolomite problem’, offering the unique opportunity to characterize complex paleo-fluid systems such as those active during subsurface dolomitization of large rock bodies.

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