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# Synthesis of hydrocarbon fluid inclusions at low temperature

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## Abstract

Hydrocarbon fluid inclusions have been synthesized in halogenide and sulfate crystals at low temperature (<100 °C) and atmospheric pressure. Water-immiscible hydrocarbon droplets were either trapped separately or with an aqueous and/or a vapor phase. Impurities on the crystal surface were verified by infrared microspectrometry, and the similarity between the initial liquid and the liquid trapped in the inclusion was documented by Raman microspectrometry for nonfluorescent compounds. This inclusion type represents a new tool for understanding inclusion-formation phenomena and for the calibration of techniques used in hydrocarbon fluid-inclusion analysis ($\mu$FT-IR, $\mu$Raman, $\mu$UV-fluorescence, gas chromatography, mass spectrometry); these inclusions allow one to obtain microthermometric calibration curves with a high precision at low temperature.

## INTRODUCTION

Synthetic fluid inclusions are often used for the calibration of analytical techniques and for thermodynamic data acquisition. Fluid inclusions have already been synthesized in laboratory-grown crystals under different temperature and pressure conditions. Shelton and Orville (1980), Sterner and Bodnar (1984), and Zhang and Frantz (1987) created synthetic inclusions in quartz crystals at high temperatures (200–850 °C) and high pressures (0.5–7 kbar) for different compositions in $CO_2$, $CH_4$, and aqueous chloride systems by healing fractures or overgrowths on an original crystal. Some researchers have synthesized hypersaline inclusions in laboratory-grown gypsum (Sabouraud-Rosset, 1969) and halite (Davis et al., 1989) below 100 °C and at atmospheric pressure. In 1987, McLimans mentioned synthetic hydrocarbon-water inclusions in calcite without procedural details.

The fluid trapped in hydrocarbon inclusions is generally a complex mixture of water, carbon dioxide, methane, alkanes, aromatics, hydrogen sulfide, etc. In order to determine the composition of these inclusions, advanced spectrometric techniques (microfluorescence, microinfrared, micro-Raman, or mass spectrometries), chromatography, or microthermometry are required. Before any routine examination, it is necessary to calibrate and to determine the detection limits of these methods by using synthetic samples with similar morphology and composition to the natural ones. The synthesis of hydrocarbon fluid inclusions represents a good tool for understanding natural inclusion-formation phenomena. The composition of the mixture in synthetic inclusions must be known and must not have been modified since trapping.

Synthetic hydrocarbon inclusions were experimentally produced below 100 °C at atmospheric pressure during crystalline growth at the hydrocarbon-water interface during solution cooling.

## PROCEDURE

Inclusions can be synthesized in crystalline chlorides, bromides, iodides, sulfates, etc. All these phases have a solubility coefficient that increases with the temperature. An aqueous solution of halogenides or sulfates, oversaturated at room temperature, is heated to the saturation point. Hydrocarbon compounds are then added to the solution in a glass test tube. This mixture is shaken and then cooled to room temperature. Some crystals grow at the hydrocarbon-water interface. The trapping temperatures range between the saturation point and room temperature. The saturation temperature of the solution must be below the boiling point of the hydrocarbon compounds. For example, a temperature range of 60 to 20 °C was used to synthesize *n*-hexane inclusions in sylvite crystals (KCl) from 100 g of saturated solution (the boiling point of *n*-hexane is 68.7 °C). Under these conditions,

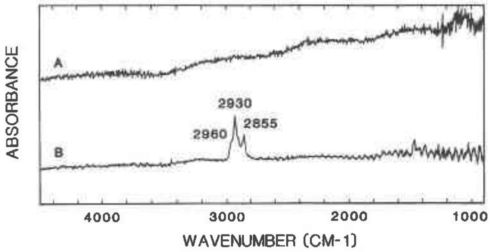

Fig. 1. Sylvite surface conditions controlled by infrared spectra obtained from a 20-$\mu$m diaphragm by 400-scan accumulations on an A-590 BRUKER microscope adapted to an IFS 88 BRUKER spectrometer. (**A**) Sylvite growing in water environment. (**B**) Sylvite growing in hydrocarbon environment. The pollution due to hydrocarbon impregnations appears from 2855 to 2960 cm$^{-1}$, the spectral range of the $CH_2$ and $CH_3$-group stretching vibrations. Interference fringes related to the crystal thickness perturb the baseline.

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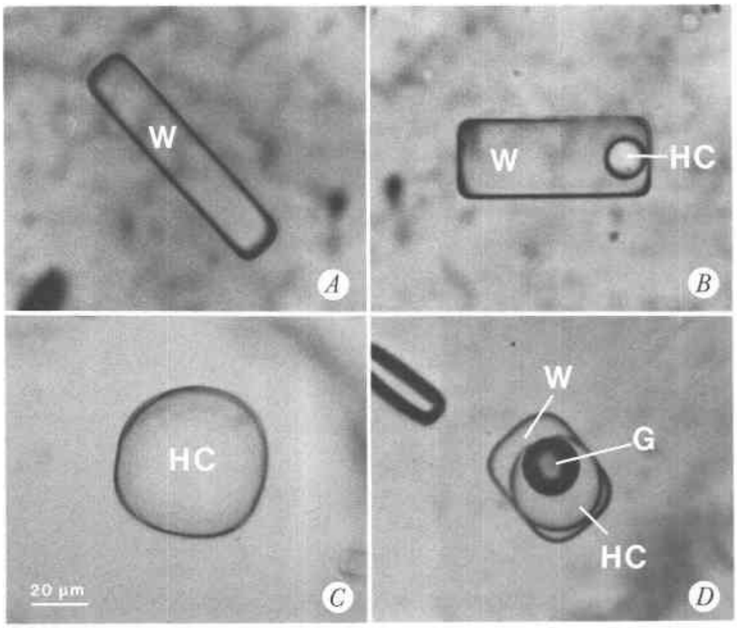

Fig. 2. Photomicrographs showing the different types of inclusions synthesized in sylvite minerals. (**A**) Aqueous inclusion, (**B**) natural oil and water inclusion; (**C**) dodecane inclusion, (**D**) natural oil, water, and gas inclusion (HC = hydrocarbon, W = water, G = gas).

5.9 g of sylvite crystals with *n*-hexane inclusions will precipitate (Table 1).

Inclusion-rich crystals are separated under a stereomicroscope and dried at 20 °C on blotting paper.

The crystals are washed in chloroform to eliminate hydrocarbon impregnation. The efficiency of this treatment can be verified by infrared microspectrometry (Barrès et al., 1987). It is possible to analyze the surface conditions by comparing crystals synthesized in water and in hydrocarbon environments (Fig. 1).

Aqueous inclusions such as water-miscible hydrocarbon inclusions (alcohols, cetones, etc.) are trapped in crystal-lattice imperfections. The size, shape, and number of inclusions depend on the cooling rate. In the case of immiscible compounds (alkanes, alkenes, aromatics, organic solvents, etc.), the inclusion-formation efficiency increases in accordance with the interface size, which is controlled by the emulsion rate of the solution. The presence of oil droplets in the aqueous phase makes formation of hydrocarbon inclusions easier.

## RESULTS AND DISCUSSION

Three different types of inclusions were synthesized: one-phase aqueous inclusions (Fig. 2A), two-phase inclusions with variable hydrocarbon/water ratios (Fig. 2B), and pseudo–one-phase hydrocarbon inclusions (Fig. 2C).

The hydrocarbon inclusions range in size from 1 to 150 µm. Aqueous inclusions are larger and more abundant. The three inclusion types often occur in the same plane inside a tabular crystal, proving that they grew from the solution-hydrocarbon interface. When the aqueous phase represents more than 20 vol% for a 50-µm inclusion, the

**TABLE 1.** Some solubility values for halogenide and sulfate compounds in water and melting and boiling points of some alkanes, aromatics, and organic solvents

| | Solubility (g/100 g saturated solution) | | | Temperature (°C) | |
|---|---|---|---|---|---|
| | 20 °C | 60 °C | | Melting point | Boiling point |
| NaCl | 26.4 | 27.0 | *n*-hexane | −95.3 | +68.9 |
| NaI | 64.1 | 72.0 | *n*-tridecane | −5.5 | +235.4 |
| KCl | 25.5 | 31.4 | cyclohexane | +6.5 | +80.7 |
| KBr | 39.4 | 46.1 | benzene | +5.5 | +80.1 |
| KI | 59.0 | 63.8 | toluene | −95.0 | +110.6 |
| CsI | 44 | 60 | carbon sulfide | −111.5 | +46.3 |
| $KAl(SO_4)_2 \cdot 12H_2O$ | 5–6 | 25 | carbon tetrachloride | −23.0 | +76.5 |

*Note:* Solubilities after Linke (1965); melting and boiling points after Weast and Astle (1979). The boiling points are determined at 760-mm Hg.

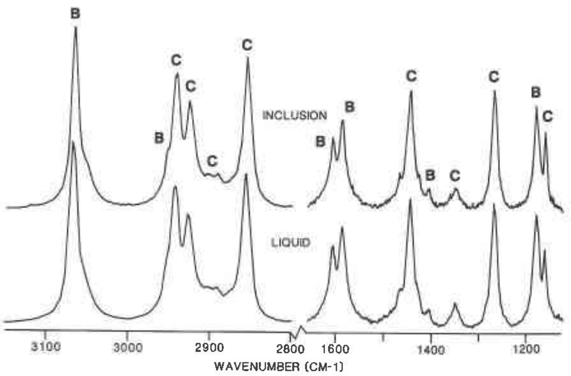

Fig. 3. Raman spectra of 50 vol% cyclohexane (C) + 50 vol% benzene (B) mixture as inclusion sample and as liquid sample. Excitation line = 514.5 nm, ⊥ polarization, laser power = 150 mW, number of accumulations = 30, integration time = 1 s ($\nu$ inc.), 3 s ($\partial$ inc.), 0.2 s ($\nu$ liq.), 0.6 s ($\partial$ liq.). The intensity in the 1650–1150 $cm^{-1}$ region ($\partial$) is magnified by 4.

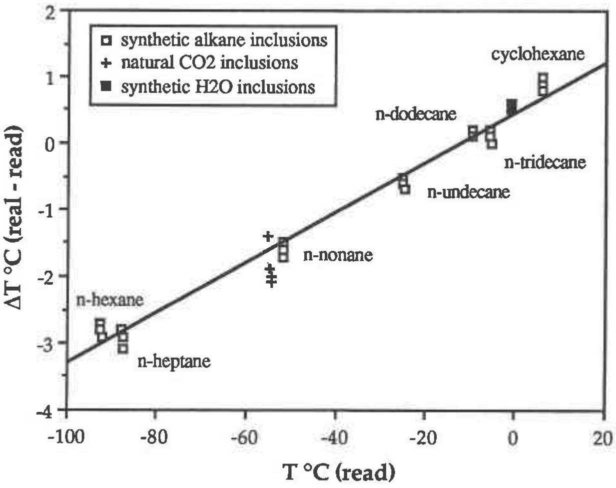

Fig. 4. Calibration curve for a Chaixmeca microthermometric stage in the low-temperature range, using synthetic hydrocarbon inclusions. The melting points of synthetic aqueous inclusions and natural carbon dioxide inclusions represent the traditional calibrating points.

inclusion has a negative crystal shape; when the hydrocarbon phase dominates, the inclusion has a spherical shape. The third type of inclusion is called "pseudo-one-phase" because water, which is invisible in transmitted light, appears in infrared spectra and seems to be located along the crystal-oil boundary. The thickness of this aqueous film is below the threshold of optical detection.

Raman analyses were made to insure that no compositional modifications occurred during trapping. The Raman spectra of a 50 vol% cyclohexane + 50 vol% benzene nonfluorescent mixture were obtained with a multichannel DILOR XY microspectrometer on the initial liquid and the liquid trapped in inclusions (Fig. 3). No difference of intensity ratios or frequencies was detected in the C-H stretching region (3150–2800 $cm^{-1}$) or in the region of the C-H bending and skeletal C-C vibrations (1650–1150 $cm^{-1}$), within the detection limits of the Raman spectrometry. The same observations were made for a 50 vol% octane + 50 vol% pentadecane mixture. This process of inclusion synthesis does not seem to produce fractionation or important structural or vibrational changes of the hydrocarbon phases.

Vapor phases are sometimes trapped in inclusions during crystal growth, inclusion-stretching, thermally induced or late decrepitation and recrystallization phenomena. These bubbles (Fig. 2D) appear in all inclusion types. Their relative volume is extremely variable, and their atmospheric content was determined by Raman microspectrometry. These inclusion types can be useful for calibration of microthermometric stages (Poty et al., 1976) with triple-point measurements at very low temperatures (Table 1); this precision is required for the determination of melting points of naturally occurring mixtures of $CO_2$ ($T_m = -56.6$ °C), $H_2S$ ($T_m = -85.5$ °C), $CH_4$($T_m = -182.5$ °C), and $N_2$($T_m = -209.9$ °C). Figure 4 shows an example of a calibration curve for a Chaixmeca microthermometric stage. Some synthetic alkane inclusions were used between $-100$ °C and $+7$ °C and compared to traditional calibrating points obtained from synthetic aqueous inclusions and natural carbon dioxide inclusions. These new references allow one to achieve more precision in the low-temperature range.

When the color and refractive index of the hydrocarbon, water, and crystal are similar, the hydrocarbon inclusions can be difficult to find. It is then convenient to use coloring agents or/and fluorescing products mixed with the water or hydrocarbon phases. Of course, these products often interfere with the analytical results, but this process can contribute to the understanding of inclusion-formation phenomena. For example, it is easier to optically identify the aqueous phase in a spherical oil inclusion.

## CONCLUSION

The procedure for hydrocarbon-inclusion synthesis described here is very easy to do and very useful in calibrating analytical techniques. Inclusions with different hydrocarbon concentrations in solvents can be used for the determination of the limit of spectrometric and chromatographic methods. Since the inclusion shape is similar to a sphere, the inclusion volume can be estimated. Chloride, bromide, or iodide crystals are more interesting than sulfates because of their nonhydrated nature. The chloride, bromide, and iodide crystals are nonabsorbing in infrared spectroscopy and their range of refractive indices is very wide. On the other hand, three-phase inclusions with liquid water, liquid hydrocarbon, and gas can be used for microthermometric-stage calibration in the problematic range of low temperatures to determine with precision the melting points of natural mixtures of $CO_2 \pm CH_4 \pm N_2 \pm H_2S$. Synthetic inclusions trapped during crystal growth are similar to those observed in natural environments (particularly fluorite, halite, and sylvite deposits) and are representative of the initial fluid; the hydrocarbon stability conditions are not modified during the inclusion synthesis.

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