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MICROCHARACTERIZATION OF FLUID INCLUSIONS IN MINERALS BY RAMAN MICROPROBE

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Abstract

Fluids trapped in inclusions in minerals are micro-amounts of ore-forming media composed of water, dissolved salts, gases and sometimes liquefied gases, liquid, hydrocarbons and solids. The aim of this paper is to summarize the contribution of the Raman scattering microspectrometry to the knowledge of fluid inclusions. After a review of the composition of fluid inclusions and a short presentation of microthermometrical investigations, a description of the Raman microprobe is given. Applications are reviewed ; identification of ionic species dissolved in aqueous phase, characterization of gases of C-O-H-N-S system, identification of solids and non aqueous liquids. The complementary characteristics of Raman microanalysis and microthermometry are underlined. The last section is devoted to comparisons with other microprobes from the point of view of chemical and mineralogical analysis of fluid inclusions.

Introduction

Although a rock is composed by solid phases, the minerals, this has not forbidden the fluid phases to play an important role via mineral-fluid interactions during and also after the formation of this rock. Some of these paleo-fluids are trapped in small cavities, with size usually from 1 to 100 μ m, called fluid inclusions. As shown by petrologists, rock-forming minerals have generally recorded a complex history. In the same way, fluid phases and paleo-fluids, found now in fluid inclusions, are a direct source of information on the initial environment of rocks and their subsequent geological history. The chemical analysis of fluid inclusions is a unique way to know the composition of the fluid phases playing a major part in the earth's crust and upper mantle.

A single crystal may generally contain several generations of inclusion fluids of various age and composition. Consequently, if one wants to reconstruct the history of fluid geochemistry of a given sample, one needs individual analytical techniques. The Raman microprobes are the tools of one of these most powerful techniques. The aim of this paper is to bring out their contribution to the knowledge of fluid inclusions.

The composition of fluid inclusions and the methods for its determination

From a chemical point of view (Roedder, 1972), fluid inclusions are a mixture of volatiles (including water), salts (generally dissolved at room temperature but sometimes crystallized out as daughter phases), minerals and organic compounds. The major volatiles belong to the system C-O-H-N-S ; they are on one hand "simple gases" such as CO₂, CH₄ and water, and on the other hand high molecular weight organic compounds of poorly known composition (Kvenvolden and Roedder, 1971; Burruss, 1981b). Fluorine compounds (Kranz, 1966) and noble gases, especially argon (Roedder, 1972) have sometimes been detected as minor components. The major trapped cations are Na⁺, K⁺, Ca²⁺ and Mg²⁺; significant amounts of iron, manganese, rubidium, tin, lead, zinc, copper and silver have sometimes been found in inclusions in quartz specimens collected in mineralized districts (Czamanske et

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al., 1963 ; Thompson et al., 1980 ; Alderton et al., 1982 ; Chrysosoulis and Wilkinson, 1983). The major anions are Cl^- and according to the bulk atomic composition and the pH and Eh values in trapped solutions, various species of the C-O-H-S system (e.g. SO_4^{2-} , HS^- , HCO_3^- , CO_3^{2-}). Amongst minor anions, one may note bromide (Grappin et al., 1979).

Until recently, most of the determinations of the chemical composition of inclusion fluids were performed by destructive methods, with noticeable exception of microthermometry. The extraction of volatiles is achieved under vacuum by crushing the samples or heating them until the decapitation of inclusions occurs. Analytical determinations were then performed either by mass spectrometry (Touray and Lantelme, 1966 ; Touray, 1968) or by gas chromatography (Mironova et al., 1974 ; Cuneo et al., 1976 ; Behar and Pineau, 1979 ; Kreulen and Schuiling, 1982). Dissolved salts are extracted after crushing the samples by leaching with water. Any sensitive method for determining trace elements in solution may be used. Special reference has to be made to Neutron Activation Analysis (Czamanske et al., 1963 ; Grappin et al., 1979) permitting one to detect various trace elements in liquid inclusions (Touray, 1976) and to the recently introduced Atomic Emission Spectrometry with an I.C.P. source (Thompson et al., 1980).

The interpretation of the chemical data obtained by such methods brings up a number of problems related firstly to the very low quantities of elements that one has to detect (pollutants, contamination from solid inclusions), secondly to artefacts related to the extraction procedure (thermal decomposition of volatile compounds, loss of ions by absorption on the inclusions walls) and, last but not least, to the mixing of the contents of inclusions with different chemical compositions. This last point explains why people endeavoured to use the various existing microprobes for analyzing fluid inclusions. As discussed in the last part of this paper, most of the attempts had only limited success until the introduction of the earlier Raman microprobes in the United States (Rosasco and Simmons, 1974) and in France (Delhaye and Dhamelincourt, 1975). These non-destructive molecular microprobes proved remarkably adapted for analyzing gases under pressure (several bars or tens of bars) and for permitting several other determinations on fluid inclusions.

Non-destructive analysis of fluid inclusions by microthermometry

Examined over a large range of temperatures, fluid inclusions hosted in sparingly soluble minerals are systems of constant composition and volume in which phase transitions (vaporization, melting etc...) occur at measurable temperatures. Accordingly, the determination of phase transitions at low and high temperatures between -200 and +600°C respectively, (during freezing and heating runs) on a dual purpose freezing and heating stage (Roedder, 1963 ; Poty et al., 1976) is a powerful non-destructive method for studying fluid inclusions with reference to appropriate

P-V-T-X phase diagrams. This type of approach is named microthermometry. Basically, two types of information may be derived from microthermometrical data :

- The "model composition" of the inclusion fluids, with reference to binary or ternary chemical systems.

- The bulk density of the inclusion fluids, as a basic information for determining the temperature and/or the pressure at the time of trapping.

Gaseous system with one, two or more components

The approach is easily illustrated for a one-component system. An inclusion made of pure CO_2 will be characterized by a melting temperature at -56.6°C, the triple point for carbon dioxide. From the temperature of homogenization, i.e. the temperature at which the phase transition $(\text{L} + \text{V}) \rightarrow \text{L}$ or $(\text{L} + \text{V}) \rightarrow \text{V}$ occurs, one may easily derive the bulk density of the inclusion with reference to P-T diagram of CO_2 (for example, Angus et al., 1973).

The situation is a bit more complex for a non-ionic binary mixture, such as CO_2 - CH_4 system. However, with a set of two parameters out of three possible (respectively TmCO_2 the temperature of melting of CO_2 , ThCO_2 the temperature of homogenization of CO_2 and Df the degree of filling of the inclusion at the temperature of melting of solid CO_2) both X CH_4 and the bulk density may be derived (Hollister and Burruss, 1976 ; Swanenberg, 1979 ; Burruss, 1981a ; Crawford, 1981 ; Heyen et al., 1982).

For ternary or higher-order multicomponent fluids in the C-O-H-N-S system, the measurements of TmCO_2 and ThCO_2 are insufficient to derive the molar volume and composition. It is necessary to know a state equation reproducing the solid-liquid-vapor equilibria. Then, from a measurement of temperatures of phase transitions and knowing the composition with the help of Raman data for example, it is possible to deduce molar volume.

Saline solutions

Trapped saline solutions are usually modeled by the known NaCl - H_2O isobaric diagram : from the depression of the freezing point of ice (or of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ on the "hydrohalite branch"), one may infer the "equivalent salinity" of the inclusion (Roedder, 1963). The determination of the eutectic temperature is a check of the validity of the model. Actually melting initiates, in a number of cases, at temperatures below -20.8°C, the eutectic temperature of the binary NaCl - H_2O system (Potter et al., 1978). A model that takes into account a ternary or a more complex system is then required (e.g. the NaCl - CaCl_2 - H_2O system).

Complex system

In "complex" inclusions where water, salts and gases are present (actually a very common case in nature...) noticeable complications arise from the formation of mixed clathrates in which gas molecules are enclosed in voids within a host crystal lattice of H_2O (Burruss, 1981a). Their presence, when they are associated with ice, may remain unsuspected during freezing runs however their formation modifies significantly the composition and molar volume of the gas phase and hence is a source of errors, as discussed further.

In conclusion, one must emphasize that fluid inclusions are delicate objects of small size, usually of variable composition from one to another in the same crystal, which permit appreciating the importance of micro-analytical techniques for determining their chemical composition.

Raman microspectroscopy

Raman effect

The interaction between a molecule and a monochromatic (laser) beam gives rise to many kinds of phenomena. So the illuminated molecule can reflect, absorb, transmit or scatter, in all directions of the space, the photons of the exciting radiation (Etz, 1979 ; Delhaye and Merlin, 1975).

The diagram in figure 1 presents the different vibrational transitions possible :

- The infrared absorption, the incident photons have an energy $hc\bar{\nu}_0$ equal to $\Delta E = hc\bar{\nu}_i = E_1 - E_0$ and through absorption, the vibrational energy of the molecule can increase by $hc\bar{\nu}_i = hc\bar{\nu}_0$.

- The scattering, the incident photons have an energy $hc\bar{\nu}_0$ very much higher than ΔE . The common use is to consider that initially the molecule is brought to an unstable temporary high level and subsequently comes to one of permitted vibrational levels by scattering a photon in any direction. When this photon has a same energy $hc\bar{\nu}_0$ as the incident one, the scattering is elastic and named Rayleigh scattering. When this photon has an energy different $hc(\bar{\nu}_0 \pm \bar{\nu}_i)$ from the incident one, the scattering is inelastic and named spontaneous Raman scattering ; the photon may either gain energy (Raman anti-stokes, $hc(\bar{\nu}_0 + \bar{\nu}_i)$) or lose energy (Raman stokes, $hc(\bar{\nu}_0 - \bar{\nu}_i)$).

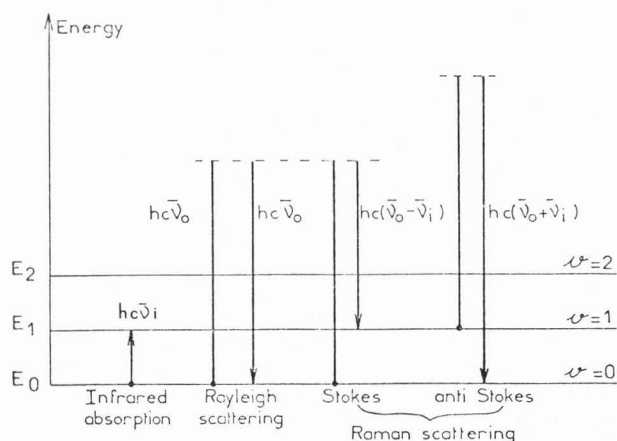


Figure 1 - Diagram illustrating the vibrational Raman effect. One electronic state with vibrational splittings is displayed.

If the incident photon energy is high enough so that other electronic states are involved, other inelastic scattering processes occur such as fluorescence. This fluorescence is a light emission with a frequency different with this incident one occurring over a broad band in the Stokes

and anti-stokes Raman spectrum. As spontaneous Raman effect is very weak, less than 10^{-3} of the scattered total photons are concerned, the laser induced fluorescence is sometimes strong enough to interfere with Raman data which cannot be easily interpreted.

The $\bar{\nu}_i$ Raman frequencies, differences between the incident and scattered radiation frequencies, are independent of the chosen exciting line. They represent the frequencies of vibration modes of polyatomic structures present in the excited sample. They are expressed in wavenumbers $\bar{\nu}_i = \nu_i / c$ (cm^{-1}) and directly read, as shown by figure 2, on the recorded spectrum whose origin is the $\bar{\nu}_0$ frequency and which consists of the anti-Stokes lines ($\bar{\nu}_0 + \bar{\nu}_i$) and the Stokes lines ($\bar{\nu}_0 - \bar{\nu}_i$), these last ones are normally studied because of their greater intensities.

The Raman spectroscopy is a molecular vibrational spectroscopy. It is complementary to the infrared spectroscopy.

A Raman spectrum, even incompletely interpreted, permits one to characterize and identify polyatomic chemical species inorganic as well as organic or biological, and to give information on their structure in all phases of matter, on the chemical bonds and on the interaction between molecules.

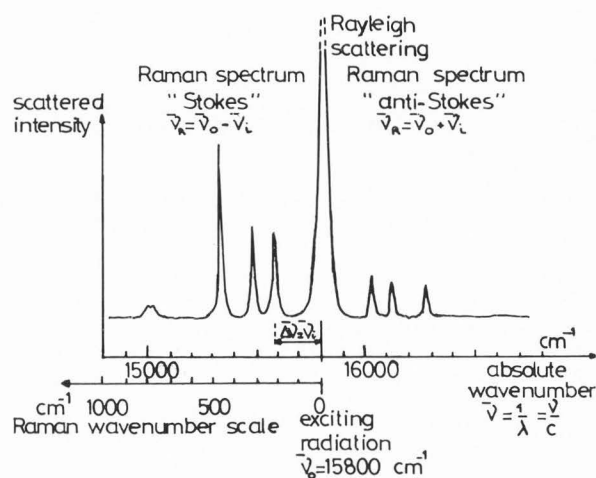


Figure 2 - Schematic representation of a Raman spectrum excited with the red line of an He-Ne laser, $\lambda_0 = 632.8 \text{ nm}$ ($\bar{\nu}_0 = 15800 \text{ cm}^{-1}$).

Raman microprobes

The main results presented below were obtained with the M.O.L.E. (Molecular Optical Laser Examiner) Raman microprobe realized by Delhaye and Dhamelincourt (1975) (Dhamelincourt, 1979a, 1982).

The principle of the M.O.L.E. as a micro-Raman spectrometer is as follows. A laser beam (monochromatic exciting radiation) is focused onto the sample with an objective of an optical microscope incorporated on the instrument. This same objective also collects the scattered light at the focal point. The scattered light is sent

onto the entrance slit of a double monochromator equipped with two concave holographic gratings. At the exit of this optical filter, there is a detector consisting of a multiplier followed by a photon counter and a chart recorder or a micro-processor (figure 3).

The M.O.L.E. also permits "mapping" the distribution of a given species on the surface of studied samples (Delhaye and Dhamelincourt, 1975 ; Dhamelincourt, 1979a). In this case, the detector is an intensifier phototube followed by a low light level TV camera and a monitor. But this capability is not used for inclusion studies.

The most important features of this analytical instrument are :

- The study "in situ" of samples without more preparation than for an optical observation or for microthermometric studies. The routine use of X160 objective requires well doubly polished samples and a depth of a maximum 100 μ m, in the mineral, for the studying inclusions. If that cannot be the case, it is possible to use other objective with lower magnification and long working distance. It is also better not to stick the sample on glass slide to avoid the interference of the glue Raman spectrum or/and its possible fluorescence with the Raman spectrum of the sample.

- A spatial resolution of few μ m, since the minimum diameter of the focal spot for a gaussian distribution of laser beam is given by the relation (Dhamelincourt, 1979a) $d_0 = 4\lambda_0/\pi\alpha$ and equal to about 1 μ m when the exciting line has a wavelength $\lambda_0 = 0.5\mu$ m and the used objective a numeral aperture $\alpha = 0.95$. Then it is possible to analyse inclusions separately and even the different phases of a single inclusion.

- The presence of an adjustable image field iris diaphragm placed in the image plane of the sample. It permits the rejection of light (from matrix or fluorescence) which does not originate from the focal point, therefore the decreasing of the spectral background level and the monitoring of the depth resolution of the probe (Dhamelincourt, 1979a, 1982 ; Adar and Clarke, 1982).

- The non-destruction of the samples during the analysis except for some highly coloured samples.

At this time, there have been developed several different types of Raman microprobes with plane holographic gratings. With these instruments, it is possible to use a large range of laser excitation wavelengths. One type is a micro-Raman spectrometer with a photomultiplier and a photon counter as detector (U1000 with microscope by JOBIN-YVON ; RTI 30 with microscope by DILOR). Another type is a micro-Raman spectrograph, with an intensified photodiode array as detector. Such a device permits one to explore, simultaneously, a large spectral range from 50 to more than 2000 cm^{-1} according to the chosen spectrograph dispersion and recording the Raman spectra more rapidly than with a scanning spectrometer : MICRODIL 28 and OMARS 89 with microscope by DILOR (Delhaye et al., 1982), (Milanovich et al., 1982) (Steinbach et al., 1982), MICRAMATE grafted onto TRIPLEMATE by SPEX (Purcell and Etz, 1982).

Applications of the Raman microprobe to fluid inclusions

Main applications fall under four headings of differing importance, relative to the partial chemical analysis of aqueous solutions, the mineralogical determination of trapped solids, the bulk chemical analysis of gases and liquefied gases and the identification of non-aqueous liquids.

Aqueous solutions

CO_2 , H_2S and even CH_4 may be detected as dissolved species in the aqueous phase when they are present at elevated pressure in the gas bubble (figure 4). Clathrates crystallized by cooling can also be analyzed at their temperature of stability. On the other hand, polyatomic ions such as NO_3^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} or UO_2^{++} are easily detected in aqueous solutions by Raman spectrometry with detection limits in the range 200-1000ppm (Dubessy et al., 1982b). Due to various reasons (such as the relatively low value of the Raman scattering cross section of HCO_3^- , $\text{pH} > 10.5$ not existing in the nature, required for CO_3^{2-} dominance with respect to HCO_3^- , low abundance of NO_3^- in natural solutions), only SO_4^{2-} has been detected in fluid inclusions (Rosasco and Roedder, 1979 ; Dubessy et al., 1983a).

Determining sulfate concentrations requires a normalization to the water content. As the Raman spectrum of water is salinity sensitive, calibration lines have been established for solutions saturated with respect to NaCl. Using appropriate standards, very accurate determinations may be performed (figure 5) which were verified by comparing primary inclusions in halite presently crystallizing in a salt marsh (Raman microprobe analysis) and the mother brine (chemical bulk analysis, table 1). Though limited to the study of inclusions in rock salt or to hypersaline inclusions with daughter halite crystals and belonging to the NaCl-H₂O system, the determination of sulfate concentrations in fluid inclusions has large potential applications for understanding the geochemical behavior of sulfur and calcium as well, with reference to the solubility product of anhydrite (Dubessy et al., 1983a).

For physical reasons, monoatomic ions, which are the great majority of dissolved species in trapped solutions, give no Raman scattering spectra. Only qualitative identification of specific hydrates, after freezing, may reveal the presence of Na^+ , Ca^{++} , Mg^{++} , K^+ and Cl^- (Dubessy et al., 1982a).

Solids

The study of minerals by Raman scattering spectrometry has been currently undertaken as an advanced topic in the field of physics of minerals (Farmer, 1974 ; Karr, 1975, for example). In fact, any solid has a Raman spectrum which is characteristic of its structure, its orientation, its composition and depends upon the polarization of the incident illumination.

In this field, investigations utilizing the M.O.L.E. aim at two principal goals :

- The identification of samples of small size "in situ" in or on polished slides or sections or in dust. This identification is made by

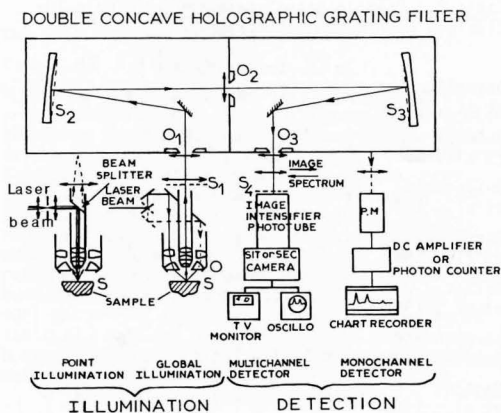


Figure 3 : Diagram of Raman microprobe microscope (M.O.L.E.) developed at CNRS-Lille, illustrating modes of sample illumination and signal detection. From Dhamelincourt (1979b).

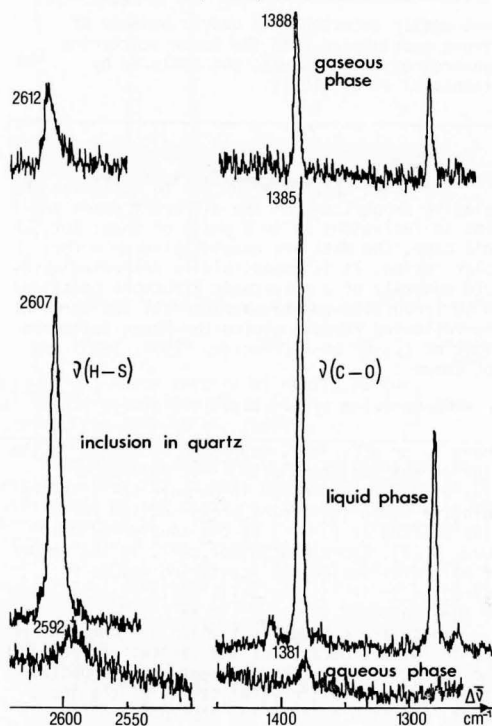


Figure 4 : Raman spectra in a single inclusion of CO₂ and H₂S in gaseous, liquid and aqueous phase. From Bény et al. (1982).

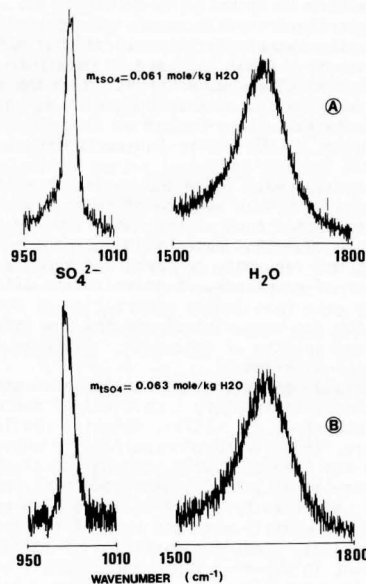


Figure 5 : Raman spectra of sulfate ($\nu_1 A_1$) and water ($\nu_2 A_1$) from A) prepared solutions and B) the aqueous phase of a natural inclusion. From Dubessy et al. (1983a).

Table 1 : Molality of sulfate in fluid inclusions. Sample A. Comparison with the brine sampled in the same pan. From Dubessy et al. (1983a).

Samples	Raman analysis		Chemical analysis	
	$\frac{I(\text{SO}_4^{2-})}{I(\text{H}_2\text{O})}$	$t\text{SO}_4$	A	σ
1	3.89	0.172		
2	3.80	0.168		
INC 3	3.71	0.165	0.168	0.002
4	3.82	0.169		
5	3.80	0.168		
F.B.n.f.	3.82	0.169		0.174
f				0.172

INC = inclusion, F.B. = free brine, n.f. = non filtered, A = average, σ = standard deviation.

comparison of the spectrum of the unknown compound with reference spectra. Bands characteristic of polyatomic groups are in well-known spectral ranges and permit one to recognize sulfate, nitrate, carbonate, chromate, silicate...

- The structural characterization of solids. Raman spectroscopy is sensitive to the local symmetry of the polyatomic groups, to their organization, to their orientation. So polymorphs such as calcite-aragonite, brookite, anatase-rutile, tetragonal GeO₂-hexagonal GeO₂ can be distinguished (Bény et al., 1980). It is also possible to follow with the help of the Raman spectra, the evolution of proportions of different elements in

compounds such as spinels (Malézieux et al., 1983). Polarization measurements can be realized to obtain the symmetry of the vibrational mode giving rise to a Raman band and to determine the Raman data can give some information on the degree of organization of compounds such as carbonaceous materials (Bény-Bassez et al., 1981; Rouzaud et al., 1983; Bény-Bassez and Rouzaud, 1985).

To easily reach these two goals, it would be interesting to have a very complete file of Raman reference spectra such as the ASTM file for X-ray diffraction. But this Raman file does not exist and it is not very easy to carry out because of the number of compounds, of polarization effect, which may give rise to the observation of several spectra for the same mineral and the low intensity of Raman spectra of numerous minerals such as micas or sulfides.

In fluid inclusions, carbonates give good spectra, easy to identify: calcite and nahcolite (Dhamelincourt et al., 1979), dolomite (Guilhaumou et al., 1981). Similarly, sulfates: anhydrite (Rosasco and Roedder, 1979), gypsum and glauberite (Dubessy et al., 1983a) have sometimes been detected. As shown by figure 6, it is also possible to differentiate with the help of the low frequency Raman bands two particles of solid sulfur present in H₂S-rich fluid inclusions: one of them is crystallized S₈ (low frequency Raman bands are present), the other is a quenched droplet of liquid sulfur which solidified as amorphous sulfur (no low frequency bands) (Bény et al., 1982). Sulfur and carbon (Guilhaumou et al., 1984) are probably amongst the most interesting trapped solids, because they act as buffers on the fugacities of O₂ and S₂ inside the inclusions which in turn determine the composition of the trapped volatiles at equilibrium (Touray and Guilhaumou, 1984).

Gases

Main analytical results. The microanalysis of "simple gases" is now routinely performed on fluid inclusions with Raman microprobes. In table 2 are collected the different gases presently detected by this technique. The outstanding feature of this list is that all the quoted gases are actually present in inclusions at room temperature. Far more exhaustive tables have been compiled in the early seventies, from a compilation of analyses of gases evolved on heating or crushing (Roedder, 1972). They indicate approximately the same compounds. However, several questions remained about the presence of nitrogen, hydrogen and carbon monoxide in the absence of evidence by non destructive bulk method. One could suspect that nitrogen resulted from atmospheric contamination, hydrogen was an artefact related to the reduction of water in the extraction device and CO the product of the reduction of CO₂ in carbon-bearing inclusions.

But, when these gases and O₂ (table 2) also are detected "in situ" by Raman microspectroscopy, there is no doubt about their existence in the studied inclusions. The spectrum obtained from the inclusions is always compared with the spectrum recorded at the same probe depth, in the matrix near the inclusion. This comparison permits one to discard any possible contribution of atmospheric nitrogen.

Table 2: "simple gases" detected in single inclusions with Raman microprobe.

	N ₂	CO	O ₂	CO ₂	H ₂	SO ₂ *	H ₂ S	CH ₄	C ₂ H ₆
Dhamelincourt et al., 1979	x			x			x	x	x
Dubessy et al., 1980	x		x		x				
Guilhaumou et al., 1981	x			x					
Bény et al., 1982				x			x		
Salot et al., 1982								x	x
Bergman and Dubessy, 1984		x		x					
Bastoul et al., 1983	x			x				x	
Clochiatti et al., 1983				x		x			
Guilhaumou et al., 1984				x			x	x	

* not easily detectable in quartz because of strong overlapping with the Raman scattering spectrum of this mineral, but analyzed by Clochiatti et al. (1983).

The Raman spectra allow one to determine the relative proportions of the different gases present in inclusions or in a phase of them. But, in this case, the data are quantitative only for molar ratios. It is impossible to determine absolute quantity of a polyatomic structure contained in an irradiated volume, because all the terms of the following formula giving the Raman scattered light at $(\bar{\nu}_0 - \bar{\nu}_i)$ cm⁻¹ (Placzek, 1934, 1962) are not known:

$$\Phi_i = dE(\bar{\nu}_0 - \bar{\nu}_i) = \sigma(\bar{\nu}_0 - \bar{\nu}_i) N_i(V) I(\bar{\nu}_0) \Omega_c \quad (1)$$

where Φ_i or $dE(\bar{\nu}_0 - \bar{\nu}_i)$, expressed in Wcm⁻³, is the flux of the radiation with $\nu_0 - \nu_i$ wavenumber, $\sigma(\bar{\nu}_0 - \bar{\nu}_i)$ or σ_i , expressed in cm²mol⁻¹st⁻¹, is the relative Raman scattering cross section for a line emitted at $(\bar{\nu}_0 - \bar{\nu}_i)$ by the considered molecule, $N_i(V)$, expressed in mol.cm⁻³, is the number of molecules inside the scattering volume V , Ω_c , expressed in st, is the solid angle of collection of the scattered light.

These are Ω_c and $I(\bar{\nu}_0)$ which are unknown for the inclusions because of the various refractions and reflections at the different phase boundaries (e.g., air-crystal, crystal-cavity of the inclusions) and also because the absorption differs from one crystal to another.

However, it is possible to calculate the molar ratios of the species present in the studied fluid inclusion phase, because Ω_c and $I(\bar{\nu}_0)$ have the same values in this case for a same analysis. For example, in a fluid inclusion gas phase, three species, i, j, k have been detected, the formula (1) gives for any species:

$\Phi_i = \sigma_i N_i(V) \cdot I(\nu_0) \Omega_c$, $i = 1 \text{ à } n$ therefore the mole fraction X_i of species i :

$$X_i = N_i(V) / \sum_j N_j(V) = (\Phi_i / \sigma_i) / (\sum_j \Phi_j / \sigma_j)$$

Φ_i and Φ_j are proportional to the intensity A_i and A_j of the Raman lines of species i and j with the Raman scattering cross sections σ_i, σ_j , whose values are found in the literature. The molar ratios and the relative proportions of the three components can be calculated, since A_i, A_j, A_k are the integrated intensities measured on the recorded Raman spectra with the help of a planimeter with a precision of about $\pm 1\%$. The spectral responses of the instrument are still not corrected because the used photomultiplier (RCA 31034A or A02) has a flat response curve on the considered spectral range and also the compared results in a same work are obtained with the same spectrometer.

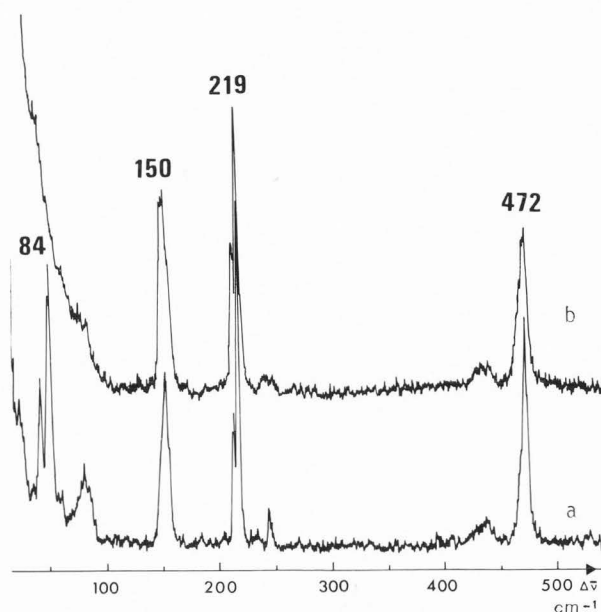


Figure 6 : Raman spectra of native sulfur, a) in a crystallized state, b) in an amorphous state. From Bény et al. (1982).

The Raman scattering cross sections are generally known for "simple gases" and depend on the wavelength of the exciting line used to obtain the Raman spectra by a term in $(\nu_0 - \nu_i)^4$ (Penney et al. 1972 ; table 3 from Fenner et al., 1973 ; Schrötter and Klöckner, 1979). But the authors do not give all the same cross section values, so it would be interesting to come to a normalization of these values at least for the fluid inclusion studies and to examine the influence of the density on them.

Equation (1) and table 3 show that it is possible to detect a smaller amount of CH_4 than N_2 . On the other hand, the detection of "simple gases" requires a certain minimum pressure in the inclusions because of the very small analyzed volume (a few cubic micrometers typically) therefore the very few excited molecules. With the M.O.L.E., for N_2 , an order of magnitude of the minimum pressure is about 1 bar when the spectra are recorded

with 1s of photon counting integration time, $20\text{cm}^{-1}/\text{mn}$ scanning speed, $500\text{ }\mu\text{m}$ for the slits and about a laser power of 30mW at the sample. It is possible that the detection limit could be lowered by analyzing the sample at longer integration time. Finally one may note that high pressures in the inclusions are probably at the origin of the frequency shifts of gas Raman lines often observed during inclusion studies (table 3, figure 4) (May et al., 1959). Some results given by Rosasco et al (1975) show that it should be interesting to realize more experiments in this field in order to obtain more information from the Raman spectra on pressure in the inclusions.

Table 3 : Relative Raman scattering cross sections for principal lines of important gases, for an exciting line $\lambda_0 = 514.5\text{nm}$.

Molecule	Frequency (cm^{-1})	Relative cross section σ
NO	1877	0.3 - 0.5
N_2	2331	1.0
CO	2145	1.0
O_2	1556	1.2
CO_2	1388	1.5
N_2O	1285	2.2
H_2	4161	2.4
H_2O	3652	2.5
NH_3	3334	5.0
SO_2	1151	5.4
H_2S	2611	6.4
CH_4	2914	6 - 8

Fluid inclusions and chemical equilibria in the C-O-H-N-S system. Two basic problems arise from the quantitative analysis of inclusion fluids belonging to the C-O-H-N-S system :

- Does the fluid composition measured over a low temperature range ($-200, +30^\circ\text{C}$) correspond to chemical equilibrium?
- What is the effect of cooling on the evolution of the molar volume and composition or, in other words, do these parameters measured in the low temperature range differ significantly from the value of these parameters in the high P-T conditions of trapping?

Some evidence shows that non-chemical equilibrated fluid compositions exist at room temperature.

$\text{H}_2\text{-O}_2$ fluids. Metastable gas mixtures have been observed in quartz samples from the uranium occurrence of Rabbit Lake (Saskatchewan, Canada) in which are present two-phase water bearing inclusions with a gas phase made up of molecular oxygen, hydrogen and minor nitrogen (Dubessy et al., 1980). Figure 7 presents the Raman bands corresponding to the vibrational stretching mode of O_2 , N_2 and H_2 and also for H_2 the Raman bands (Q_1) due to the rotational transitions. With respect to the quality of the Raman spectra (figure 7) and assuming a detection limit in the range 0.5 to 1 bar, one may infer that, at room temperature, the partial pressures of oxygen and hydrogen are respectively as high as several tens of bars and five to ten bars.

These figures are clearly in contradiction with thermodynamic constraints arising from the

value at 25°C of the dissociation constant of water which forbids, at equilibrium, the coexistence of detectable amounts of O_2 and H_2 . Additionally, in geologic fluids buffered by volatile rock interactions, one may recall that equilibrium oxygen fugacities are always very low, even at high temperature. Accordingly an oxygen partial pressure higher than ten bars cannot result from water-rock equilibria. The proposed explanation (Dubessy et al., 1983b) is the radiolysis of water by alpha irradiation, possibly before the trapping of fluids.

$H_2S-CH_4-CO_2-H_2O$ fluids. A discussion of the stability of H_2S-H_2O -carbon bearing inclusions has been performed at 25°C on a $\log f_{O_2} - \log f_{S_2}$ diagram. Under equilibrium conditions, methane may be an additional component but CO_2 cannot (Touray and Guilhaumou, 1984). Accordingly, complex inclusions with H_2S , CH_4 , CO_2 , H_2O and carbon which have been described in calcite cements from oolitic limestone collected in deep boreholes (Guilhaumou et al., 1984) are not at chemical equilibrium.

In conclusion, these results show that fluid inclusions of the C-O-H-N-S system are probably quenched equilibrium mixtures at an unknown temperature of their natural cooling history.

Concerning the second question, chemical thermodynamic calculations, carried out on inclusion fluids of the C-O-H system originating from chemical processes, have shown that the V-X properties determined over the low temperature range do not differ more than a few percent from their values in the high P-T conditions of trapping for which chemical equilibrium is assumed (Dubessy, 1984). These thermodynamic simulations assume chemical equilibrium during the cooling path of the inclusion fluid until 300°C. These theoretical results demonstrate that fluid inclusions can be used to model some chemical equilibria in the C-O-H-N-S system and estimate the oxygen fugacity, which is an essential parameter in the understanding of some ore deposition (Dubessy, 1984).

Non-aqueous liquids

In fluid inclusions there have already been detected some non-aqueous liquids such as aliphatic or aromatic hydrocarbons (Guilhaumou, 1982) (figure 8). These are not always easy to specify, however it is possible to distinguish the two kinds of hydrocarbons with the help of the wavenumbers of their characteristic Raman bands. Nevertheless pentane has been precisely identified by Dele-Dubois et al (1980) in inclusions in emeralds. Sometimes it is impossible to record a spectrum of these non-aqueous liquids because of their intrinsic fluorescence and/or their fragility under the laser beam, which allows one to say only that there is a complex mixture of hydrocarbons probably similar to natural mineral oil in the studied inclusion and nothing else.

The complementary nature of optical microscopy, microthermometry and Raman microprobe investigations

For careful optical examinations at high magnifications (objective lens x160 without immersion oil), it is necessary to doubly polish the studied

slides or sections. These are used, without any other preparation, to perform the microthermometric and Raman studies. Presently, in routine studies, freezing runs are performed before any Raman microprobe determinations in order to choose, from their microthermometric parameters, fluid inclusions representative of the paleofluid history. Furthermore, microthermometry is also performed after Raman analysis to ensure that no modification occurred under the laser beam as noticed by Rosasco et al. (1975) in a hydrocarbon mixture due to high irradiance level.

Apart from these basic rules, the complementary nature of microthermometry and Raman microprobe may be understood in two ways. Firstly microthermometry assumes that the phases, for which temperatures of phase equilibria are measured, are known. In some circumstances, a micro-Raman characterization is absolutely necessary. On the other hand, in the non-aqueous part of fluid inclusions from C-O-H-N-S system, it is better to derive the chemical composition from Raman-microanalysis and to use it for determining the molar volume of this part from temperature of liquid-vapour equilibrium.

Various Raman determinations have been performed at low temperature. The first application is to concentrate by solidification a gas that is present as a minor component and to identify it. For example, in methane-rich inclusions from quartz collected in the French Alps near Barcelonnette (Barlier et al., 1973), minor amounts of CO_2 have been identified from the analysis of small solids that disappear in the range of -92 to -103°C (Dubessy et al., 1984). Another application presently qualitative, is the determination of the various clathrates (e.g. the H_2S bearing clathrate, Bény et al., 1982) whose presence reveals traces of water (Guilhaumou et al., 1984) or salt hydrates that appear on freezing. On figure 9 are given the Raman scattering spectra obtained for different hydrates from frozen solutions of known composition. Three out of these spectra, respectively for $NaCl \cdot 2H_2O$, $CaCl_2 \cdot 6H_2O$ and $KCl \cdot MgCl_2 \cdot 6H_2O$, have been recorded from frozen inclusions (Dubessy et al., 1982a). Such phase determinations may allow a qualitative identification of the dissolved cations, especially calcium and magnesium. The detection of K^+ appears more difficult, it requires the formation of carnallite because no hydrated potassium chloride is known. On the other hand, this type of identification would facilitate the microscopic investigations. Theoretically, with the help of the ternary diagram $NaCl-CaCl_2-H_2O$ or a section of the quaternary diagram including $MgCl_2$ at the proper value of $CaCl_2/MgCl_2$, one may deduce the bulk composition of the brine from the last melting temperatures of ice and $NaCl \cdot 2H_2O$ (Crawford, 1981). However, the optical distinction of ice from hydrohalite is not always straightforward and a Raman microprobe outfitted with a freezing stage permitting the scanning of the sample would probably be of great help.

Two types of comparisons between microthermometric data and Raman microprobe determinations are of interest: firstly, a qualitative and quantitative explanation (in terms of chemical composition) of the phase behavior of gas-rich

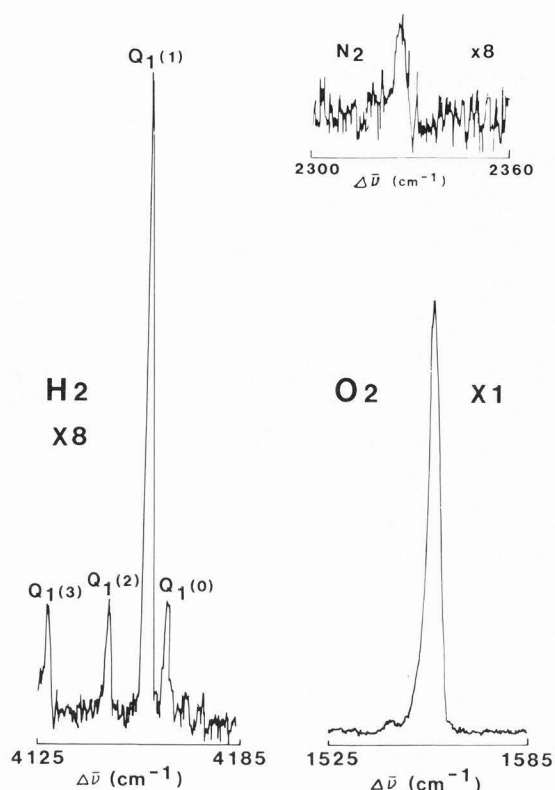


Figure 7 : Raman spectra of H_2 , O_2 and N_2 in a natural inclusion from the Rabbit Lake uranium ore deposit. From Dubessy et al. (1980).

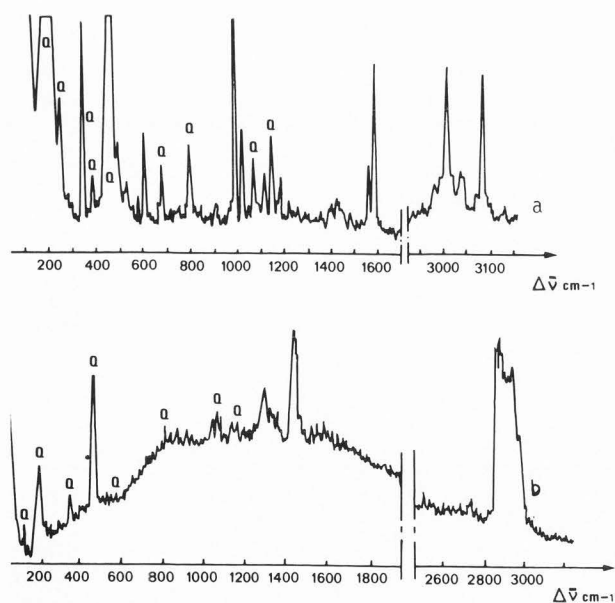


Figure 8 : Raman spectra of inclusions with liquid hydrocarbons. a) aromatic hydrocarbon, b) aliphatic hydrocarbon. From Guilhaumou (1982).

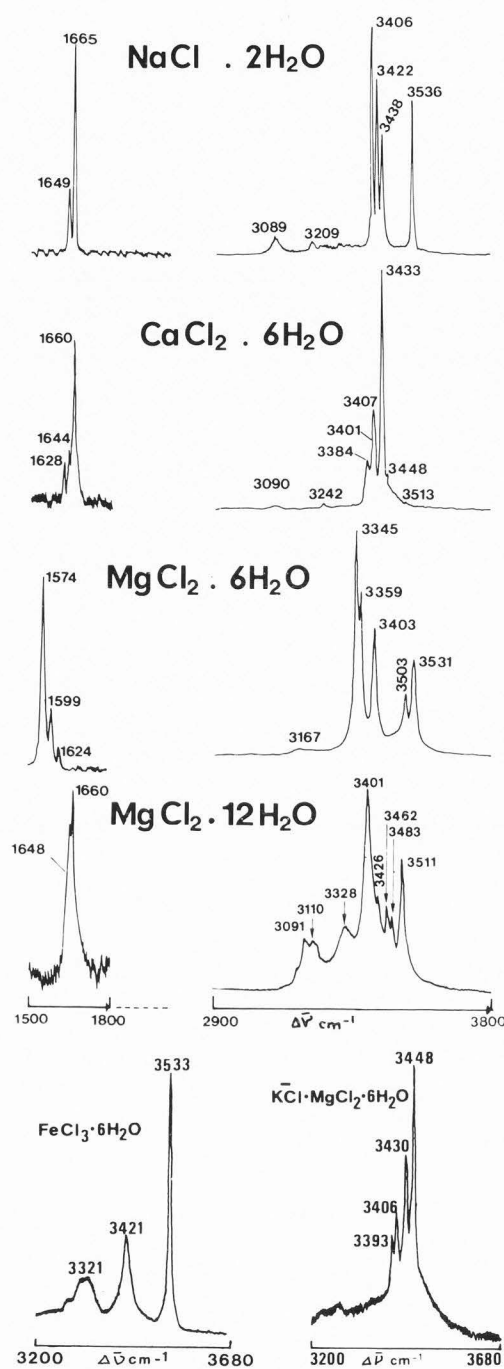


Figure 9 : Raman spectra of various hydrates at -170°C . From Dubessy et al. (1982a).

inclusions at low temperature and secondly, a comparison of chemical data obtained by both techniques.

The first approach may be illustrated by the behavior at low temperatures of inclusions representative of the system N_2 - CO_2 as synthesized in figure 10. Both composition and phase behavior of N_2 - CO_2 inclusions have been determined on a set

of inclusions trapped in quartz and dolomite. Therefore it was possible to depict, for various compositions, the behavior of N_2 - CO_2 inclusions on cooling and subsequent heating (Guilhaumou et al., 1981) and to establish an empirical phase diagram at low temperature for N_2 - CO_2 system (Touret, 1982). At high nitrogen content ($X_{N_2} \geq 0.57$), solid CO_2 grown on cooling does not melt but is consumed by sublimation on further heating. Liquid nitrogen is always visible at very low temperatures and homogenization occurs in the range -151 to $-147^\circ C$ (critical temperature of N_2). For lower nitrogen contents, solid CO_2 grown on cooling melts at temperature significantly lower than the triple point of CO_2 (figure 10). A CO_2 -rich liquid is observed between -51 and $-22^\circ C$. Near the CO_2 end member, the liquefaction of nitrogen is not observed. The only indication of an extra component is a limited shift of the temperature of melting of solid CO_2 , with respect to pure carbon dioxide and a homogenization temperature very low for a pure system. This behavior may be compared with most observations on CO_2 - CH_4 inclusions for which the liquefaction of methane is not reported. However, the exact limit between freezing behaviors of type I and II is density dependent. In this respect, type I inclusions with nitrogen mole fraction lower than 0.5 have been found in quartz veins from Les Boudons, Cévennes, France (Bastoul, 1983). The second approach is also readily illustrated by the N_2 - CO_2 inclusions in which the nitrogen content is high enough (types I and II, figure 10). From a determination in flat inclusions of the volume fraction respectively occupied by liquid nitrogen and solid (or liquid) CO_2 at specified temperatures, and from the densities of these phases at same temperatures, the $N_2/(N_2+CO_2)$ ratio may be readily established (Guilhaumou et al., 1981). The agreement with Raman microprobe determination appears fairly good (figure 11). When the most volatile gas component fails to liquefy on cooling as commonly illustrated in CO_2 - CH_4 inclusions both composition and density may be derived from microthermometric investigations. Occasionally, contradictions arise when water is present, due to possible formation of clathrates in addition to ice and salt hydrates. In these compounds CO_2 is more easily sequestered than CH_4 . As a net result, the gas phase becomes enriched in methane which in turn lowers the melting temperature of CO_2 . In this situation, the composition derived from microthermometry will be clearly in error. Fortunately, clathrates are not always present at low temperatures. Due to kinetic reasons, these compounds may fail to nucleate with ice on cooling and forms on heating ("inverse double freezing", Collins, 1979; Ramboz, 1980). In this case the two methods will give compatible compositions.

Another example of the complementary nature of the two methods is the study of H_2S -bearing inclusions. H_2S has been detected in fluid inclusions by destructive methods (e.g. Rankin & Sheperd, 1978). However, it has been evidently shown to be a major component in fluid inclusions only from Raman microprobe analysis (Bény et al., 1981). It is now possible to give the "freezing

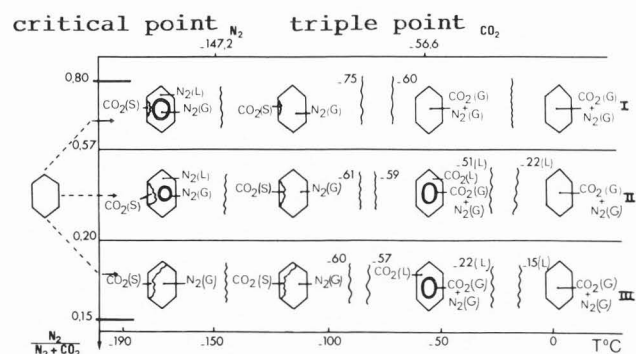


Figure 10 : Different observed cases in relation with the molar ratio $N_2/(N_2+CO_2)$, G, L, S : gas, liquid, solid. From Guilhaumou et al. (1981).

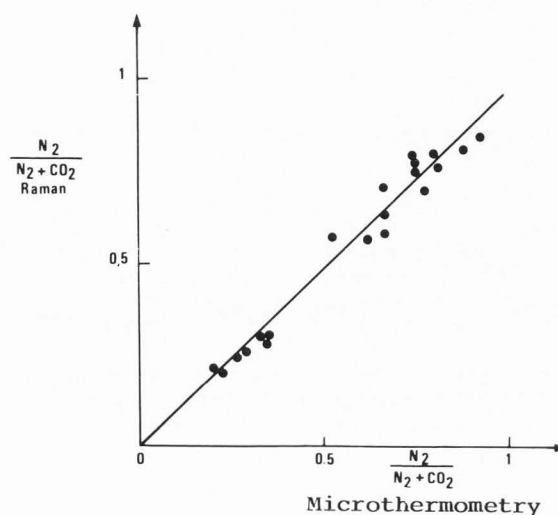


Figure 11 : Comparison between molar ratio $N_2/(N_2+CO_2)$ values measured by Raman spectroscopy and microthermometry. The trend has a slope of one. From Guilhaumou et al. (1981).

signature" of CO_2 - H_2S - H_2O and CH_4 - H_2S - CO_2 inclusions with reference to phase behavior, at low temperature, of inclusions of known composition (Touray and Guilhaumou, 1984). The presence of H_2S significantly depresses the melting temperature of CO_2 in CO_2 - H_2S melts (Bény et al., 1982). Homogenization temperatures are sometimes but not always higher than the critical temperature of CO_2 ($+31^\circ C$). The compositions of CH_4 - CO_2 - H_2S inclusions have been correlated with phase transitions observed by microscopy between -190 and $+25^\circ C$ (Guilhaumou et al., 1984). Two peculiarities were noticed : an immiscibility between a CH_4 -rich and a H_2S -rich liquid and the crystallization of solid H_2S melting between -99 and $-91^\circ C$. This determination derives from the Raman analysis of solids at low temperature ($-170^\circ C$) (figure 12). On the other hand, spectra characteristic of solids that disappear between -103 and $-92^\circ C$ in CO_2 - CH_4 bearing inclusions (CH_4 -rich) (Dubessy et al., 1984). It gives evidence that in inclusions of very different compositions (CO_2 - CH_4 and CO_2 - CH_4 - H_2S) the disappearance of solid CO_2 or H_2S may be

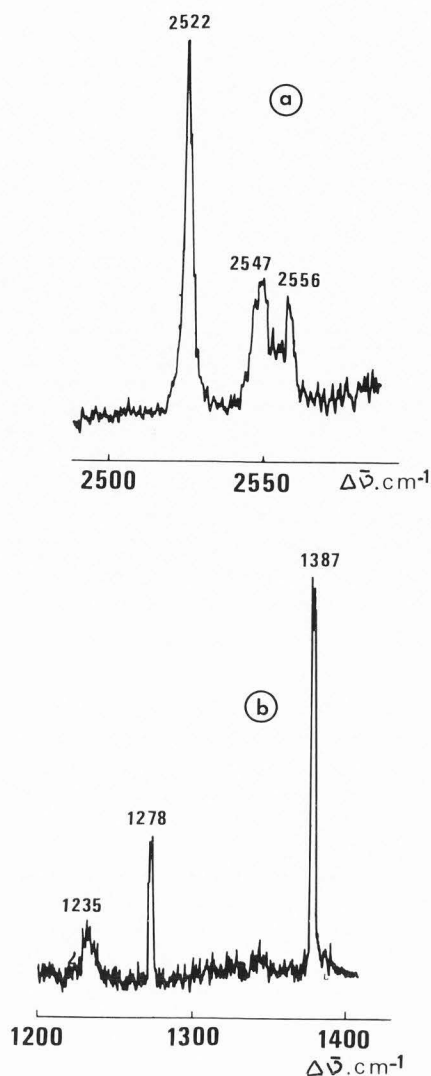


Figure 12 : Raman spectrum at -170°C of a) solid H_2S , b) solid CO_2 . From Dubessy et al. (1984).

observed in the same range of temperature during microcryoscopic runs. In this respect, the comparison of solubility curves (S+L+Vloci) in the binary system $\text{CO}_2\text{-CH}_4$ (Davis et al., 1954) $\text{CO}_2\text{-N}_2$ (Touret, 1982) $\text{CO}_2\text{-H}_2\text{S}$ (Sobocinsky and Kurata, 1959) and $\text{CH}_4\text{-H}_2\text{S}$ (Kohn and Kurata, 1958) confirms these observations. Raman microprobe determinations are hence essential for any qualitative interpretation of such freezing data.

Comparison of results obtained with the help of Raman microprobe and other microprobes

Besides the Raman microprobe, the determination of the composition of single inclusions may involve various types of microprobes, but these are generally of the sample-intrusive type. Their application to fluid inclusion studies are now reviewed.

Aqueous solutions

The determination of the composition of dissolved salts in single inclusions is today the

major analytical challenge we are faced with. From the Raman microanalysis, one may at least derive the sulfate content. Various destructive techniques, including laser probe mass spectrometry have been suggested to analyse composition of aqueous volumes (Deloule and Eloy, 1982 ; Eloy, 1984) or proton microprobe (Horn, 1983).

Electron probe microanalysis (Eadington, 1974 ; Chrysosoulis and Wilkinson, 1983) is at best semi-quantitative. After raising the temperature until decrepitation, precipitates are formed on the surface of the polished wafers under investigation. Owing to surface irregularities, the analysis of these precipitates is carried out using scanning.

The ion microanalyzer (Nambu and Sato, 1981) applied to inclusions kept frozen to prevent rapid evaporation in vacuum is probably the most promising technique for analyzing trapped solutions in the microgram range. However, this method is limited by inaccuracies caused by a rather bad signal reproducibility, the heterogeneity of the frozen solutions and also by the lack of the required spatial resolution due to the presence of daughter phases and/or trapped solids.

Solids

The determination of trapped and daughter minerals usually requires more sophisticated methods than microscopy alone. By optical means, only halite, sylvite, hematite and magnetite may be quickly identified. Tentative determinations of carbonates, anhydrite or chalcocopyrite are sometimes possible. For identification purposes, micromineralogical methods (Kalyuzhnyi, 1958) have sometimes been applied to "giant inclusions".

At the present time, scanning electron microscopy of opened cavities is a successful approach for identifying daughter minerals in small size inclusions (Metzger et al., 1977 ; Le Bel, 1979). The inclusions are exposed by fracturing or cleaving the host crystal. A preliminary SEM examination includes observations of number, proportion and morphologies of daughter crystals. Then a semi-quantitative analysis of selected crystals is performed by focusing the electron beam on them. The characteristic X-ray spectrum produced by electron bombardment is sensed by a solid state X-ray detector and displayed on the screen of a multichannel analyzer. By comparison with the spectra of known compounds run under the same conditions, mineralogical identifications are possible in most instances. General limitations and source of errors in the SEM techniques arise from interferences from surrounding minerals, difficulties in comparing the spectra of unknowns and standards and the inability to detect elements lighter than sodium, thus making it difficult to distinguish hydrates and oxides from carbonates. Finally, one has to underline the possible introduction of artefacts related to investigations under vacuum, because it is not certain that the studied species have not been modified.

The use of the Raman microprobe is very important for studying species with covalent bonding or ionic species with, at least, one polyatomic ion. But, that precludes any identification of alkali halides which are easily characterized by SEM (Nesbitt and Kelly, 1977) and which make up the majority of daughter minerals. However, by

Raman spectroscopy, it is always possible, during a routine analysis of trapped gases to try to determine a trapped solid. As Raman spectroscopy permits one to work "in situ" and is non-destructive, complementary SEM studies may be then performed. On the other hand, small sized solids adhering to the gas-water interface (i.e. native sulfur, Bény et al., 1982, figure 6) or in suspension (i.e. carbon, Guilhaumou et al., 1984), even invisible with the microscope, are identified with the Raman microprobe whereas it would be impossible by using SEM.

Gases

No other microanalytical tool appears to give equivalent results to the Raman microprobe. All gases can be easily detected except when their characteristic Raman lines are overlapped by matrix bands, for example, SO_2 is difficult to detect in inclusions in quartz. There are also problems when the matrix or some species in the studied inclusion are fluorescent. In this case, one cannot distinguish the Raman bands from the important background or above the noise. A possible solution to this problem would be to change the wavelength of the exciting laser radiation.

Non-aqueous liquids

Many of these non-aqueous liquids, presumably mixture of hydrocarbons, are often fluorescent and/or can be destroyed by the laser beam. However, one may attempt to record and interpret their Raman spectra.

Another method, infrared microspectroscopy, could theoretically give interesting information. Some experiments have been made with the Nanometrics infrared microscope (Hausdorff and Coates, 1982) but the spectral resolution is presently not good enough.

Conclusion

Fluid inclusions are small cavities (1 to 100 μm in size) found in minerals and filled with fossil fluids testifying to ancient geochemical processes. The knowledge of the composition and the molar volume of these inclusion fluids is essential to retrace the chemical P-T conditions of rock formation. A single mineral may contain fluid inclusions of different origin, age and hence composition. Accordingly, the study of fluid inclusions requires microscopic analytical techniques.

Among these, Raman microspectroscopy has a paramount place. Recent developments of lasers and high quality optics have permitted the design of Raman microprobes providing non-destructive "in situ" analyses of microsamples such as fluid inclusions. In these, it is possible to determine the gas mole fraction, to identify most of the solid phases and to derive information on the liquid aqueous and non-aqueous phases. Raman microprobe analysis complements freezing data, permitting a more accurate determination of the molar volume of the trapped fluids. On the other hand, from thermodynamic data and chemical equilibrium formula, it has now become possible to calculate fugacities of gases and pressure-temperature relationships for entrapped volatiles in the C-O-H-N-S system.

To improve and complement the micro-Raman measurements, it would be of great interest to outfit the Raman microprobe with a freezing stage. This device would permit crystallization of gas compounds present in too small amounts to be detected as they are, and formation of salts hydrates allowing one to better use the phase diagrams $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ or $\text{NaCl-CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$ by identifying, for example, hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$).

After the very good and abundant results obtained using the earlier scanning monochannel Raman microprobes and recent improvements in the technology of photodetectors, a second generation of Raman microprobes has been designed. In such devices, the detector is an intensified photodiode array permitting one to explore simultaneously a large spectral range. Such multichannel Raman microprobes are now under development in various laboratories.

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Discussion with Reviewers

E.S. Etz : To achieve a spatial resolution of a few micrometers -as claimed- the physical/optical properties of the mineral specimen need to be ideal for inclusion studies. What are the critical factors determining the exact location and dimensions of the effective sampling volume ?
Authors : If a sample is very well doubly polished and the microscope adapted to the spectrometer has various appropriate objectives, the exact location of the interesting inclusion or inclusion phases is easy and realized as in optical microscopy. Sometimes there are problems when a gas bubble (especially when it contains much CO₂) moves during the observation in white light, which heats the sample ; there are two possibilities when the white light is switched off, either the bubble is as attracted by laser beam and the study can be made or the bubble moves because of the temperature variation and it is necessary to be patient and to succeed after several attempts in keeping the bubble under the laser beams. The critical factor determining the dimensions of the effective sampling volume is the curvature radius of the inclusion, because it turns the laser focal point into a focal segment whose length depends on this curvature radius.

E.S. Etz : In the analysis of daughter crystals found in brines, is there any evidence that laser-induced heating effects are less severe -for optically absorbing phases- due to effective heat transfer by the surrounding liquid ?

Authors : We have no exact evidence, that, in the case of multiphase inclusions, the laser-induced heating are less severe for optically absorbing trapped and daughter solids, but we have observed, for example, in S₈ bearing inclusions that there are some convection movements. The surrounding liquid causes the solid to move (whose recorded spectrum is really that of S₈).

E.S. Etz : With the developments of spectrographic/multichannel Raman microprobes spectra can be acquired more rapidly, thereby exposing the sample to much shorter period of laser irradiation. Are these instrumental developments likely to have a significant impact on the application of the technique to fluid inclusion studies, especially from the point of view of increasing the detection sensitivity and reducing the possibilities of laser-induced sample modification ?

Authors : Actually we may hope that the use of spectrographic/multichannel Raman microprobes will be interesting for the inclusion studies. As a spectral range, larger than 50cm^{-1} , is simultaneously monitored, each spectral element is analyzed during longer time than with a scanning device for a same whole analysis time, therefore the sensitivity must be better. With regard to the laser-induced modifications, we may also hope that they are reduced by using this type of Raman microprobes either because the power of the laser can be lowered since the sensitivity is better or only because the sample is not illuminated during the whole analysis time when accumulations are realized, actually one illumination period is followed by a dark period and the second recorded signal is subtracted from the first one for each accumulation to obtain the Raman spectrum.

P. Dhamelincourt : Could the authors comment on proposed future development of a "freezing-heating" stage especially designed to fit Raman microprobes ?

Authors : The future "freezing-heating" stage must be used to obtain various new data on natural or synthetic samples. It could permit one for example

- To characterize the solid phases such as clathrates, salt hydrates obtained from known composition mixtures.

- To follow the evolution of the Raman scattering cross section versus the temperature.

- To record Raman spectra of homogenized inclusions before decrepitation.

- To calibrate the Raman shifts of the bands characteristic of CH_4 , CO_2 , H_2S , $\text{CH}_4\text{-CO}_2$, $\text{CH}_4\text{-N}_2$, $\text{CO}_2\text{-N}_2$, $\text{H}_2\text{S-CO}_2$, ... versus the density and the composition of the inclusion fluids.

P. Dhamelincourt : The authors mention the difficulties in identifying alkali halides which are the major part of daughter minerals. Could they comment on the possible use of the LAMMA (Laser Microprobe Mass Analyzer) ?

Authors : There are two types of laser microprobes

- the LAMMA 1000 in which the plasma temperature is at about 8000°C , and

- the LPMS (Laser Probe Mass Spectrometer) (Deloule and Eloy, 1982 ; Eloy, 1984) in which the plasma temperature is between 20000 and 30000°C . The results obtained by Deloule and one of the authors (unpublished), with the help of the two microprobes, show that the identification of monoatomic ions is possible without any problem. However, at present, no quantitative data have been obtained because the plasma temperature is unknown whereas this parameter is essential to determine the ionization yields.

P. Dhamelincourt : Could the authors discuss in further detail, if possible in terms of sensitivity and speed of analysis, the prospects for quantitative analyses using multichannel Raman microprobes ?

Authors : We have performed only few attempts with a new multichannel Raman microprobe and compared the results with those obtained with the M.O.L.E. working for several years. The comparison has been made in terms of analysis time and signal/noise ratios but no quantitative analyses (giving, for example, the molar fractions of the various gases present in an inclusion) have been made by us. So it is difficult to answer the question. Actually, the sensitivity seems to be better with the multichannel device than the monochannel one for the same analysis time. We think also that the multichannel Raman microprobe is very good to obtain qualitative information rapidly on the various components of inclusions with the help of the large simultaneously monitored spectral range until 2000cm^{-1} , but that is at the expense of the spectral resolution which must be good to obtain quantitative results from very sharp Raman bands such as characteristic gas bands. So, to have quantitative data, it is necessary to record another spectrum on an appropriate spectral range.

E.S. Etz : In the Raman spectra of the vitrinite portions of coal (figure 8) the half width (i.e., the full width at half maximum, FWHM) of the band centered at 1600cm^{-1} is shown to vary with the sample reflectivity. What is the explanation for this observation ? How is the shape of the carbon band at 1350cm^{-1} affected ?

Authors : The answer to this question is given in detail in the paper by Beny and Rouzaud (1985) in this volume.