

## LOW TEMPERATURE PHASE TRANSITIONS IN METHANE-RICH INCLUSIONS IN QUARTZ FROM THE SOUTH WALES COALFIELD

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### Introduction

Methane-rich inclusions are common in diagenetic and low temperature hydrothermal minerals from sedimentary environments. Usually they are small (<20µm), but larger inclusions of this type may occur in large quartz crystals from vugs and fissure veins in carbonaceous sediments or low grade metamorphic rocks (e.g. Mullis, 1976). Here we report on a combined Raman and microthermometric study of methane-rich inclusions of exceptional size and abundance in rock crystal associated with the Carboniferous Coal Measures of south Wales (UK). These inclusions show exceptionally clear phase transitions on cooling/heating and a remarkable consistency in the temperatures at which these transitions occur. In particular, the triple point of CH<sub>4</sub> at -182.5 °C is consistent and easy to observe. Raman spectroscopic studies have shown that although the inclusions may also contain small amounts of CO<sub>2</sub> and H<sub>2</sub>O these are strongly partitioned into a solid clathrate leaving a residue of pure CH<sub>4</sub> which is ideal for use as a calibration standard.

### Sample location, methods of study and description of inclusions

The inclusions occur in euhedral quartz crystals up to 3cm long, with small carbonate overgrowths. The samples were provided by Dr N Hollinsworth (NERC) and were collected from the lower benches of the Nant Helen Coal mine. Analyses were carried out using a Linkham TH600 stage attached to a Renishaw Laser Raman probe and an Ar ion laser. At room temperature two main compositional types of large, primary inclusions were recognised. Monophase **methane-rich** inclusions, which make up about 95% of the population, and co-existing, two phase (V+L) low salinity, **aqueous** inclusions (Th <110°C) which constitute the remaining 5%. Raman analyses of the CH<sub>4</sub>-rich inclusions showed that 10-11 mole% CO<sub>2</sub>, was consistently present. No other gases were detected. Occasionally, a small amount of liquid water was observed in very thin inclusions, but mostly water was undetectable at room temperature in these inclusions.

### Behaviour of methane-rich inclusions on cooling/heating

On rapid cooling, L and V appear at about -70 °C, and a solid phase (S1) appears at about 110 °C. Heat-cool cycling was used to grow a single euhedral crystal of this phase (Figure 1). Further cooling to -195 °C resulted in complete crystallisation of the remaining liquid to form a separate solid phase (S2). On heating the following phase transitions were noted (consistent to within 1°C):

-183°C	Melting of S2	(S1 + S2 + V → S1 + L + V)
- 75°C	Melting of S1	(S1 + L + V → L + V)
- 67°C	Homogenisation	( L + V → L/V with faint meniscus)

Raman analysis at -195°C (Figure 2) confirmed that S1 mostly comprises CO<sub>2</sub> clathrate with typical peaks at 1278 and 1382 cm<sup>-1</sup> (Murphy and Roberts, 1995) and distinctive shape (Bakker & Thiery, 1994). Further Raman analyses at different temperatures showed a strong partitioning of CO<sub>2</sub> into S1, as previously reported (Murphy and Roberts, 1995) and also the partitioning of CH<sub>4</sub> between vapour and liquid (Table 1). With the first appearance of vapour the mole % CH<sub>4</sub> in the liquid decreases as it partitions preferentially into vapour. On further cooling CO<sub>2</sub> is totally extracted into S1 leaving pure CH<sub>4</sub> behind in the residual liquid. It is noteworthy that the main Raman peak for liquid CH<sub>4</sub> decreases as temperature decreases.

### Conclusions

Observation of the triple point of pure CH<sub>4</sub> is rare in inclusion studies, so the inclusions reported here are exceptional in that solid CH<sub>4</sub> is easy to form at -195 °C and this transition is easy to observe. By growing S1 during heat-cool cycling it is possible to "purify" the remaining CH<sub>4</sub> liquid and vapour and produce a reliable and suitable low temperature calibration standards for heating/freezing stage studies.

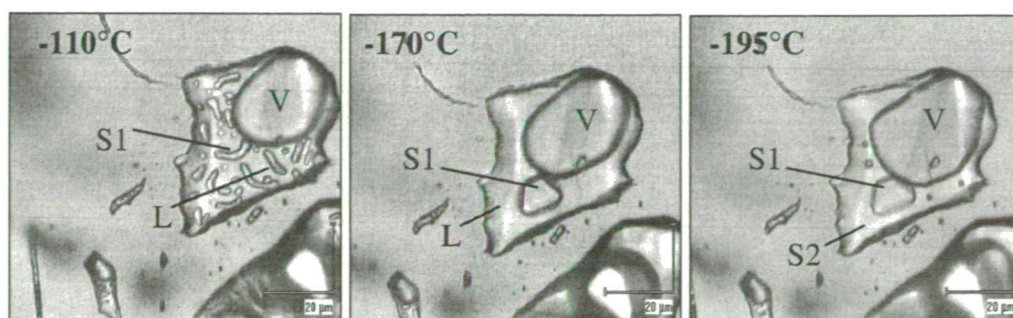


Fig. 1. Development of CO<sub>2</sub>-clathrate (S1) and solid methane (S2) on cooling. At -110 °C multiple crystals of S1 develop and on heat-cooling cycling a single crystal is grown (-170 °C). Solid methane appears at -195 °C.

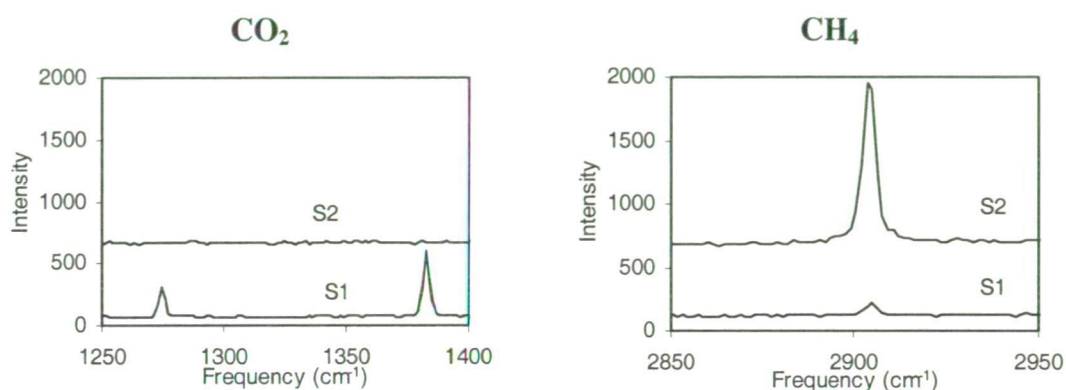


Fig. 2. Raman spectra of solid phases at -195°C: S1 = CO<sub>2</sub>- rich clathrate (1275 and 1382 cm<sup>-1</sup>) with minor CH<sub>4</sub>, S2 = methane (2905cm<sup>-1</sup>). Note the weak CH<sub>4</sub> band in S1 may be due either to minor CH<sub>4</sub> within the clathrate phase, or to scattering from the larger S2 solid.

	L		V		S1	
temperature	mol%CH <sub>4</sub>	mol%CO <sub>2</sub>	mol%CH <sub>4</sub>	mol%CO <sub>2</sub>	mol%CH <sub>4</sub>	mol%CO <sub>2</sub>
40	88.7	11.3				
-34	86.6	13.4				
-74	83.8	16.2	100.0	0.0		
-95	100.0	0.0	100.0	0.0	19.4	80.6
-135	100.0	0.0	100.0	0.0	3.9	96.1
-165	100.0	0.0	100.0	0.0	6.2	93.8
-195	S2: 100.0	0.0	0.0	0.0	21.8	78.2

Tab. 1. Variation of the phase-composition with temperature changes

### References

- BAKKER R. J. & THIERY, R. (1994). Application of Clathrates to Fluid Inclusion Studies, 191-208, In: Fluid inclusions in Minerals: Methods and Application (De Vivo & Frezzotti, Eds.). IMA Short Course notes, Siena, 1994.
- MULLIS, J. (1976). Das Wachstumsmilieu der Quatzkristalle im Val d'Illiez (Wallis, Schweiz). Schweiz. Min. Pett. Mitt., v. **56**, 219-268.
- MURPHY, P. M. & ROBERTS, S. (1995). Laser Raman spectroscopy of differential partitioning in mixed-gas clathrates in H<sub>2</sub>O-CO<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub> fluid inclusions: Implications for microthermometry. Geochim. Cosmochim. Acta, v. **59**, 4809-4824