

## Metastable melting behaviour in fluid inclusions in sphalerite from the Angouran Zn(Pb) deposit (NW Iran)

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The Angouran Zn(Pb) ore deposit in Northwestern Iran consists of a Zn-rich sulphide ore (38 mass% Zn) and Zn-rich hypogene zinc carbonate ore (smithsonite) that formed in two successive mineralization stages. Microthermometric measurements of the primary (L+V) fluid inclusions in sphalerite (Fig. 1) yielded unusually low first melting temperatures, commonly below -59 to -66 °C (Daliran et al., 2009).



Fig. 1. L+V fluid inclusion in sphalerite (15 µm in diameter).

Because optically the formation or melting of salt-hydrates were not identified, these low temperatures were interpreted as an indication of the presence of ZnCl<sub>2</sub> in the ore-forming brines (Daliran et al., 2009). The eutectic temperature of the binary H<sub>2</sub>O-ZnCl<sub>2</sub> system is about -62 °C (Linke, 1965). The final melting temperatures of these fluid inclusions are -33 to -21 °C, commonly between -24 and -26 °C, suggesting the presence of a highly saline brine. Total homogenizations (LV→L) occur between 150 and 155 °C and occasionally up to 160 °C. The primary fluid inclusions in sphalerite are commonly irregularly shaped, but locally negative crystal shapes occur (Fig. 1).

To properly understand the behaviour of these fluid inclusions in microthermometric experiments at low temperatures, cryogenic Raman spectroscopy was applied at the Montanuniversitaet of Leoben.

Laser Raman spectroscopy studies reveal the presence of ice and hydrohalite at low temperatures (e.g. -140 °C, Fig. 2).

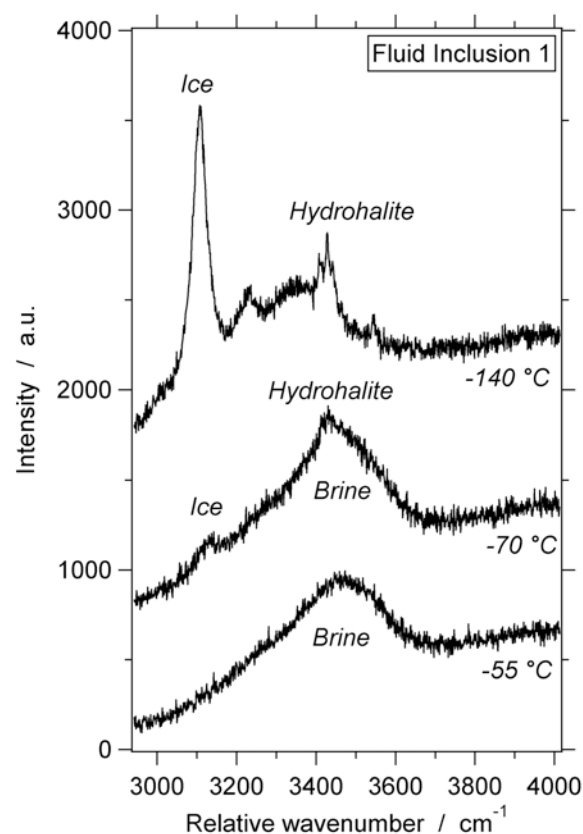


Fig. 2. Raman spectra of a fluid inclusion at -140 °C, -70 °C and -55 °C

At -70 °C, the Raman spectrum reveals the presence of ice, hydrohalite and a brine, which indicates that the melting has already started

before it is optically noticed. At -55 °C, both ice and hydrohalite have completely melted in part of the inclusions, whereas ice is still present in other inclusions, illustrating a variation in salinities.

In conclusion, the optically observed "first melting" is not corresponding to phase changes at an eutectic point of the fluid system in the inclusions, but only reflects the first amount of visible brine. The presence of ZnCl<sub>2</sub> in the brine cannot be proven with microthermometry, whereas Raman spectroscopy clearly evidenced the presence of NaCl in the fluid (in the form of hydrohalite at low temperatures). However, this brine must contain another type of salt, most probably ZnCl<sub>2</sub>, which remains metastable in the liquid aqueous solution, even at extreme low temperatures.

The role of chloride complexing on metal solubilization in high salinity acid fluids is considered as the most important mechanism of Zn, Pb (and Ag), as well as Cd (e.g. Bazarkina et al., 2010), and could explain the formation of Zn-rich ore deposits, such as the Angouran deposit.

#### REFERENCES

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