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Raman spectrometry and microthermometry data on CO_2-CH_4-bearing fluid inclusions in late-orogenic quartz from the Saxberget Zn-Pb-Cu-Ag deposit, Central Sweden

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Introduction

Several studies have recently been performed on the sulfide ores of central Sweden, using a multidisciplinary approach with methods as stable isotopes, rare-earth elements, geochemistry of main and trace elements in combination with conventional microscopy (Johansson & Rickard, 1985; Karlsson, 1981; Arvanitidis & Rickard, 1981; Vivallo, 1984, 1985; Billström, 1985).

Van den Kerkhof (1987) investigated the fluids involved in the formation of the Harmsarvet Ag-Pb-Zn deposit. The present work deals with fluid phases associated with another deposit in central Sweden, the Saxberget Zn-Pb-Cu-Ag ore.

Geological setting

The volcanogenic, massive sulfide ore at Saxberget Vivallo & Karlsson (1986), is emplaced between two sets of supracrustal rocks: (1) a banded quartz-feldspar-biotite gneiss to the north under the moderately south-dipping ore lens, and (2) an almandine-bearing quartz-biotite gneiss in the hanging wall to the south. The supracrustal rocks have an unknown basement, and they were affected by the Svecokarelian orogeny (1700–1800 Ma: Lundqvist, 1979; Moorman et al., 1982). Several intrusive bodies of late-orogenic granites surround the Saxberget area along the general E-W strike of the lithological units. These granites constitute a complex formation of different generations (Karlsson, 1980; Vivallo & Karlsson, 1986). Intrusions of amphibolite and diorite also occur. The area is bordered by large masses of early-orogenic granites, both to the north and to the south.

Karlsson (1980) suggested on the basis of mineral assemblages that the Saxberget supracrustal rocks underwent two low-pressure metamorphic events. One event was of high grade and of regional extent, characterized by temperatures of about 600° C and with water pressure lower than total pressure; it was caused by the intrusions of the early-orogenic granites. This was followed by a static event of medium grade, apparently of only local extent. It is characterized by temperatures of about 500–550° C and pressures of about 200–375 MPa (Vivallo & Karlsson, 1986); this event is related to the intrusion of the late-orogenic granitic rocks.

The sulfide ores have been divided into three types (Karlsson, 1980): (1) ball ore, a rich massive sulfide ore with rounded wall rock inclusions of different sizes, (2) ore in anthophyllite-bearing

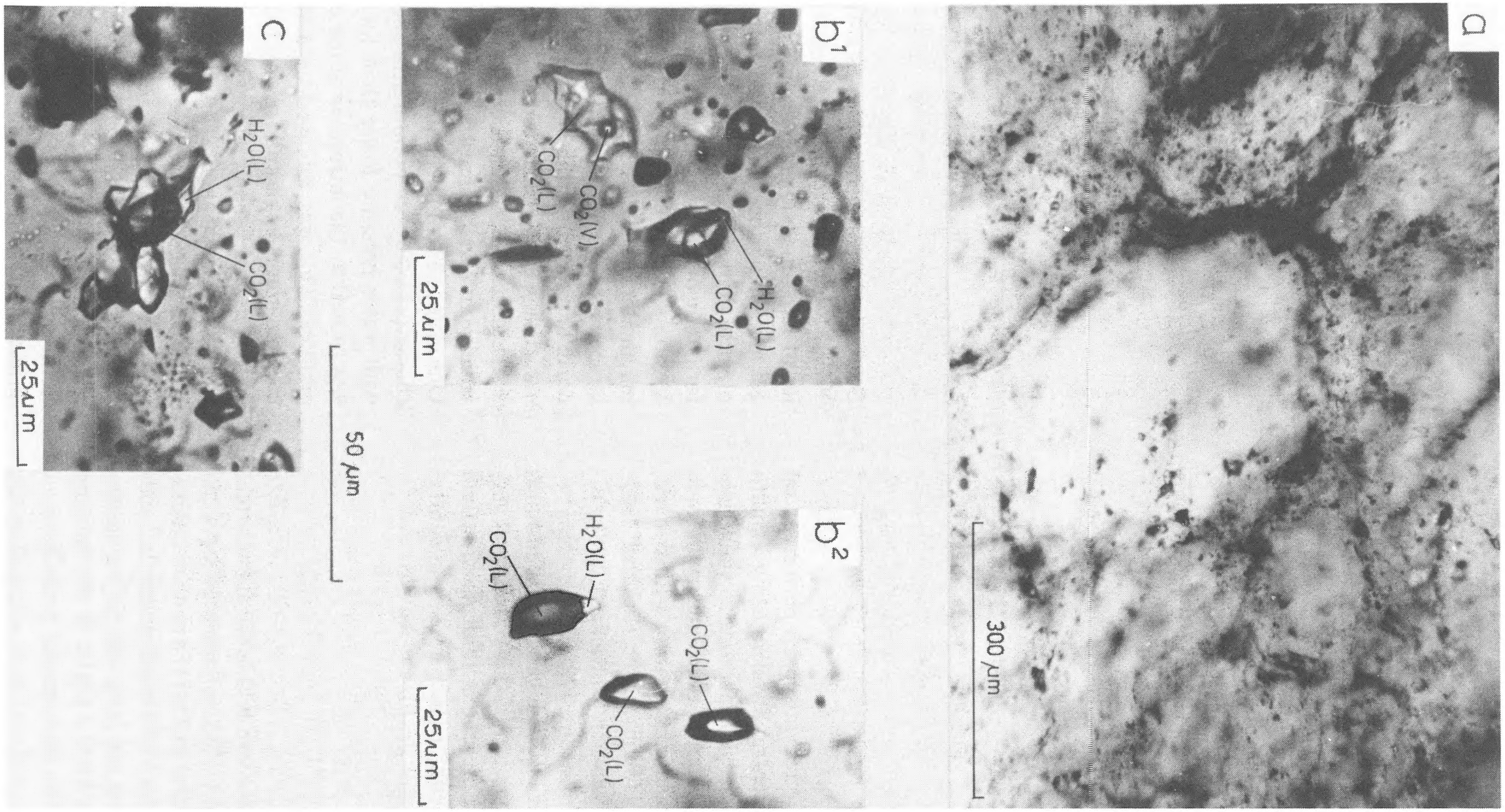

Fig. 1. Fluid inclusions in quartz from Saxberget. (a) A slightly deformed equigranular texture with grain boundaries and fluid-inclusion trails and clusters. (b) Carbonic inclusions with mainly CO_2; the presence of H_2O may be observed at irregular corners in some inclusions. (c) A relatively large irregular inclusion: P. [$CO_2(V)$ = gas carbon-dioxide, $CO_2(L)$ = liquid carbon-dioxide, $H_2O(L)$ = water.]

host rock, and (3) ore in serpentized rocks or in marble. In all three types the ore minerals are sphalerite, galena, chalcopyrite, pyrrhotite, magnetite and pyrite in varying proportions. Pyrrhotite dominates over pyrite, and the iron sulfides make up about 15 vol. % of the ore.

Vivallo & Karlsson (1986) have assembled evidence which points to a volcanogenic origin of the ore, related to submarine hydrothermal activity. The present mineralogy and wall-rock textures are the result of subsequent deformation and metamorphism, which affected both ore and country rocks.

Description of sample and inclusions

The present study concerns a single sample of massive, milky-white finely-crystalline quartz. It originates from a post-mineralization, quartz-rich pegmatite in the central part of the ore body, spatially associated with the massive ore. Qualitative observations indicate that the sample is representative for a large number of pegmatites observed in the area. These pegmatites are connected to one of the late-orogenic granites.

The quartz specimen has an annealed and equigranular texture, which subsequently underwent deformation, fracturing and healing. Large relatively clear quartz crystals are surrounded by areas abundant in inclusions (Fig. 1a). All inclusions have a secondary mode of occurrence, and appear to follow more or less distinct trails. Two types of inclusions have been observed: (1) rare two-phase inclusions of irregular shape; thermometry indicates that they contain an aqueous solution; (2) CO_2 inclusions with one, two or three phases; they sometimes contain a narrow border of liquid H_2O (Fig. 1b).

Microthermometry

Measurements of aqueous inclusions on the freezing/heating stage (Chaixmeca; *Poty et al.*, 1976) gave ice final-melting temperatures (Tm ice) of -3 to -5° C, indicating a salinity of less than 8 equivalent wt. % NaCl. Three homogenization temperatures (Th) gave respectively 138.2, 163.5 and 201.2° C. All aqueous inclusions occur closely together and show the same salinity; the observed range of Th can be explained by phenomena as necking-down, boiling or leaking, but the number of measurements is too small to allow further interpretation.

Microthermometry results indicate that the majority of the inclusions contain CO_2 as the major phase (Fig. 1b). Homogenization temperatures (to the liquid phase) (Th) ranged between +16.9 and +24.3° C, with a modal temperature of +22° C (Fig. 2). Melting temperatures (Tm) of CO_2 ranged between −58.0 and −57.4° C, with a distinct mode at −57.8° C (Fig. 2). No relation was found between $ThCO_2$ and $TmCO_2$. Four inclusions yielded clathrate-melting temperatures at +8.0, +8.2, +8.4 and +11.4° C. One single inclusion (P in Fig. 1c) is fairly large with many irregular corners; this made the observation of phase changes difficult, and this inclusion gave temperatures different from the others: $TmCO_2 = -58.0$° C and Tm clathrate = +11.4° C, but no $ThCO_2$.

There is no apparent relation between the size of the inclusions and their water content. The large inclusion P shows a large amount of water (Fig. 1c).

Raman spectrometry

Fifteen inclusions have been analysed with a multichannel laser Raman microspectrometer (Microdil-28). The instrument and the measurement conditions for fluid inclusions have been described by Burke & Lustenhouwer (1987). Only CO_2 and CH_4 have been detected in the Saxberget inclusions; components searched for, but not detected, include N_2, O_2, SO_2, H_2S, CO, H_2, NH_3 and C_2H_6. The instrument was run with the following parameters: laser power 600 mW at the source, exciting line 514.5 nm, slit width 200 μm, integration time 3 seconds and 50 accumulations for each spectrum. Mole percentages of CO_2 and CH_4 in the 15 inclusions were calculated from the peak areas using the following relative Raman-scattering cross-sections: $\sum CO_2 = 1.21$ and $\sum CH_4 = 8.9$. The accuracy

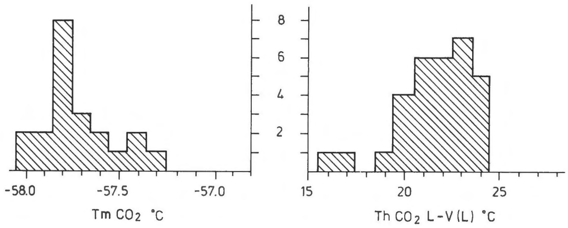

Fig. 2. Melting temperatures (Tm) and homogenization temperatures (Th) of CO_2 inclusions.

of the results is within a 10% relative error for the minor component, in this case CH4.

Most inclusions contain more than 90 mole % CO_2, and between 3 and 7 mole % CH_4. Two inclusions have a higher CH_4 content: 11 and 15 mole %. The latter result was obtained on inclusion P with the anomalous microthermometry results. Plotted as a histogram, the CH_4 contents have a mode around 5 mole %. This value can be taken together with the Th of + 22° C to calculate a molar volume for further isochore calculations: this would give a V = 65 cm^3/mole (Ramboz, 1980).

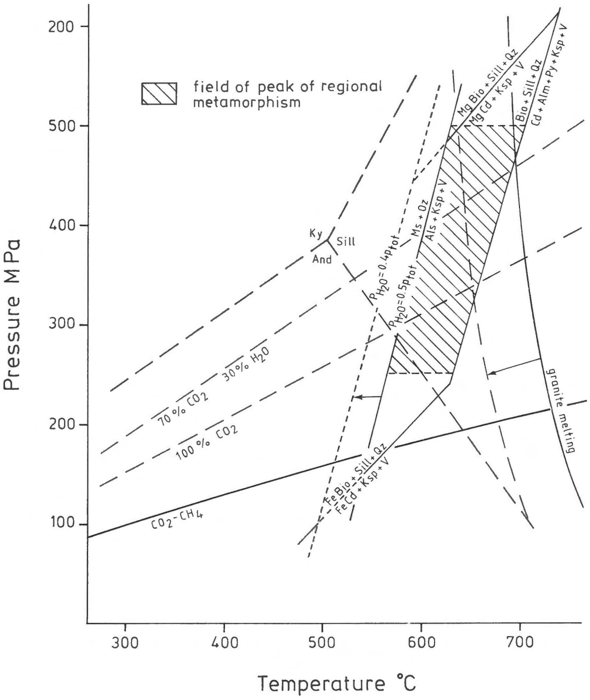

Fig. 3. Pressure and temperature conditions for regional metamorphism at Saxberget. The field of peak metamorphism is hatched. A calculated CO_2-CH_4 isochore passes below this area and intersects the granite melting field at about 700° C and 200 MPa in a water-deficient system ($P_{H2O} = 1/2P_{tot}$). Data from Kerrick (1972) and Holdaway & Lee (1977). Al_2SiO_5 stability relations from Holdaway (1971). CO_2-H_2O isochore from Bowers & Helgeson (1983).

Discussion

The Saxberget sulfide deposit has been metamorphosed to a higher degree than most other deposits in Bergslagen. This is manifest from structures and mineral assemblages throughout the ores (Karlsson, 1980; 1986; Vivallo & Karlsson, 1986). The quartz specimen used in the present study, however, represents a later metamorphic event as it was formed during one of the late-orogenic granitic intrusions. The quartz was subjected to later fracturing and subsequent healing, as indicated by trails of fluid inclusions in the quartz. This is in agreement with observations by Karlsson (1986), relating the present mineral textures to the late-orogenic events.

The majority of the abundant CO_2-rich inclusions are two-phase, but a third phase (liquid H_2O) can be seen as a thin film along the borders of some inclusions, and clathrate formation has been observed in a number of inclusions. It is concluded that water is present as a separate phase, sometimes with as much as 10 vol. %, but usually in smaller amounts.

The occurrence of rare purely aqueous inclusions indicates that an aqueous solution has influenced the quartz by healing late-stage fracture planes, thereby probably altering the composition of many CO_2- rich inclusions. A striking but extreme example of this process is shown by inclusion P (Fig. 1c).

A CO_2-H_2O system in which the amount of water is less than 10% can be approximated to the pure CO_2 system if the density of CO_2 is high (Swanenberg, 1980). This applies to Saxberget, where the CO_2 inclusions have a density of 0.8 g/cm^3. Moreover, the pure CO_2 isochore then represents a minimum value compared to any CO_2-H_2O mixture with the same CO_2 density: this is due to the much steeper slope of H_2O isochores than the ones for CO_2. For these reasons, the carbonic system as defined by Raman analyses (95 mole % CO_2, 5 mole % CH_4, molar volume of 65 cm_3/mole) can be used for the construction of a 'minimum'-isochore for the sample, according to a calculation by Holloway (1981). This isochore evidently passes well below the P-T field calculated from mineral assemblages for the peak of metamorphism (Fig. 3). The isochore obviously represents lower pressures than those of the regional metamorphism, the event associated with the early-orogenic granite intrusions. The isochore also passes below the P-T field of the second, more local metamorphic event (500–550° C and 220–375 MPa). Taking into account, however, the presence of a certain amount of water in the system (as evidenced by the inclusions), the slope of the isochore will be steeper, thus fitting very well the formation of the CO_2-rich inclusions with the field of local metamorphism caused by the late-orogenic granite intrusions (500° C and 250 Mpa).

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