

TEMPERATURES, SALINITIES AND EVOLUTION OF BARITE-FLUORITE- MANGANESE MINERALIZATIONS OF THE VÄTTERN BASIN, SOUTH SWEDEN

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Mn-Ba-F mineralizations of inferred Permian age occur at Bölet, Spexeryd and Medevi located along Lake Vättern, a fault-controlled basin within the Protogine Zone of south Sweden. The Protogine Zone is a major lineament, the age and origin of which are still poorly understood. Assessment of temperatures and depths of formation of these mineralizations and the source of water of ore-forming solutions is vital to a correct interpretation of ductile and brittle structures and crustal depths along the Protogine Zone. For this reason, we have studied fluid inclusions in transparent crystals of calcite, quartz, barite and fluorite using thermometric, cryometric and chromatographic analysis of volatile constituents. Stable isotope analysis includes ¹⁸O and ¹³C.

Alterations

Wall-rock alteration is most intense along mylonitized zones of the normally massive wall-rock granite. Potassic alteration resulted in thick masses of biotite. Fluoritization led to formation of fine-grained fluorite in association with quartz and sericite; as monomineralic veins, or as quartz-fluorite mineral zones with sericite.

Silicification occurred as replacement of wall-rock minerals by fine, idiomorphic quartz crystals. Quartz occupies small fissures in microcline; such fissures are often cut by veinlets of calcite and barite. Quartz grew either simultaneously with fluorite or slightly later: both minerals occupy fractures in crystals, but quartz frequently replaced or coated cubic crystals of fluorite. Zones of quartz and calcite with corrosive grain boundaries replace earlier quartz and quartz-fluorite veins. Inner parts of composite veins/veinlets are frequently filled by transparent quartz crystals containing no gas-liquid inclusions and displaying no traces of tectonic activity; druses of quartz also occur.

Carbonatization and baritization accompanied fluoritization and silicification. This process led to the formation of zones of quartz-calcite and quartz-fluorite-calcite. Calcite occurs in fissures with quartz and fluorite. Grain boundaries of fluorite and calcite are usually non-corrosive. A black variety of calcite is impregnated by pyrolusite and psilomelane. Barite formed monomineralic (up to 6 m wide) veins but also occurs in narrow veins composed of quartz-barite, calcite-barite and fluorite-barite. Narrow monomineralic barite veins are characterized by fibrous texture; oblong crystals of constant length grew across the vein.

Manganite is the main ore mineral, occurring as massive or aggregates of needles. It is often partially replaced by a network of pyrolusite, or by earthy aggregates of pyrolusite and psilomelane. Acicular, dendritic, and globular aggregates of ore minerals occur in various cavities and in microfissures and within druses of fluorite. Iron hydroxides occur as coatings on transparent crystals of quartz and fluorite.

Homogenization temperatures

Fluorite: 19% of measurements fall within the temperature range of 240-350°C; 30% between 160-240°C and 51% between 100-160°C. See Figure 1!

Quartz: 12% of measurements fall within the temperature range of 240-300°C; 34% between 160-240°C and 54% between 85-110°C. Calcite: 10% of measurements fall within the temperature range of 200-220°C; 80% between 180-200°C and 10% between 160-180°C. Barite: 70% of measurements fall within the temperature range of 160- 240°C; 30% between 85-100°C.

Composition of fluids and gases

Cryometric analysis of gas-liquid inclusions in quartz and fluorite indicate two main groups of fluids: aqueous salt systems and mixed gas-liquid systems (CO₂ or CH₄). Concentrations and salt composition of solutions differ slightly between quartz and fluorite. While inclusions hosted in quartz are characterized by calcium and sodium salts, those in fluorite have more varied contents of cations (Mg, Ca, K, Fe, Na). The concentrations of solutions were determined as follows: 22-30.2% CaCl₂ (quartz); 19.7% KCl (fluorite) and 11-13% NaCl (quartz and fluorite).

Chromatographic analysis was performed on quartz, barite, fluorite within the temperature ranges 120-160°C and 160-260°C in order to define the vapor phase of inclusions in these minerals. In addition opal and collomorphic goethite were analyzed. In the gas phase of solutions, carbon dioxide is prevalent (70-96%), also hydrocarbons (CH₄, C₂H₄, C₂H₆), CO, H₂ and a little of N₂, and NO are present. The presence of CO, H₂, CH₄ indicate a reducing character and hypogene origin of the gas phase; this is suggested also by the presence of nitrogen in the absence of oxygen.

Estimation of depths of formation

Fluid pressures were estimated from the isochore for specific fluid density (19.7% KCl_{eq}) and measured T_h (256-280°C). Inclusions (10-20 μm large) in fluorite were used. Using the PT plot with isodensities and defining liquid CO₂ density from

tabulated data, pressures of 400-500 bar were obtained. For a regional geothermal gradient of $\sim 30^{\circ}\text{C}/\text{km}$, the depth of mineral formation at temperatures between $256\text{-}280^{\circ}\text{C}$ would be nearly 9 km, suggesting substantial additional heat.

Stable isotopes

Analysis of calcite ($T_h = 210^{\circ}\text{C}$) in quartz-fluorite-calcite veins in mylonitic granite yielded $\delta^{18}\text{O} = +18.6\text{‰}$; $\delta^{18}\text{O}_{\text{H}_2\text{O}}\text{SMOW} = +9.6$ compatible with magmatic water of ore-forming fluids. $\delta^{13}\text{C}\text{‰} = -3.7$, compatible with hydrothermal origin.

History of mineralization

The data obtained indicate three stages of mineral formation resulting in three mineral associations. During the first stage, fluorite, quartz and sericite formed at temperatures of $350\text{-}260^{\circ}\text{C}$ and ductile conditions of the wall-rock deformation, as evidenced by isoclinaly folded quartz-biotite-sericite fabrics.

The second stage is represented by quartz, barite, fluorite, calcite that form veinlets and veins and also occupy fissures and the matrix of brecciated wall-rock. Ore minerals, rhodochrosite and colloform seams of goethite entered central parts of veins and the interstices of crystals. The extensive temperature range of mineral formation ($250\text{-}120^{\circ}\text{C}$) and the shape of crystals and inclusions suggest prolonged and slow circulation of mineralizing solutions under brittle conditions of rocks deformation.

The third stage is represented by well-faced and transparent crystals of quartz, fluorite and barite, and needles or dendrites of ore minerals grown largely in open cavities. Perfect crystal shapes and the lack of secondary inclusions healing microfissures indicate quiet tectonic conditions.

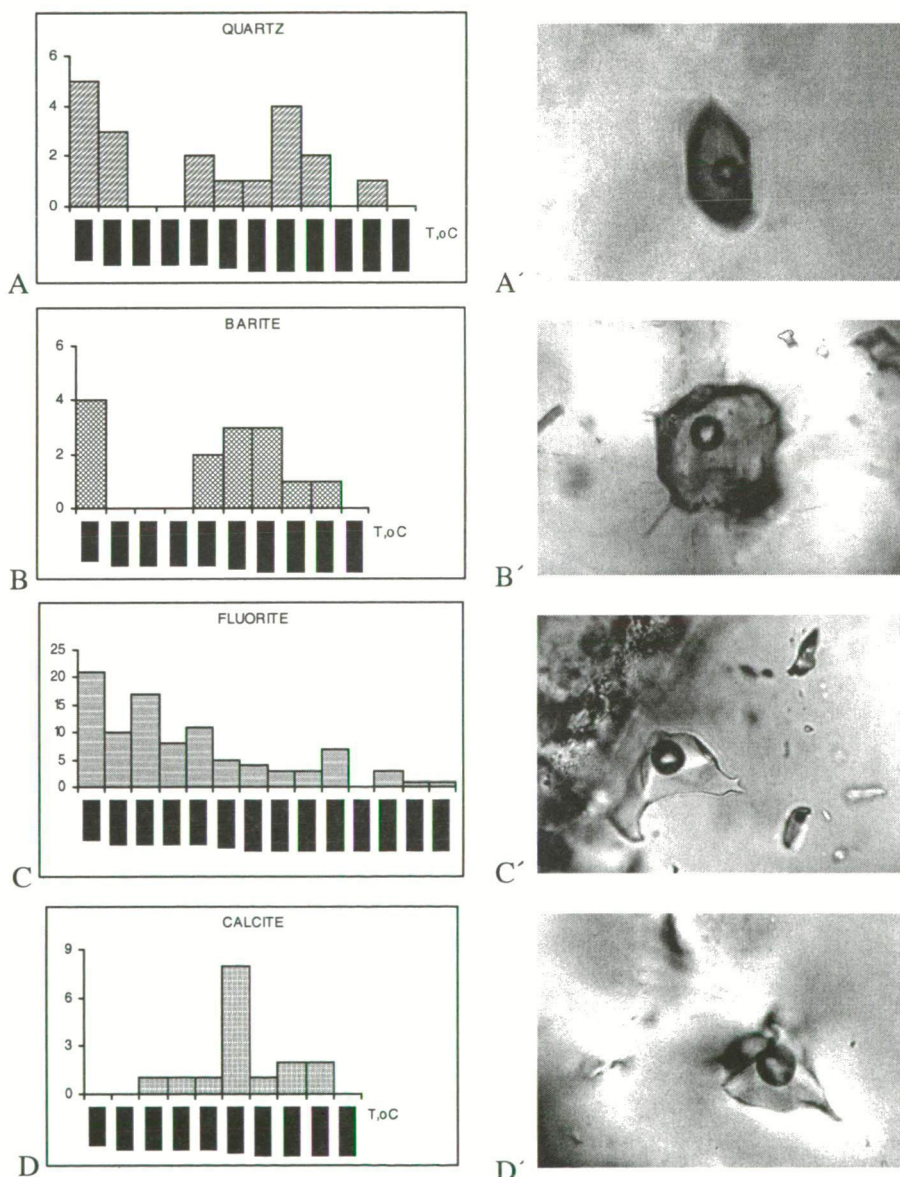


Figure 1. Homogenization temperatures (A-D) and primary two-phase fluid inclusions in transparent minerals (A'-D') of the Bölet Mn-Ba-F mineralization A'= inclusion in quartz; size $7\mu\text{m}$. B'= inclusion in barite; size $20\mu\text{m}$. C'= inclusion in fluorite; size $12\mu\text{m}$. D'= inclusion in barite; size $9\mu\text{m}$.