

# The genesis of mineralising brines in the South West Massif Central, France

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**Geological setting.** The base-metal, fluorite and barite deposits of the SW Massif Central are hosted by EW-trending vertical fractures that transect Lower Cambrian to Lower Carboniferous nappe sequences in the Rouergue, Albigeois, northwestern Montagne Noire and Monts de Lacaune regions of the Hercynian Massif. To the north, base-metal and fluorite veins outcrop in a Cambro-Ordovician series of pelites, quartzites and metabasites. South of the Albigeois, base-metal veins outcrop in a weakly metamorphosed sequence of Cambrian black shales, sandstones and volcanoclastics. In the eastern Monts de Lacaune, karst-vein-hosted barite deposits occur in dolomites and limestone of Devonian age and in the adjacent Triassic clastics of the Causses Basin.

**Mineral paragenesis and microthermometric data.** Base-metal - fluorite mineralisation in the SW Massif Central is associated with a number of generations of gangue quartz that are distinct in terms of their texture and mineral associations. They may be regional in extent and occur in a variety of different lithologies.

Four major stages of quartz deposition have been identified.

1. Quartz 1 typically takes the form of a silicified tectonic breccia and is known regionally as 'B.T.H.' (brèche tectonique hypersilicifiée). Sheared fragments of local wall-rock are cemented first by chalcedony and then by successive generations of zoned prismatic quartz giving rise to characteristic cockscomb textures. B.T.H. may occur independently and is found as prominent EW-trending 'dykes' throughout the region. Where B.T.H. occurs in association with Pb-Zn-F-Ba mineralisation it typically forms the wall-rock to the deposit. Primary fluid inclusions have aqueous two-phase fills with salinities between 20 and 24 wt.% NaCl equiv. and homogenisation temperatures of 85 to 130°C. First

melting temperatures indicate that CaCl<sub>2</sub> is also present (-52°C).

2. Quartz 1a is referred to as lamellar quartz and consists of interlocking, randomly orientated lamellae of quartz. Lamellar quartz may occur in association with silicified breccias though relationship between the two are ambiguous. Lead-Zinc sulphides may fill angular vugs between lamellae. Quartz 1a occurs in the Rouergue and Monts de Lacaune regions of the Massif Central but is not present in the Albigeois and NW Montagne Noire. Fluid inclusions are similarly CaCl<sub>2</sub>-bearing liquid-vapour fills where temperature of final ice melting indicate salinities of approximately 26 wt.% NaCl equiv. Homogenisation temperatures range from 185 to 213°C.

3. Quartz 2 occurs in association with sulphide cockade ores in the NW Montagne Noire and Rouergue regions. Local host-rock, silicified breccia and lamellar quartz are brecciated and cemented by siderite and sphalerite. Coarse prismatic quartz fills terminal vugs within the sphalerite matrix. Primary inclusions show aqueous two-phase fills with salinities that vary between 20 and 22 wt.% NaCl equiv. (including CaCl<sub>2</sub>) and homogenisation temperatures range of 117 to 166°C.

4. Quartz 3 occurs in association with massive blue fluorite veins in the Albigeois, as drusy quartz fills of terminal vugs. Fluorite stage mineralisation, is seen to cross-cut sulphide ores in the deposit of Peyrebrune in the NW Montagne Noire. Fluid inclusions in quartz associated with the fluorite are CaCl<sub>2</sub>-bearing liquid-vapour inclusions with salinities of 20–26 wt.% NaCl equiv. and homogenisation temperatures range of 125–170°C.

Although pressures prevailing during mineralisation are presently unknown, Munoz *et al.*, (1994) find good correlation between homogenisation tempera-

tures and calculated, suggesting that any correction for pressure would be small.

**Stable isotope analyses.** Oxygen isotope analyses were carried out on all four generations from deposits across the SW Massif Central. In addition, examples of each were fragmented and analysed in detail to investigate potential variation in the oxygen isotope signature across individual samples. A total laser fluorination system was used in both cases.

Quartz 1 shows a broad range of  $\delta^{18}\text{O}_{\text{Qtz}}$  from +12.5 to +22.3‰<sub>SMOW</sub>. Deposits in the Albigeois and NW Montagne Noire fall towards the lower end of this bracket whilst deposits in the Monts de Lacaune exhibit heavier values. Quartz 1 shows only slight variation in isotopic composition within samples. In contrast, quartz 1a, 2 and 3 show much narrower ranges (+17.9 to +20.8‰<sub>SMOW</sub> respectively) but significant variations (up to 5‰) within samples. Using measured fluid inclusion homogenisation temperatures and a standard quartz-water fractionation equation, the calculated fluid  $\delta^{18}\text{O}$  range for each generation is: Quartz 1: -10.5 to +6.0 ‰<sub>SMOW</sub>; Quartz 1a: +3.0 to +10.5‰<sub>SMOW</sub>; Quartz 2: +1.5 to +5.5‰<sub>SMOW</sub>; Quartz 3: -2.0 to +5.5‰<sub>SMOW</sub>.

Results show that the isotopic composition of fluids responsible for the deposition of quartz 1 varies with geographical location and host-rock lithology. This suggests either that mineralising fluids have separate sources or that their isotopic composition is controlled by the equilibration of similarly sourced fluids with local host rocks. For deposits in the Albigeois and NW Montagne Noire,  $\delta^{18}\text{OH}_2\text{O}$  values are within the range expected for surface waters. This is consistent with the  $\delta^{18}\text{O} - \delta\text{DH}_2\text{O}$  data of Munoz *et al.*, (1994, 1997) which plot close to the meteoric water line.

Quartz 1 fluids are heaviest in deposits from the Monts de Lacaune and in the Triassic rocks of the adjacents Causses Basin. If quartz 1 fluids in this region were also meteoric in origin then there has been a positive shift in isotopic composition due to fluid-rock interaction. Whilst fluid  $\delta^{18}\text{O}$  differ geographically, there is little variation in values measured within samples. This may imply that fluids in the Monts de Lacaune were fully equilibrated with their host at the time of quartz 1 deposition – if an independent fluid with separate isotopic evolution is invoked to account for the geographical disparity in the isotope data then it might be expected that the evolution of the isotopic signature is recorded as quartz growth proceeds.

For each of quartz generations 1a, 2 and 3,  $\delta^{18}\text{OH}_2\text{O}$  varies only slightly between deposits but differs more significantly within individual samples.

Isotopic composition may therefore be representative of the source and subsequent evolution of an infiltrating fluid rather than its equilibration with the host-rock during deposition. In all cases,  $\delta^{18}\text{OH}_2\text{O}$  values can be interpreted in terms of a surface-derived fluid that has shifted to more positive values during fluid-rock interaction in the hydrothermal system.

**Halogen analyses.** For deposits in the Albigeois and NW Montagne Noire, processes of brine formation have been investigated through the analysis of halogen ratios in fluid inclusion leachates.

Whilst the absolute concentration of chloride remains relatively constant through the paragenesis, Br/Cl ratios decrease from values greater than that of seawater to values that are equivalent or less. Such a trend implies that initial fluids were either bitterns or brines generated through the incongruent dissolution of halite by a dilute fluid. If such scenarios were true then the chloride concentration (being less than that at halite saturation) requires that the high Br/Cl brine is diluted. In both cases, continual flushing of the evaporite by the hypothesised surface-derived fluid would serve to dilute and gradually deplete the Br reservoir such that successive fluids would exhibit decreasing Br/Cl ratios. However, given that the salinity is near uniform across all deposits throughout the paragenesis, ratios of mixing would have to be sustained spatially but modified with time to maintain this value. As this would seem difficult to achieve it is possible that an independent process is operating to keep salinity constant. Br/Cl ratios for all stages are not consistent with ratios indicative of magmatic-hydrothermal activity (Böhlke and Irwin, 1992).

## Conclusion

Isotope data from this study and the work of Munoz *et al.*, (1994, 1997) would suggest that the ore-forming brines in the SW Massif Central were surface-derived but have undergone isotopic modification through exchange with country rocks in the hydrothermal system. In order to account for their high salinities, Munoz *et al.*, (1994, 1997) have postulated that such fluids flowed through and interacted with Mesozoic evaporite-bearing horizons in adjacent sedimentary basins. Br/Cl ratios in fluid inclusion waters would imply that this involved either an initial « flush out » of trapped bitterns followed by congruent dissolution of evaporite or incongruent dissolution of an evaporite horizon and gradual depletion of the Br reservoir as successive 'packets' of fluid pass through.