Fluid inclusions in the Outokumpu Deep Drill Core: implications for paleofluid evolution and composition of modern deep saline fluids

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The drill hole, which was finished in January 2005 at a depth of 2516 metres, transects the Paleoproterozoic Outokumpu formation and was intended to encounter the Archaean basement. The Outokumpu formation represents a 1-5 km thick remnant of folded and imbricated overthrust terrain, consisting of mica schist with black schist interlayers, serpentinite, skarn rocks, and pegmatitic gneisses, which are underlain by Archaean basement. The formation was strongly deformed during the Svecofennian orogeny (1.9 Ga) (Gaal et al., 1975).

Mica schist, biotite mica schist, and biotite gneiss contain quartz, biotite, chlorite, and feldspars as main components and accessory minerals like hematite, pyrrhotite, garnet, and tourmaline. Fine-grained quartz is oriented along bedding planes and/or foliation. Some grains show undulous extinction and incipient recrystallisation. Biotite defines bedding planes and/or foliation and is partly replaced by chlorite. Plagioclase is rarely replaced by white mica and alkali feldspar shows signs of incipient alteration. The mineralogy and texture of the ultramafic rocks of the Outokumpu assemblage show an amphibolite facies overprint (Peltonen et al. 2008). The samples studied are addressed as serpentinites. Microscopically serpentine, calcite, Mg-chlorite, and sericite can be distinguished. Because of the strong serpentinisation and the metamorphic conditions, no relicts of the primary magmatic minerals could be identified. In addition, magnetite and pyrite occur as opaque phases. The skarn rock mainly consists of diopside and tremolite, which are arranged in a herringbone pattern. Talc, carbonates, and opaque phases are also present. The opaque phases, like pyrrhotite and chalcopyrite, replace the primary minerals. The skarn rocks are often penetrated by calcite veins (Piribauer et al. 2011)

In addition to these main lithologies other strongly carbonatized rock types were found. The pegmatites and pegmatitic granites consist of alkali feldspar, plagioclase, muscovite, quartz, and garnet. Apatite, epidote, and opaque phases occur as accessories. Quartz shows partly undulous extinction and no recrystallisation has been observed. The strip-shaped plagioclase shows beginning alteration and a myrmekitic intergrowth with quartz. Alkali feldspar is not as strongly altered as plagioclase and muscovite forms large crystals within the interstices (Piribauer et al. 2011).

The primary, pseudosecondary, and secondary fluid inclusions observed in quartz veins contain up to three different phases: vapour phase (V), liquid phase (L), and sometimes a solid phase (S) as accidentally trapped crystals. Within the veins, fluid inclusions occur on intragranular trails, on transgranular trails, in clusters or as single inclusions in the veins. Fluid inclusions within the carbonate veins are smaller than 5 µm and cannot be analysed with microthermometry. Four different types of primary isolated fluid inclusions can be distinguished within the quartz veins, based on their composition:

> Type 1: LV = H_2O-NaCl
> Type 2: LV = H_2O-$CaCl_2$-NaCl
> Type 3: L = CO_2
> Type 4: LL = H_2O-CO_2

Type 1 fluid inclusions show a melting temperature (T_m) between -2 and -22 °C, which corresponds to a salinity of 2 – 22 eq mass% NaCl. The size of the inclusions range from <2 µm

to 40 μm. The homogenisation temperatures (T_h (LV→L)) of the type 1 fluid inclusions plot between 100 and 400 °C. Type 2 fluid inclusions have a lower eutectic melting (T_e) than type 1 fluid inclusions. T_e is between -30 and -60 °C, which suggests the presence of $CaCl_2$ in addition to NaCl. Final melting occurs between -45 and -5 °C, which points to a variable salinity of the fluid inclusions next to a variable composition of the $CaCl_2$-rich type. The CO_2 bearing, type 3, inclusions are characterised by a Tm(ice) between -57° and -60°C, which indicates the presence of another gas phase, most likely CH_4. They show different homogenisation temperatures T_h(CO_2 LV→L) between -11 °C and +6 °C. The homogenisation of the CO_2 occurs into the liquid phase. Type 4 H_2O-CO_2 fluid inclusions show melting temperatures of CO_2 between -57.9 and -62.5 °C, CO_2 homogenisation occurs into the liquid phase between 8.7 and 22.6 °C. It was not possible to measure T_h(total) due to decrepitation. Ice and clathrate melting temperature also suggest the presence of an additional salt component within the H_2O, which is assumed to be NaCl (Piribauer et al. 2011).

The results of crush-leach analyses show cation ratios of Ca/Na (0.255 – 0.948 molar), K/Na (0.097 – 0.204 molar), Li/Na (0.001 – 0.085 molar), and Mg/Na (0.024 – 0.344 molar), which are partially higher than seawater (Ca/Na 0.022; K/Na 0.021; Li/Na >0.001; Mg/Na 0.113; seawater values from Turekian, 1968). The Li/Na ratio rises in the vicinity of the deeper pegmatites, which suggests an influence of magmatic water. Within the Cl/Br-Na/Br diagram most of the crush-leach samples differ significantly from the seawater evaporation trajectory (SET). They also plot mainly below the 1:1 line, indicating a change of the Cl/Br-Na/Br ratios during halite precipitation and halite dissolution. The molar Cl/Br ratios range from 100 to 400 and are significantly lower than seawater, suggesting a higher Br concentration than seawater. The molar Na/Br ratios are between 80 and 580 and are similar to seawater ratios (Piribauer et al. 2011).

The δ^{18}O values of the fluid inclusions were calculated under the assumption of isotopic equilibrium between the fluid phase and the host mineral (quartz, Hu & Clayton 2003) at a temperature of 500 - 540°C, as indicated by geothermometry. The δD values of the fluid inclusions show a broad scatter; however, all values plot in the field of metamorphic fluids with the biotite values being distinctly lighter in δ^{18}O straddling the field of magmatic fluids. In contrast, the isotopic composition of the Outokumpu groundwater (Nurmi et al., 1988) plots to the left of the meteoric water line (Piribauer et al. 2011).

Deep groundwaters in the Outokumpu crystalline basement deviate significantly from fluid inclusions in their stable isotope ratios, which plot to the right of the global meteoric water line in a δD - δ^{18}O diagram. This suggests that they may have formed as a mixture of meteoric and saline waters. In addition, Cl/Br and Na/Br ratios point to chemical exchange with the host rocks. Many models have been proposed to account for the enhanced salinity of deep groundwaters and the shift in the stable isotopes, but our data indicate that the saline fluids are derived primarily through water–rock interaction. The role of fluid inclusions as important contributors to the saline fluids is not supported (Piribauer et al. 2011).

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