

## Trace element sulfide geochemistry as an indicator of vent fluid pH

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Study of actively venting seafloor massive sulphide deposits allows quantitative links to be made between vent fluid and deposit compositions. Models that reproduce mineral assemblages using measured vent fluid compositions and considering transport within the deposits indicate greatest sensitivity to the large ranges in temperature, and lesser but still significant sensitivity to the ranges in pH, present within the deposits; sensitivity to variations in oxygen and sulphur fugacity, which are small except at deposit exteriors, is not as significant (Tivey, 1995). Interest in finding an indicator of past pH from seafloor vent deposits stems from the ranges in pH (~2 to ~6) exhibited in fluids venting from seafloor sulphide deposits (Von Damm, 1995), and calculated for pore fluids within vent deposit interiors (Tivey, 1995). It also stems from our understanding that the pH of the highest temperature, lowest Mg vent fluids provides information about subsurface processes (e.g., temperatures of water-rock reaction, substrate composition, interactions with organic matter and sediment, input of magmatic volatiles).

Trends observed within bulk geochemical datasets obtained from deposits within a number of different active vent fields suggest that distributions of certain trace elements can be used as indicators of pH. For example, Ag/Fe correlates well with Zn/Fe in massive sulphide deposits from vent fields where vent fluid pH is low (<3.5 at 25°C). In contrast, Ag/Fe does not correlate well with Zn/Fe in massive sulphide deposits from vent fields where vent fluid pH is considerably higher (>4 at 25°C). The latter is consistent with wurtzite or sphalerite precipitating at higher temperatures from higher pH fluids and Ag remaining in solution, partitioning at lower temperatures into other sulphide minerals (e.g., pyrite and chalcopyrite). This behaviour, reported for Main Endeavour (high pH) versus Snakepit (low pH) vent fields (Tivey *et al.*, 1999), holds for many additional vent fields, e.g., those along the Eastern Lau Spreading Center. The consistency of these correlations to vent fluid pH suggests that detailed in situ chemical analyses may allow estimates of pH to be made within vent deposits (e.g., inside chimney walls).

### References

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## How to cool a supersaturated solution and 'watch' in real-time the nucleation and growth of silica nanoparticles?

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The mechanisms and kinetics of silica nanoparticle formation in natural environments has been the subject of extensive laboratory investigations, yet, silica polymerization was usually induced by lowering the pH to near neutral values where silica solubility is at a minimum. However, in natural systems (e.g., geothermal pools or deep-sea vents) silica polymerization and silica colloid formation is a result of rapid cooling of a supersaturated near neutral fluid. So far, experimental challenges to simulate natural geothermal processes precluded the quantification of the kinetics and mechanisms of silica nanoparticles formation from cooling hot fluids.

Here we present data from X-ray and light scattering experiments that followed the nucleation and growth of silica nanoparticles *in situ* and in real-time with the polymerization being induced by rapid cooling of a supersaturated silica solution. A novel flow-through geothermal simulator system that was designed to work on-line with a synchrotron-based Small Angle X-ray Scattering (SAXS) or conventional Dynamic Light Scattering (DLS) cell and detector system was used. Silica solutions ([SiO<sub>2</sub>] = 600 or 1'500ppm, and ionic strengths of 0.02 and 0.22) were equilibrated in this flow-through set-up to 230°C (all silica monomeric) and silica polymerization was initiated by continual rapid cooling of the flowing fluid to between 90°C to 20°C. This way the polymerisation of monomeric silica from a supersaturated hot spring fluid upon discharge at the Earth's surface was simulated. SAXS, DLS (and complementary cryo-TEM) data pertaining to changes in size and polydispersity of the nucleating and growing silica nanoparticles as a function of temperature, concentration and ionic strength will be discussed.