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Fluid Geochemistry at Depth:
What characterization techniques are best suited
to determine the geochemistry of fluids at depth?

I. Sampling challenges

• Sequence of deep borehole activities – who goes first? geochemistry? geophysics? hydrogeology? Careful planning is required

• If geochemical sampling does not have priority then sample integrity can be substantially compromised by other downhole measurements; borehole is already compromised by the effects of drilling; further perturbations must be avoided

• An important decision is how to collect the sample
  • bring it to the surface through a sampling line or
  • use in-line downhole sampling vessels
    • Has the advantage of keeping sample at T and P
    • Amount of gas separation can be measured and corrected on opening
    • Borehole must be large enough to accommodate several sampling lines and lines for inflating packers, T and P measuring devices, and several sampling vessels; equipment must work at 100-200°C
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I. Sampling challenges (cont’d)

• Substantial sources of contamination or chemical changes on sampling that must be avoided
  • Oxidation from air
  • Chemical changes from decrease in T and P
  • Mineral precipitation
  • Degassing
  • Water mixing from shallow to deep and vice versa
  • Drilling mud
  • Containment vessels and/or sampling lines (e.g. teflon, or something similar, other plastics will leach organics)
  • Microbial samples should be taken from water and from drillcores
  • Sterile equipment must be used for microbial sampling
Sampling with packers

Samplers – pumped or evacuated or not? evacuted, open, N₂ or Ar filled?

Swiss style gold standard – teflon-coated stainless steel vessels with remote-switch valves

Any device will have a higher probability of failure when T >150°C

Volume of sampling vessel must be large enough for small concentrations of radioisotopes (several Ls)
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II. Analytical challenges

• Samples must be kept under anoxic conditions (N\textsubscript{2} or Ar) continuously from depth to analysis for redox sensitive constituents
• Gases should be collected during degassing of samples at surface so that subsurface chemistry can be adequately reconstructed
• High salt concentrations can severely contaminate analytical instruments
• The samples have to be diluted for some constituents to be in the instrument working range
• When samples are diluted, some constituents go below their detection limits
• High salt concentrations can interfere with trace element determinations
• Some isotopic determinations also can experience interference at high salt concentrations
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What are the implications of the expected saline and reducing groundwater conditions at 3-5 km for solubilities of minerals and retardation factors of radionuclides?

• High salt and high sulfide concentrations along with high temperatures should greatly increase corrosion rates for most inexpensive metals comprising canister material.

• Chloride, sulfide, bicarbonate, and organic complexes can be expected to form and keep radionuclides and other metals dissolved and highly mobile.

• Quantitative predictions of mineral solubilities requires geochemical modeling suitable for high ionic strength solutions at elevated temperatures and pressures.
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Geochemical modeling challenges

- Thermodynamic properties of fluids, fluid chemistry, minerals, mineral solubilities, minerals that would uptake radionuclides are incomplete (missing some enthalpies, entropies and heat capacities)

- Only the Pitzer method and the SIT method are adequate to model water-rock interactions with high salinities or brines but the necessary specific ion interaction parameters are not all available, especially at high T and P; internal consistency of data is always an issue but less so with Pitzer and SIT; however there are several Pitzer or SIT databases to choose from and the internal consistency of any database must be evaluated for consistency

- Solid-solution data are important for uptake of radionuclides but only limited aqueous-solution/solid-solution properties are known; modeling is more qualitative than quantitative; numerous assumptions such as gas-solid-fluid equilibrium

- Retardation factors or distribution coefficients are too condition-specific to be helpful; mostly not known for situations involving brines
“Don’t mind him. As we take out the coal, he fills in the spaces with nuclear waste.”