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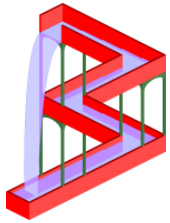
Fluid Geochemistry at Depth:

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

Fluid Geochemistry at Depth:
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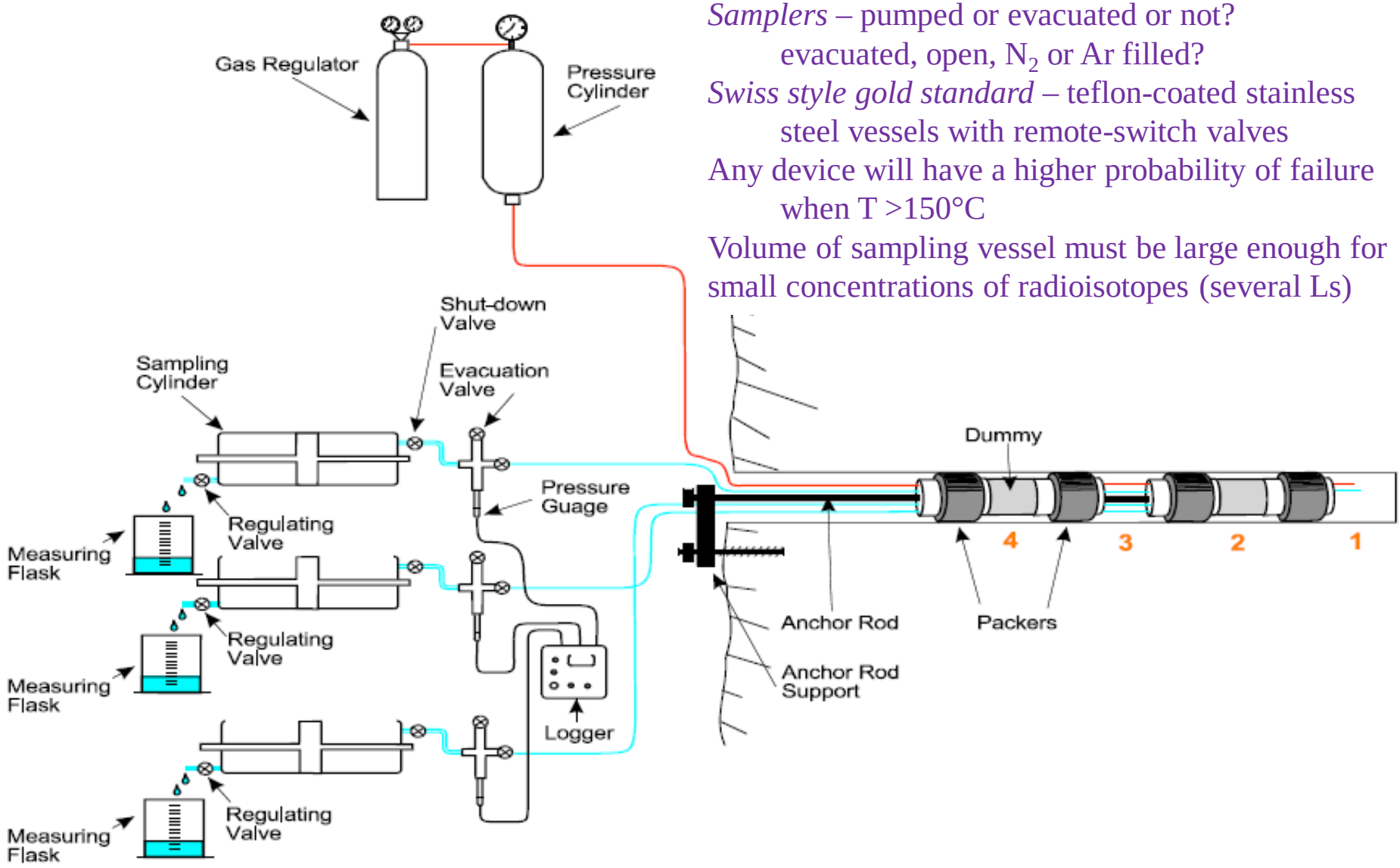
I. Sampling challenges (cont'd)

- 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?
evacuated, open, N_2 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)

Fluid Geochemistry at Depth.

II. Analytical challenges

- Samples must be kept under anoxic conditions (N_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

Fluid Geochemistry at Depth.

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

Fluid Geochemistry at Depth.

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."