Inorganic geochemical composition of Appalachian Basin formation waters – Preliminary examination

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Unlike many oil and gas producing basins in the U.S., inorganic geochemical data for Appalachian Basin formation waters are scarce. In a preliminary effort to characterize the formation waters, we have examined publically available data for five states: NY, PA, OH, WV, and KY, e.g. [1, 2]. The samples were obtained from oil/gas wells producing from Pennsylvanian – Cambrian age reservoirs, with the majority of samples taken from reservoirs of Devonian and Silurian age. The median salinity is ~250, 000 ppm TDS (total dissolved solids), and values range to nearly 400, 000 ppm. Piper diagrams show that the waters are predominantly Na-Cl type, with Na/Ca mole ratios of >3; concentrations of K, Mg, SO_4, and HCO_3 are comparatively minor. Cl/Br and Na/Br ratios in samples from eastern Ohio indicate that evaporative seawater concentration was the dominant salinity source, rather than dissolution of evaporites. Although, thus far, we lack the Br analyses needed for a similar investigation of the formation waters from the other states, strong similarities in total salinity, Na/Ca, and other major element ratios across the data sets suggest a common origin for the brines.

Additionally, we examined fluid inclusion salinity data published in studies of MVT (Mississippi Valley type) ore deposits (commonly of Late Paleozoic age) within and at the margins of the Appalachian Basin. Fluid inclusions preserve microscopic samples of formation fluid trapped during the growth of the host crystal. The inclusion fluids are similar to the formation waters in several ways: 1) high total salinities, generally 150, 000–350, 000 ppm TDS, 2) Na-Cl type fluids with Na/Ca ratios similar to those of the formation water samples, and 3) Cl/Br ratios indicative of surface evaporative concentration of seawater as the salinity source. These observations suggest that highly saline formation waters in the Appalachian Basin might be remnants of Paleozoic connate fluids. Unravelling their history may help in predicting the distribution of brines within the basin.

[1] Sanders (2001) *AAPG Bull.* **75**, 1593-1608. [2] Breit (2002) http://energy. cr. usgs. gov/prov/prodwat/index. htm.

Climate sensitivity to atmospheric CO_2 during the Phanerozoic

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The equilibrium temperature response to doubled atmospheric CO_2, a common measure of climate sensitivity, provides a wealth of information about the climate system because it integrates a wide variety of climate feedbacks such as clouds and other greenhouse trace gases. In deep geologic time, over Myr timescales, an equilibrium temperature response includes additional feedbacks, for example the waxing and waning of ice sheets and the chemical weathering of silicate minerals. This long-term climate sensitivity is sometimes called Earth system sensitivity. In an earlier study, we calculated an average Earth system sensitivity of 2.8 °C per CO_2 doubling for the past 420 Myrs. This was done by minimizing the misfit in CO_2 between proxy records and GEOCARBSULF, a long-term carbon- and sulfur-cycle model that includes Earth system sensitivity as a parameter. However, because a single mean value was calculated, it was not clear whether Earth system sensitivity was constant or variable during the Phanerozoic. We will report an extension of the earlier study using an updated CO_2 proxy data set and carbon cycle model (GEOCARBSULFVOLC) to calculate a more finely-resolved record of Earth system sensitivity (~50 Myr time slices). In particular, we focus on potential differences in sensitivity during glacial and non-glacial times. We will compare with independent estimates of Cretaceous and Cenozoic Earth-system sensitivity that correlate proxy estimates of CO_2 and tropical sea surface temperature.