Ca^{2+} and HCO_3^- concentrations in some natural waters II: observations

The plot in Part I of this set of pages shows the Ca^{2+} and HCO_3^- concentrations of some natural waters from different settings. The vertical axis is $HCO_3^- + CO_3^{2-}$ because dissociation of HCO_3^- becomes significant at high pH. Some noteworthy observations are . . . . .

1. The scale is logarithmic, and thus the plot represents a huge range of concentrations.

2. Dilute waters fall largely on a trend extending from rainwater toward greater concentrations of Ca^{2+} and HCO_3^-. That's not surprising if those dilute lake waters, stream-and-river waters, and groundwaters originate as rain water and acquire Ca^{2+} and HCO_3^- as the result of weathering of bedrock. That trend parallels, but is on the HCO_3^- -rich side, of the 1:1 molar line, which is again not surprising because chemical weathering that yields HCO_3^- as the conjugate base of H_2CO_3 liberates other cations in addition to Ca^{2+}.

3. The saline lakes fall in a diagonal band (the blue field) that is dictated by equilibrium with precipitation of calcite and by equilibrium exhange of CO_2 with Earth's atmosphere.

4. The largest bodies of saline surface water (the ocean and the largest salt lakes) are near the middle of the plot and near the end of the trend for dilute waters. On the other hand, ...

5. Smaller saline lakes plot across a vast swath of the diagram, from very HCO_3^--and-CO_3^{-2-} rich (very alkaline) and Ca^{2+}-poor at the upper left to the opposite (very Ca^{2+}-rich and HCO_3^--poor) toward the lower right. That suggests that lake chemistries take odd turns of fate. Some (increasingly to the upper left) have sufficiently little Ca^{2+} that, as the concentration of HCO_3^- increases with evaporation but the product of Ca^{2+} and HCO_3^- is held constant by

$$K_{sp\text{-}calcite} = a_{HCO_3^-} \times a_{Ca^{2+}}$$

Ca^{2+} is driven to virtually zero. Others (increasingly to the lower right) go the opposite route and have so much Ca^{2+} relative to HCO_3^- that, as Ca^{2+} increases with evaporation, the concentration of HCO_3^- is driven down to a small value. That thinking follows from the model of Hardie and Eugster (1970).

The imbalance of Ca^{2+} and HCO_3^- suggests, in the case of Ca^{2+}-poor and HCO_3^--rich waters, drainage basins with slilicate rocks containing little Ca^{2+}. Such rocks might be rich in alkali feldspars, as in syenites and trachytes. The opposite case, that of Ca^{2+}-rich and HCO_3^--poor waters, suggests drainage basins rich in Ca^{2+}-bearing minerals whose weathering doesn't produce HCO_3^-, such as anhydrite.

6. In the context of Observation 5, seawater and the waters of the largest saline lakes are among those saline waters that have *not* gone off into the wilds of tremendous imbalance of Ca^{2+} and HCO_3^-. That may be because they are the drainage waters of very large basins (in the case of seawater, the drainage water of the whole world), and so they drain basins unlikely to be atypical in their general geology - for example, unlikely to be dominated by trachytes or anhydrite.

7. Almost all of the saline lakes are supersaturated with respect to calcite, and some of them are strikingly so.

8. Deep brines reach equilibrium with calcite at lower values of pH because (a) non-release of CO_2 makes them more acidic but (b) large concentrations of Ca^{2+} nonetheless maintain equilibrium with calcite and thus depress a_{CO3} and a_{HCO3}.

9. Groundwater evolves to greater Ca^{2+} and HCO_3^- concentrations as it evolves from recharging rainwater to progressively deeper groundwater (see Part 1a). That's true regardless of the nature of the bedrock through which the water moves, because weathering of silicates produces HCO_3^- as the conjugate base of H_2CO_3.

Sources:
Saline lakes: Drever (1997) citing Hardie & Eugster (1978);
Brine in Jurassic carbonates: Moldovanyi & Walter (1992);
Brines in Silurian carbonates: Wilson & Long (1993);
Brines in Cretaceous carbonates of Texas: Land & Prezbindowski (1981);
Georgia groundwater: Data set of Railsback et al. (1996);
Freshwater lakes, rivers, and streams: Livingstone (1963).