Using ^{222}Rn, water isotopes and major ions to investigate a large alpine through-flow lake

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Session 22a. Tracing Groundwater Variability

Geochemical and isotopic tracers in groundwater and surface water studies in montane catchments have become increasingly popular because monitoring wells are often sparse and terrain is complex (e.g. fractures and folds), which makes physical hydrogeologic methods difficult to characterize quantitatively. In this study several geochemical tracers (^{222}Rn, δ^2H, δ^{18}O, and major ions) were collected spatially in Georgetown Lake, Granite County Montana, a large montane lake with a surface area of 1489 ha. The geochemistry of nearby precipitation, surface water, and groundwater was also characterized to assess the chemistry of source waters mixing with the lake. Physical and chemical measurements were used to i) construct a water balance for the lake, ii) characterize groundwater flow locations and amounts with the lake, and iii) develop a conceptual model for geologic controls on groundwater-lake interactions. Stable isotopes were used in an endmember mixing analysis to separate the relative fractions of source waters mixing with the lake, a physical water budget was used to quantify the difference between groundwater inflows and outflows, and a radon mass balance was used to characterize the groundwater flow locations and amounts to the lake.

Results from the stable isotopes show three endmembers mix with the lake. They are precipitation (39%), groundwater (26%), and a strongly evaporated endmember (35%). The evaporated endmember is most likely groundwater and/or surface water that later evaporated after entering the lake. The physical water budget suggests little difference between groundwater inflows and outflows, but could not be used to quantify groundwater inflow or outflow amounts. The radon mass balance suggests that groundwater inflows to the lake are substantial. Based on the physical water budget, this implies that groundwater outflows are also significant and the lake is a through-flow lake. Radon measurements also show that nearly all of the groundwater inflows occur along the eastern side of the lake, which is underlain by carbonate bedrock. The western portion of the lake (~75% area) is underlain by western dipping Precambrian metasedimentary bedrock. The steep dip and limited groundwater elevations suggest that the western portion of the lake is losing. It appears that groundwater enters through fractures, caverns, and shallow alluvium from the carbonates, and groundwater exits through the western dipping bedding planes and fractures in the metasedimentary rocks.

The use of ^{222}Rn for determining groundwater discharge locations and amounts provides a simple, but crucial, method for developing the conceptual model in this study. The spatial measurements of ^{222}Rn elucidate groundwater interactions that could not be assessed by geology, water levels and physical water budgets alone. Even conservative water isotope mass balances were limited in characterizing the nature of groundwater-lake interactions.

The crystallization of Amorphous Calcium Carbonate (ACC), and the effects of magnesium and sulfate

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Many organisms use transient ACC during biomineralization, as a means to control the particle shape/size and structure (e.g. calcite, aragonite or vaterite) of the crystalline calcium carbonate formed. For example, sea urchin larvae produce highly elongated single crystals of calcite by the controlled deposition and transformation of ACC [1]. Organisms also adjust or control the crystallization pathway using inorganic ions, organic molecules and/or membrane structures. Resolving the mechanisms and kinetics of ACC crystallization in abiotic systems, and evaluating the role of inorganic additives (e.g. Mg and SO_4) is key to underpinning our understanding of biologically-controlled calcium carbonate formation. In particular, the pathway of crystallization from disordered hydrated ACC to fully crystalline calcite needs to be quantified.

Using *in situ* small and wide angle X-ray scattering (SAXS/WAXS) at fast time resolution (1 sec.) we studied the crystallization of ACC to vaterite/calcite in the absence and presence of variable Mg and SO_4 concentrations. We show that pure ACC crystallizes via a multi-stage process [2]. Firstly, hydrated and disordered ACC forms, then rapidly transforms to more ordered and dehydrated ACC; in conjunction with this, vaterite forms via a spherulitic growth mechanism. This is followed by Ostwald ripening of the vaterite particles, and finally transformation to calcite via a surface controlled growth mechanism. The presence of Mg in ACC significantly reduced the rate of crystallization and led to the direct formation of calcite (Mg = 10%), or various Ca-Mg-CO_3 polymorphs (Mg > 10%), including monohydrocalcite and dolomite (T>60°C) [3]. The presence of SO_4 did not alter the overall ACC crystallization mechanism, but reduced the rate of vaterite nucleation, growth and ripening due to surface adsorption [2]. Also, SO_4 dramatically increased the stability of vaterite compared to the pure system (i.e. stable for hours/days).

These results provide a comprehensive mechanistic description of the abiotic ACC crystallization pathway, with the final crystalline product being controlled by the initial ACC composition (e.g., Mg or SO_4 content). These abiotic crystallization mechanisms are similar to those observed in marine organisms [1], where it has been shown that secondary calcite nucleates within ACC, a process comparable to the secondary (vaterite) and tertiary (calcite) nucleation and growth observed in our systems.

[1] Killian *et al.* (2009) *J. Am. Chem. Soc.* **131,** 18404-18409. [2] Bots *et al* (2012) *J. Am. Chem. Soc* (Submitted). [3] Rodriguez-Blanco et al (2012a,b) *Geochim. Cosmochim. Acta*. (In Review)