Regional evaluation of catchment-scale weathering: surface-water chemical indicators of lithology, and mechanical and biological effects

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In central Colorado, USA, samples were collected from 227 alpine streams between 2004 and 2007 [1] to evaluate the effects of catchment lithology on stream-water chemistry, aquatic communities, and weathering mechanisms. The study area, about 55,000 km^2, includes catchments with a variety of lithologies. The area also includes zones of hydrothermal alteration which have added metals such as Zn, Pb, Cu, Cd, Au, and Ag to the rocks. Abandoned mines in some of the catchments have introduced these metals to the weathering environment.

In altered and mined catchments, rapid weathering of sulfide minerals such as pyrite dominates the aqueous geochemical signature (low pH and high metal and SO_4 concentrations). In unaltered and unmined catchments, catchment lithology determines certain aspects of stream-water quality, including pH, salinity, and relative and absolute concentrations of major and trace elements. Dissolved Ge concentrations are greater in streams draining certain lithologic groups, including the Pikes Peak Granite, although secondary chemical effects, such as the relation between Ge and F, are possible. Prior studies of Ge/Si systematics in lithologically homogeneous areas like Hawai'i [2] have traced weathering processes, but in this study lithologic effects appear to play a stronger role in Ge variations.

Average catchment slope was calculated using GIS software. Steeper slopes likely promote exposure of fresh mineral surfaces because of mechanical processes and decreased soil and vegetation. Across a wide range of lithologies, our data show a small ($r^2 = 0.08$) but significant ($p<0.01$) increase in average weathering rate with increased slope. The effect is greater in catchments with hydrothermal alteration and historical mining.

Benthic macroinvertebrates (n=153) were collected in 125 streams to evaluate effects of trace-metal concentrations on insect abundance and diversity. As metal concentrations increase, sharp drops in diversity and abundance are observed, beginning at lower metal concentrations than were previously reported [3], and likely the result of synergistic effects of several metals on stream biota.

[1] Wanty, Verplanck, SanJuan, Church, Schmidt, Fey, DeWitt, Klein (2009) *App. Geochem.* **24**, 600-610. [2] Kurtz, Derry, Chadwick (2002) *Geochim. Cosmochim. Acta* **66**, 1525-1537. [3] Schmidt, Clements, Mitchell, Church, Wanty, Fey, Verplanck, SanJuan (2010) *Env. Tox. Chem.* **29(11)**, 2432-2442.

Isotopic and geochemical evidence for the natural migration of Marcellus-like brine to shallow drinking water in northeastern Pennsylvania

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The recent increase in production of natural gas from the unconventional shales of the Appalachian Basin represents an important new energy resource. But the drilling and hydraulic fracturing processes required to obtain the gas have generated an increased concern over possible contamination of shallow drinking water resources [1]. Reports of shallow groundwater contamination caused by natural gas drilling are often dismissed based on the large vertical separation between the shallow drinking water wells and the shale-gas formations. Assessing the possible risk to shallow drinking water hinges on the hydraulic connectivity between the shale gas formations and the overlying aquifers.

In this study, we analyze the geochemistry of water samples from three principle aquifers, Catskill, Lockhaven, and Alluvium located across six counties of northeastern Pennsylvania (NE PA). We hypothesize that a detailed analysis of major (Br, Cl, Na, Ba, and Sr) and trace (Li) element geochemistry, coupled with utilization of a specific spectrum of isotopic tracers ($^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$), could provide evidence of potential hydraulic connections between shallow drinking water aquifers and deep formation waters from the Marcellus or other deep formations. Findings suggest that mixing relationships between a fresh, shallow groundwater and a Marcellus-like brine could cause the groundwater salinization observed in some locations of NE PA. The occurrence of the saline water does not appear to be correlated with the location of shale-gas wells and the same water type was reported prior to the recent and rapid shale-gas development in the region [2]. However, the presence of these pathways could suggest specific areas in NE PA where shallow drinking water resources are at greater risk of contamination with deeper formation brines and gases during drilling and hydraulic fracturing of shale gas.

[1] Osborn *et al.* (2011) *PNAS* **108**, 8172-8176. [2] Williams, Taylor and Low (1998) *Pennsylvania Department of Conservation and Natural Resources* **Water Resources Report 68**, 1-89.