Strontium Isotopic Signatures of Flowback and Co-Produced Waters Associated with Marcellus Shale Natural Gas Extraction, Pennsylvania

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A byproduct of natural gas extraction from shales of the Middle Devonian Marcellus Formation is flowback and co-produced water from hydraulic fracturing, often with high levels of total dissolved solids (TDS) that present a major challenge to gas producers and regulators (Blauch et al, 2009, SPE 125740). Determining the source of these dissolved salts, whether from the shale itself or associated saline aquifers, and understanding local and basinal variations in TDS have direct relevance to exploration methodologies and water management and reclamation. Another important concern involves verification of the safe and environmentally benign disposal of this high-TDS water; any increase in TDS of ground or surface waters can potentially be attributed to Marcellus flowback leakage or improper disposal. We have initiated a strontium (Sr) isotope study of Marcellus flowback and co-produced waters to (1) determine the source of dissolved salts that are abundant and ubiquitous in Marcellus waters; and (2) identify unique isotope "fingerprints" of Marcellus waters to aid in verification of safe disposal.

In order for the isotope ratio of strontium to be used successfully as a natural tracer in ground and surface waters, the isotope ratios ($^{87}Sr/^{86}Sr$) of the potential endmembers must be distinct. Our previous work on flowback from a series of wells in Bradford County, northern Pennsylvania, demonstrated a tight clustering of $^{87}Sr/^{86}Sr$ ratios from 0.7103 to 0.7108 (Chapman et al., 2011, NE-NC Sect. GSA Abstr. Prog 43 no.1:76). Additional work has expanded the geographic range to southwestern Pennsylvania. Flowback and co-produced samples from the southwestern-most counties (Greene and Washington) expand the range of values slightly to 0.7101-0.7111, while a subset from adjacent Westmoreland County cluster at distinctly higher values (0.7120-0.7121). Other fossil-fuel-related fluids that could introduce dissolved solids into streams include coal mine drainage, coal fly ash disposal ponds, and brines from shallow abandoned gas wells that are common throughout the Marcellus exploration area, such as those that tap upper Devonian Venango Group. Strontium isotope data from these sources over a wide geographic and stratigraphic range indicate that most are isotopically distinct from Marcellus waters, and that influxes from these sources at any given location tend to fall within a fairly restricted range. These data, when combined with the extreme concentrations of Sr in flowback waters (up to 5,000 mg/L), demonstrate that the Sr isotope ratio is likely to be an extremely sensitive tracer that can be used for verification of safe flowback water disposal.

The $^{87}Sr/^{86}Sr$ ratios of Marcellus waters measured here fall well above Phanerozoic seawater values (Burke et al., 1982, Geology 10:516-519). Thus, while the Marcellus brines may have a significant seawater component, this has clearly been augmented by a more radiogenic source, possibly originating from dissolution of minerals within the shale itself. The bimodal clustering of flowback values so far identified in this study could be a result of gas (and water) production from different members of the Marcellus Formation. Ongoing leaching studies of Hamilton group core material is addressing the detailed origins of the high TDS in flowback and co-produced waters and have potential application to exploration methodologies as well as reduction of environmental risks.