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The strontium isotopic evolution of Marcellus Formation produced waters, southwestern Pennsylvania

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ABSTRACT

The production of natural gas and natural gas liquids from unconventional tight shale formations involves hydraulic fracturing and subsequent removal of fluids co-produced with the gas. The chemistry of the returning fluid reflects the original composition of the injection water, mobilized constituents in the shale formation, and co-mingled formation waters liberated by hydraulic fracturing. Produced water from unconventional gas wells tapping the Middle Devonian Marcellus Formation is characterized by high total dissolved solids (TDS), including very high strontium concentrations. In this study, the strontium isotope composition ($^{87}Sr/^{86}Sr$) was measured in produced waters from four horizontally drilled, hydraulically fractured Marcellus shale gas wells in southwestern Pennsylvania, sampled from the first day after commencement of flowback to as much as 27 months later. The $^{87}Sr/^{86}Sr$ of the waters tended to change rapidly over the first few days of water return, and then approached (but did not reach) a constant range of values from 0.7113 to 0.7114, which appears to be characteristic of this part of the Marcellus play. In contrast, the concentration of Sr rose more slowly and appeared to hit a steady state value (up to 3000 mg/L) by the end of the first year. Taken together with results from earlier work, these data suggest mixing between injected frac fluid and high-TDS formation water, highly enriched in Sr, and isotopically relatively uniform throughout the Marcellus shale gas play. This brine could exist within porous lenses of organic matter in the shale, in pre-existing fractures within the shale, and/or originate from fluids that migrated from adjacent formations at some point during the post-depositional history of the basin.

1. Introduction

Development of the Appalachian Basin Marcellus Shale, now one of the world's largest natural gas plays, was made possible by the successful application of directional drilling and hydraulic fracturing (Engelder and Lash, 2008; Milici and Swezey, 2006; Soeder et al., in this issue). Unconventional drilling techniques involve the use of millions of liters of water, combined with drilling fluids (slickwater, composed primarily of water with proppants and chemical additives; Gregory et al., 2011) that is pumped down into the well. Most of this fluid remains in the formation, but when the pressure is released, some fluid flows back out of the well, initially at a high rate (up to 1000 m^3/day; GWPC and ALL Consulting, 2009), then slowing down over the life of the well. The initial fluid is sometimes referred to as flowback; in this paper, all of the post-hydraulic fracturing fluid returned from the well is referred to as produced water, and identified by date collected and source (tank or gas–water separator). This returned water is high in total dissolved solids (TDS); produced water from unconventional Marcellus shale gas wells ranges from 30,000 to over 300,000 mg/L TDS and is high in constituents such as sodium (Na), calcium (Ca), chloride (Cl), barium (Ba) and Sr (Blauch et al., 2009; Hayes, 2009), and there is evidence for spatial variations in geochemistry across the basin (Barbot et al., 2013; Chapman et al., 2012; Dresel and Rose, 2010; Haluszczak et al., 2013; Hayes, 2009; Poth, 1962). To comply with regulations, produced water is collected at the well site and either recycled for other hydraulic fracturing ("frac") jobs, disposed of in deep injection wells, or sent to brine treatment plants (Shaffer et al., 2013).

Although the success of unconventional gas development has radically changed the energy portfolio of the US and other countries, environmental concerns regarding these high TDS fluids have arisen (U.S. Environmental Protection Agency, U.S. EPA, 2011); one area involves surface water quality, including the impact of increased total suspended solids (TSS) related to shale gas waste treatment

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(e.g., Entrekin et al., 2011; Olmstead et al., 2013; Rozell and Reaven, 2012), and potential generation of drinking water contaminants related to bromine released by wastewater treatment plants (Warner et al., 2013; Wilson and Van Briesen, 2012, 2013). Another issue involves subsurface mobility and the potential for hydraulic fracturing-induced migration of methane and brines to shallower aquifers via conduits such as subsurface faults and fractures or compromised well casings. While hydraulic fracturing-related migration of methane from the Marcellus shale into shallow aquifers has been suggested (e.g., Osborn et al., 2011), the presence of thousands of shallow Upper Devonian gas wells and high background levels of thermogenic methane in some areas makes identification of its source and origin difficult (Baldassare et al., 2013; Molofsky et al., 2013; Révész et al., 2010). In addition, the potential for hydraulic fracturing to cause groundwater contamination by upward migration of Marcellus shale-related brines remains controversial (e.g., Engelder, 2012; Myers, 2012a,b; Saiers and Barth, 2012; Vengosh et al., 2013; Warner et al., 2012a,b). Accidental spills and improper disposal of brine and fluids related to both conventional and unconventional gas production have the potential to contaminate surface and ground water with barium, radium, bromine and other constituents from deep brine and injected fluids. These concerns highlight the need for research that improves our understanding of the source, composition, and long-term evolution of subsurface brines from unconventional shale gas wells, and for sensitive methods that can discriminate between multiple potential contaminant sources in areas affected by over a century of legacy mining and hydrocarbon exploration.

1.1. Application of Sr isotopes

Strontium consists of four natural isotopes with atomic masses 84, 86, 87, and 88; ^{87}Sr is produced by the decay of ^{87}Rb. The $^{87}Sr/^{86}Sr$ ratio has been used as a chemostratigraphic tool, as a tracer of water–rock–soil interactions, and to identify sources of ground and surface water contamination (e.g., Banner et al., 1994; Bayless et al., 2004; Capo et al., 1998; Keating et al., 2011; Leung and Jiao, 2006; Stewart et al., 1998; Vinson et al., 2011). Sr isotopes have also been used to track the interaction of coal mine discharges (AMD), coal fly ash and coalbed methane produced waters with the environment (e.g., Brinck and Frost, 2007; Brubaker et al., 2013; Frost et al., 2002; Hamel et al., 2010; Sharma et al., 2012; Spivak-Birndorf et al., 2012). Strontium isotope ratios can be expressed using ε_{Sr}^{SW} notation, where the $^{87}Sr/^{86}Sr$ ratio of the sample is normalized to the globally uniform $^{87}Sr/^{86}Sr$ ratio of present-day seawater:

$$\varepsilon_{Sr}^{SW} = 10^4 \left(\frac{^{87}Sr/^{86}Sr_{sample}}{^{87}Sr/^{86}Sr_{seawater}} - 1 \right).$$

Strontium isotopic ratios of produced waters collected from Marcellus shale gas wells over a geographic range of ~375 km across southwestern to northeastern Pennsylvania define a relatively narrow set of values (Chapman et al., 2012). Our results to date indicate that this range ($\varepsilon_{Sr} = +14$ to $+42$; $^{87}Sr/^{86}Sr = 0.7101–0.7121$) is distinct from most western Pennsylvania acid mine drainage and from Upper Devonian (Venango and Bradford) oil and gas units (Fig. 1).

These data suggest that Sr isotope ratios can be a sensitive natural tracer of the source of surface or groundwater contamination in areas potentially affected by AMD, fly ash, or produced waters from legacy Upper Devonian gas wells or unconventional Middle Devonian Marcellus wells. For example, Sr isotope analysis of contaminated discharges from a series of abandoned gas wells in western Pennsylvania indicated that they resulted from the interaction of AMD with siderite-cemented aquifers, and that there was no upward migration of Upper Devonian oil and gas brines (Chapman et al., 2013). This demonstrated the capability of Sr isotopic analysis to differentiate between coal- and oil/gas-related inputs (e.g., shallow AMD vs. deep brines) into natural waters, and to distinguish between mineralogically identical but stratigraphically different sources of dissolved Sr in subsurface waters.

Because Marcellus Formation produced waters can have Sr concentrations that are an order of magnitude greater than those of the Upper Devonian waters in this region, the Sr isotopic composition of the latter ($\varepsilon_{Sr} = +151$ to 166; $^{87}Sr/^{86}Sr$ 0.7199–0.7209; Kolesar et al., 2013) is sensitive to small (<1–2%) intrusions of the former. Comparison of $^{87}Sr/^{86}Sr$ of water samples from local spring water and active conventional Upper Devonian gas wells (>3000 ft above the Marcellus shale and ~2000 ft below freshwater aquifers) spanning a period of six months before to four months after hydraulic fracturing of horizontal Marcellus gas wells in the same area did not indicate migration of Marcellus-derived fluids into local groundwater or the Upper Devonian wells (Kolesar et al., 2013).

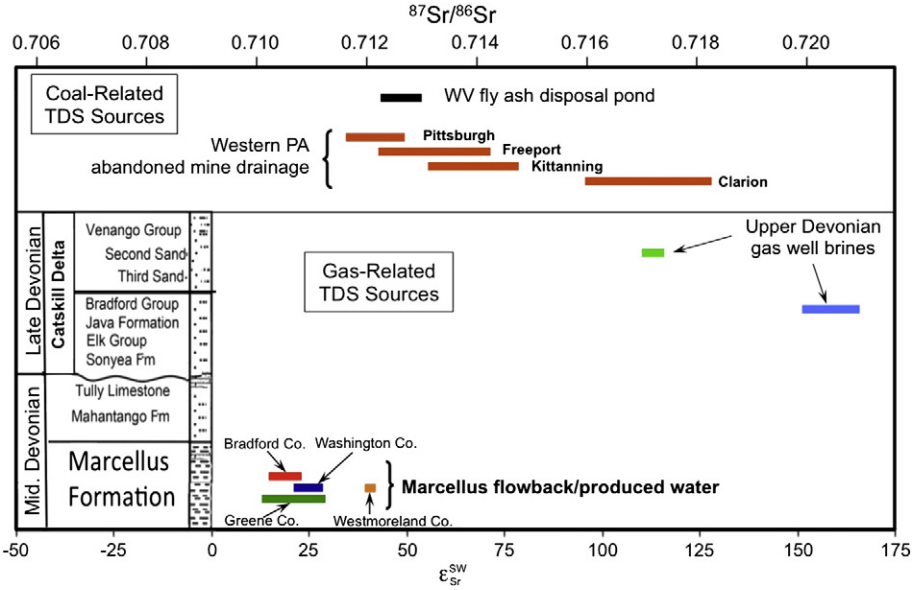

Fig. 1. Comparison of Marcellus Formation Sr isotope ratios with those of other TDS sources in western Pennsylvania, modified from Chapman et al. (2012). Upper Devonian brine data are from Chapman et al. (2013) and Kolesar et al. (2013).