



Rapid desorption of radium isotopes from black shale during hydraulic fracturing. 1. Source phases that control the release of Ra from Marcellus Shale

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ABSTRACT

Hydraulic fracturing of the Marcellus Shale produces wastewaters that are hypersaline and highly enriched in isotopes of radium. Radium is understood to derive from the Marcellus Shale itself, but its source phases and their contributions to wastewater production have not been described. Using sequential extractions and experimental leachates, we characterize two distinct end-members that could contribute Ra to wastewaters, (1) a mineral phase, which hosts *labile* ²²⁸Ra and has ²²⁶Ra/²²⁸Ra atom ratios ~250, and (2) an organic phase, which hosts *exchangeable* ²²⁶Ra and has ²²⁶Ra/²²⁸Ra ~10,000. In leaching experiments we observed rapid extraction of Ra from these phases, with high ionic strength solutions leaching up to 14% of Ra from the shale in just hours. Radium concentrations and ²²⁶Ra/²²⁸Ra ratios increase with [Ca²⁺] of the leaching solution, and solutions approaching 1 M Ca²⁺ produce ²²⁶Ra/²²⁸Ra ratios compatible with Marcellus wastewaters. In contrast, pure water removes < 0.5% of Ra from the shale with low ²²⁶Ra/²²⁸Ra ratios incompatible with wastewaters. Experimental results and wastewater data together provide a coherent picture, that the distinctive Ra isotopic signature of Marcellus wastewaters results from contemporaneous water-rock interactions that promote desorption of ²²⁶Ra from organics during hydraulic fracturing.

1. Introduction

Production of natural gas from black shales such as the Devonian Marcellus Shale by high-volume hydraulic fracturing (HVHF) requires the injection of 5 to 15 million liters of water, sand and chemicals into a well bore that has been drilled down and then horizontally for kilometers through the host rock. The pressurized mixture of fluid and sand fractures the shale and allows natural gas to flow to the surface. About 60–90% of injected water is imbibed by the fractured formation (Engelder, 2012; Engelder et al., 2014), but the remainder returns to the surface as wastewater¹ once pressure has been relieved at the wellhead. The wastewater, is saltier than seawater by a factor as high as 20–40 (Vidic et al., 2013; Rowan et al., 2015) and highly enriched in isotopes of radium (Haluszczak et al., 2013; Rowan et al., 2011, 2015; Warner et al., 2013), thus requiring regulation and handling as hazardous material with limited treatment and disposal options (Gregory et al., 2011; Lutz et al., 2013; Vengosh et al., 2014).

Developing strategies to mitigate wastewater production ultimately

requires a comprehensive understanding of its production. Geochemical trends over the duration of wastewater flowback provide some insight into this problem. Major element concentrations and total salinity (Hayes, 2009; Haluszczak et al., 2013; Rowan et al., 2015), as well Ra concentration (Rowan et al., 2011, 2015), increase continuously with time during wastewater flowback, prompting interpretations that wastewater is produced when injected fluids mix with Na-Ca-Cl formation water (brines) within either the fracture network (Haluszczak et al., 2013; Rowan et al., 2011; Engle and Rowan, 2014; Kondash et al., 2017) or shale pore network (Balashov et al., 2015). Deep brines found throughout the Appalachian Basin and in formations adjacent to the Marcellus Shale share a common Na-Br-Cl brine signature with Marcellus wastewaters (Haluszczak et al., 2013; Engle and Rowan, 2014) and are frequently enriched in radium (Dresel and Rose, 2010). However, Marcellus wastewaters are orders of magnitude higher in both total Ra concentration (= [Ra]) and ²²⁶Ra/²²⁸Ra isotopic composition versus other Appalachian Brines. Median [Ra] are 450 pg L⁻¹ for brines and 4550 pg L⁻¹ for Marcellus wastewaters, with ²²⁶Ra/²²⁸Ra = 250

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¹ Hydraulic fracturing industry describes these waters as flowback when recovered before gas production commences, and produced water after production; collectively we term them wastewaters as they cannot be discharged to the environment or waste facilities without treatment.

for brines and 1848 for wastewaters (see our companion paper, Landis et al., 2018). Ra isotopes thus provide strong evidence that Ra in hydraulic fracturing wastewater originates from within the Marcellus Shale itself (Rowan et al., 2015).

The Marcellus Shale is highly enriched in uranium due to its high organic content (Leventhal et al., 1981), and thus has both high ^{226}Ra concentrations and high $^{226}\text{Ra}/^{228}\text{Ra}$ ratios that distinguish it from other lithologies in the basin. Moreover, short half-lives of ^{226}Ra (half-life 1600 years) and ^{228}Ra (half-life 5.8 years) require that their occurrence in wastewater is supported by contemporary radioactive decay from U and Th-bearing solids within the shale. Half-life restrictions thus provide assurance that $^{226}\text{Ra}/^{228}\text{Ra}$ ratios in wastewaters reflect those of Ra source phases, and may thus provide insights into mechanisms of Ra extraction and wastewater production. However, while constituent phases of Marcellus Shale must constitute the principal sources of wastewater Ra, the nature of these phases and the timescale over which they contribute Ra to wastewaters are not yet known.

Limited available data, provided by Rowan et al. (2011, 2015), yield some insight into Ra behavior, showing that in measurements reported for a single well over a year, [Ra] is positively correlated with total dissolved solids (TDS) in wastewater (Fig. 1a). Significantly, in these data we find a stronger relationship between the ratio of divalent to monovalent cations $[\text{Ca}^{2+}]/[\text{Na}^+]$ versus [Ra] (Fig. 1b). The strength of this relationship underscores the importance of $[\text{Ca}^{2+}]$ ion exchange reactions that are likely to control Ra release from the shale, a behavior which is well documented for Ra in aquifers (Sturchio et al., 2001). We have attributed similar behavior to Ba in wastewaters (Renock et al., 2016). Intriguingly, the $^{226}\text{Ra}/^{228}\text{Ra}$ ratios for time-series data reported by Rowan et al. (2011, 2015) also increase with $[\text{Ca}^{2+}]/[\text{Na}^+]$ in systematic, temporal trends (Fig. 1c). The strength of this relationship suggests a specific role of Ca^{2+} in regulating release of Ra isotopes from different sources within the shale during flowback. Since wastewater samples integrate a fracture network with a path-length of several tens of km (Hammack et al., 2014), increasing wastewater $^{226}\text{Ra}/^{228}\text{Ra}$ ratios likely reflect release of ^{226}Ra over ^{228}Ra from the shale in response to increasing ionic strength and Ca^{2+} concentration of water, rather than variation among U/Th ratios of shale facies. Water-rock reactions may thus play a significant role in regulating wastewater [Ra] and $^{226}\text{Ra}/^{228}\text{Ra}$ isotopic composition.

These observations raise a key question: what are the sources in Marcellus Shale that control release of Ra? We sought to answer this question by measuring [Ra] and $^{226}\text{Ra}/^{228}\text{Ra}$ isotope ratios in drill core samples of Marcellus Shale, and in sequential extractions and experimental leachates at both low and high pressures similar to those

generated during hydraulic fracturing. We first use sequential extraction data to describe source phases of ^{226}Ra and ^{228}Ra in the shale, to provide a basis for understanding Ra that may be leachable during wastewater production (Section 4.2). We then focus on the susceptibility of Ra to leaching from aqueous solutions under conditions similar to those produced by hydraulic fracturing (Section 4.3). We next characterize the organic phase of Ra in the shale, due to its importance in hosting ^{226}Ra and in driving the distinctive $^{226}\text{Ra}/^{228}\text{Ra}$ composition of Marcellus Shale and wastewaters (Section 4.4). Finally, we discuss how Ra host phases may promote extraction of Ra from the shale (Section 5).

2. Background

Radium isotopes ^{226}Ra and ^{228}Ra are produced through radioactive decay of ^{238}U and ^{232}Th , respectively. In rocks that have remained a closed-system, the decay rates (activities) of each parent-daughter pair converge over ~ 6 half-lives of the daughter radionuclide to reach a condition of secular equilibrium. Marcellus Shale, like other black shales, displays high bulk U/Th ratios due to preferential binding of U to organic matter (Leventhal et al., 1981). Based on reported U/Th ratios, bulk shale has distinctly high $^{226}\text{Ra}/^{228}\text{Ra}$ atom ratios as high as 10,000, which greatly exceed crustal average of about 250 (Fig. 2). Here we present $^{226}\text{Ra}/^{228}\text{Ra}$ atom ratios, which may be converted to $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio using the following relation, $A = N\lambda$ so that $A_{228}/A_{226} = (N_{228}/N_{226})(\lambda_{228}/\lambda_{226})$, and $\lambda_{228}/\lambda_{226} \approx 278$. Here N specifies number of atoms, A specifies radioactivity. Thus, $^{226}\text{Ra}/^{228}\text{Ra}$ atom ratios are converted to activity ratio A_{228}/A_{226} as $278 \cdot (^{226}\text{Ra}/^{228}\text{Ra})^{-1}$.

Constituent phases of the shale may contribute Ra to wastewater or leaching solutions, with Ra isotopic composition related to their U/Th ratio. Based on sequential extraction results, Galindo et al. (2007) attributed U in Moroccan black shale to organic phases, and Th to both organic and silicate phases. In a similar round of extractions Phan et al. (2015) attributed a fraction of U in Marcellus Shale from Greene Co. PA to carbonate and oxidizable phases, but found the majority to reside in refractory (silicate) minerals; Th was not measured in their procedure. Based on this preliminary assessment, we expect organics and carbonates to host Ra with moderate to high $^{226}\text{Ra}/^{228}\text{Ra}$ ratios, and silicates to host Ra with low to moderate $^{226}\text{Ra}/^{228}\text{Ra}$ ratios. Authigenic or secondary minerals including phosphates (apatite) or sulfides (pyrite) might acquire minor amounts of U or Th during diagenesis, hydrothermal alteration or via recoil effects (Galindo et al., 2007). However, U^{4+} is insoluble under anoxic conditions and Th^{4+} is highly-particle

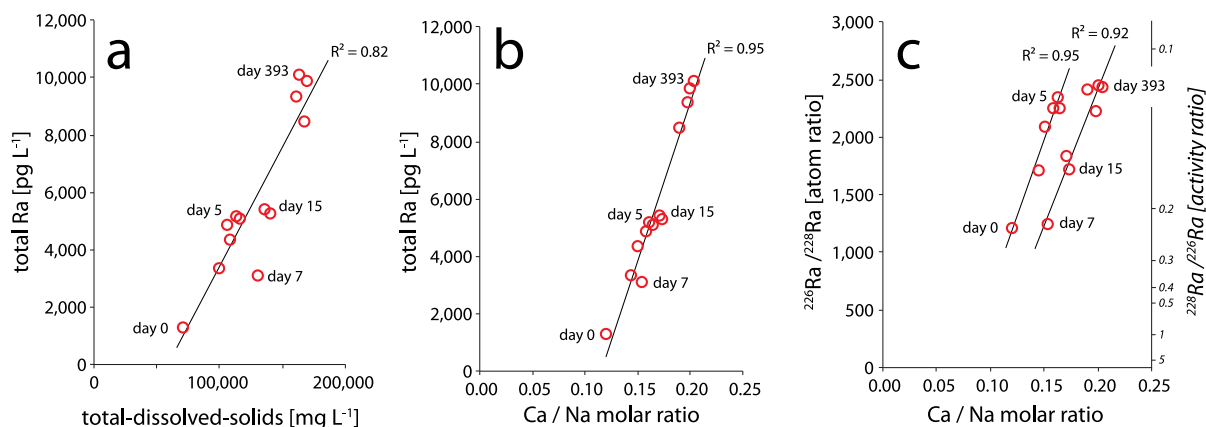


Fig. 1. Total [Ra] and $^{226}\text{Ra}/^{228}\text{Ra}$ ratios in flowback time series reported by Rowan et al. (2011, 2015). Total [Ra] is correlated with total-dissolved-solids in panel (a), but is better predicted by Ca/Na molar ratio of the wastewater as in panel (b). Evolution of $^{226}\text{Ra}/^{228}\text{Ra}$ over the duration of flowback is similarly well-described by Ca/Na in panel (c). A departure in both [Ra] and $^{226}\text{Ra}/^{228}\text{Ra}$ on day 7 of the time series has been attributed to a change in flowpath within the fracture network (Rowan et al., 2015). Consistent with this interpretation, Ra isotopic data conform to similar [Ca]/[Na] relationships before and after this departure. Solid lines show linear regression best fits.

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