



Reductive weathering of black shale and release of barium during hydraulic fracturing



Devon Renock*, Joshua D. Landis, Mukul Sharma

Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA

ARTICLE INFO

Article history:

Received 6 May 2015

Received in revised form

28 October 2015

Accepted 2 November 2015

Available online 11 November 2015

Keywords:

Barium

Barite

Hydraulic fracturing

Marcellus Shale

ABSTRACT

Hydraulic fracturing is an important technological advance in the extraction of natural gas and petroleum from black shales, but water injected into shale formations in the fracturing process returns with extraordinarily high total-dissolved-solids (TDS) and high concentrations of barium, Ba. It is generally assumed that high TDS comes from the mixing of surface water (injected fluid) with Na–Ca–Cl formation brines containing elevated Ba, but the mechanisms by which such mixing might occur are disputed. Here we show that Ba in water co-produced with gas could originate from water-rock reactions, with Ba levels observed in produced waters reached on a time scale relevant to hydraulic fracturing operations. We examined samples from three drill cores from the Marcellus Shale in Pennsylvania and New York to determine the possible water-rock reactions that release barium during hydraulic fracturing. Two samples, one containing microcrystalline barite (BaSO_4) and one without barite, contain elevated concentrations of Ba relative to the crustal average for shale rocks. A third sample is slightly depleted in Ba relative to the crustal average. Micro-XRF measurements and SEM/EDS analysis combined with chemical sequential extraction methods reveal that a majority of the Ba in all samples (55–77 wt.%) is present in clays and can only be leached from the rock by dissolution in hydrofluoric acid. Thus, a majority of barium in our samples is relatively inaccessible to leaching under hydraulic fracturing conditions. However, the balance of Ba in the rocks is contained in phases that are potentially leachable during hydraulic fracturing (e.g., soluble salts, exchangeable sites on clays, carbonates, barite, organics).

We next studied how shale reacts with water at elevated temperatures (80 °C), low Eh (–100 to –200 mV), and a range of ionic strengths ($\text{IS} = 0.85\text{--}6.4$) that emulate conditions prevalent at depth during hydraulic fracturing. Our experimental results indicate that the amount of Ba released from the bulk rock has a positive correlation with the ionic strength of the reacting fluid. Between 5 and 25% of the total Ba in the rock can be leached from shale under ionic strength conditions and leachate compositions typical of produced waters over a contact time of just 7 days. We suggest that reductive weathering of black shale occurs during hydraulic fracturing due to: 1) Ba^{2+} in clays exchanging with Na^+ and Ca^{2+} ions that are present in high concentrations in produced water, and 2) increased solubility and dissolution kinetics of barite under high ionic strength conditions. At the low Eh conditions prevalent during hydraulic fracturing the sulfate deficient water allows Ba to be dissolved into the produced water. Based on Ba yields determined from laboratory leaching experiments of Marcellus Shale and a reasonable estimate of the water/rock mass ratio during hydraulic fracturing, we suggest that all of the Ba in produced water can be reconciled with leaching directly from the fractured rock.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Water co-produced with gas (i.e., flowback and produced water) following the hydraulic fracturing of the Marcellus Shale (MS) has a

peculiar chemical composition. While the major dissolved ions are sodium, calcium and chloride, the produced water can reach salinities that are $10 \times$ greater than seawater with total dissolved solid (TDS) content often exceeding 150,000 mg/L (or ppm) (Blauch et al., 2009; Chapman et al., 2012; Haluszczak et al., 2013). Produced water contains appreciable amounts of other dissolved ions, as well, including magnesium, strontium, barium, uranium, radium, arsenic, vanadium, and molybdenum. Barium (Ba) and especially

* Corresponding author.

E-mail address: Devon.J.Renock@Dartmouth.edu (D. Renock).

radium (Ra) are of particular concern due to their toxicity in drinking water (Baldi et al., 1996; EPA, 2014; Warner et al., 2013; Zhang et al., 2015a); Barium and Ra are alkaline earths and their geochemical behaviors are similar. Barium concentrations and Ra activities in produced water: 1) have been shown to increase over days following the start of pumping exceeding 1400 mg/L (Ba) after only 7 days of pumping and reaching activities of 5000–16,000 pCi/L (Ra), and 2) are often strongly correlated with total dissolved solids (TDS) (Chapman et al., 2012; Rowan et al., 2011; Warner et al., 2012). High concentrations of Ba^{2+} and Ra^{2+} in produced water is also problematic due to the possibility of precipitation of highly-insoluble scale-forming barite, $BaSO_4$, upon mixing with sulfate-bearing surface water (Hamlat et al., 2003; Zhang et al., 2015a). The barite thus formed sequesters available Ra^{2+} ions and forms radioactive radiobarite, $(Ba,Ra)SO_4$ (Zhu, 2004). The source and fate of Ba thus becomes important to understand if we wish to consider ways of reducing its production during Marcellus gas extraction. The key questions that must be resolved are: 1) what are the source phases of Ba in the MS, and 2) what mechanisms govern its release from each phase into produced water?

The generation of highly saline produced waters is widely assumed to occur through the mixing of injected fluid with formation water or 'basin brine', based on binary mixing models (i.e., Br–Cl, Na–Ca, TDS, and oxygen isotopes) of injected fluid with a homogeneous basin brine end-member (Capo et al., 2014; Rowan et al., 2015; Warner et al., 2012). Appalachian basinal brines are thought to permeate the MS and adjacent rock units and are generally thought to be derived from a concentrated end member comprised of residual Paleozoic seawater expelled from the Salina group (Silurian) based on observed chloride and bromide relationships (Chapman et al., 2012; Dresel and Rose, 2010; Osborn and McIntosh, 2010, 2012; Stueber and Walter, 1991; Warner et al., 2012). In this model, fluid migration throughout the basin dissolves salts and mixes with or incorporates capillary-bound relict seawater via a mechanism such as that proposed by Balashov et al. (2015). Heterogeneities in brine geochemistry in the Appalachian Basin also suggest varying stages of alteration due to water-rock interactions (e.g., dolomitization of carbonates, sulfate reduction, brine-aquifer rock interactions, and dilution (Dresel and Rose, 2010; Osborn and McIntosh, 2010, 2011; Warner et al., 2012)). Brines in permeable host formations ranging in age from Ordovician to Devonian have been reported to contain up to a few thousand ppm Ba (Dresel and Rose, 2010). A possible explanation for such high Ba concentrations is sulfate deficient brines reacting with Ba-containing minerals in the rock (e.g., silicates and carbonates) (Dresel and Rose, 2010). However, the mechanism and rates of these reactions are considered highly speculative.

Multiple episodes of brine migration in the Marcellus Formation have been documented with events dating back to basin subsidence in response to the Alleghenian orogeny (Evans, 1995). Due to the low permeability of the black shale matrix, brine migration into the MS most likely occurred through horizontal and vertical fractures within the unit. The physical and chemical nature of brines within the MS is not well known. These brines are variously described as adsorbed water films on clays, capillary water, or free-flowing brine. Desiccation of brines can also leave dried salt residues along prior fluid conduits. A schematic illustrating the potential sources of brine and mechanisms by which brines or dried salts are incorporated into injected fluids and returned to the surface as produced water is shown in Fig. 1. Incorporation of ions into Ba-free injected fluid is thought to occur either when fractures induced by hydraulic fracturing cross pre-existing fractures that have been conduits for brine migration, or when injected fluid dissolves autochthonous salts within the MS itself (Blauch et al., 2009; Capo et al., 2014; Rowan et al., 2015; Warner et al., 2012).

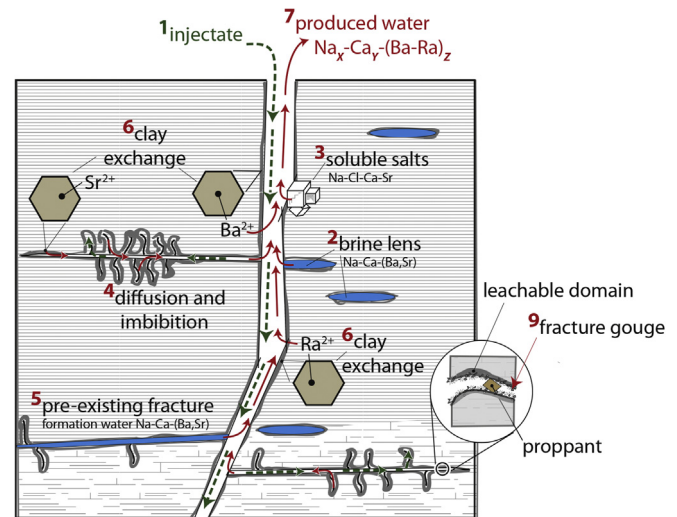


Fig. 1. Possible mechanisms contributing to the generation of produced water alkaline-earth (i.e., Ca, Sr, Ba, Ra) cation composition. These include: (1) injected fluid containing Na and Ca if recycled from previous wells; (2) hydrofracture crossing pre-existing formation water conduit (Warner et al., 2012); (3) brine inclusion in discrete lens, e.g., (Capo et al., 2014); (4) diffusion of capillary-water from pores, e.g., (Balashov et al., 2015) and imbibition of injected fluids (Engelder, 2012); (5) dissolution of soluble salts, e.g., halite (Blauch et al., 2009); (6) Ba and Ra released from leachable domain by cation exchange between host rock and saline leachate (e.g., Renock et al. herein); (7) inset shows micro-fracture with proppant (sand) and fracture 'gouge', pulverized shale which may greatly increase reactive surface area and leachable domain in the fracture zone; (8) produced water with composition determined by multiple sources and processes, and concentrations increased by factors, X Y and Z.

However, well logs and other observations indicate that MS contains very minor amounts of free brine (Engelder, 2012; Engelder et al., 2014). In response, Balashov et al. (2015) propose a model in which salt concentration, including Ba, in produced water is explained by diffusion from capillary-bound brine in the shale matrix into the injected fluid.

None of the proposed scenarios for Ba enrichment in produced water include the role of contemporaneous water-rock interactions, though others have suggested that water-rock interactions may be relevant for other elements. For example, Chapman et al. (2012) suggest that modification of formation brines by radiogenic clays in the MS is required to explain Sr isotopic composition in flowback water. Similarly, while Rowan et al. (2015) conclude that flowback salinity is derived from formation brine, they also observed that the Ra isotopic signature of the MS, specifically, is imprinted on flowback water from this unit. We consider the occurrence of Ra isotopes in flowback to be unequivocal evidence for a significant role of water-rock interactions in generating the composition of Marcellus produced water. Due to the short half-lives of ^{226}Ra (1600 years) and ^{228}Ra (5.8 years), radium isotope activity in the Marcellus formation must be supported by radioactive decay from their precursors $^{238}U > ^{230}Th$ and ^{232}Th , respectively. The activity of U and Th in seawater is very low (Chen et al., 1986), and given its half-life restrictions, Ra occurrence in MS flowback cannot be explained by its inheritance from paleo seawater. Furthermore, preliminary Ra isotopic measurements of shale leachates are incompatible with a dispersed, soluble Ra source to produced water (Landis et al., 2015). Instead, Ra isotope activity must be supported by U and Th decay within the formation rock. Leaching of Ra from shale, even if occurring over long time scales of contact between rock and a pre-existing brine, versus the short timeframe of hydraulic fracturing, is more than a matter of semantics. It argues for active leaching of the host rock, and in this case the rates of leaching reactions become of paramount relevance to our understanding of the generation of produced water composition.

Download English Version:

<https://daneshyari.com/en/article/4435590>

Download Persian Version:

<https://daneshyari.com/article/4435590>

[Daneshyari.com](https://daneshyari.com)