



Factors controlling Li concentration and isotopic composition in formation waters and host rocks of Marcellus Shale, Appalachian Basin



Thai T. Phan^{a,b,*}, Rosemary C. Capo^a, Brian W. Stewart^a, G.L. Macpherson^c,
Elisabeth L. Rowan^d, Richard W. Hammack^b

^a Department of Geology and Environmental Science, University of Pittsburgh, Pittsburgh, PA 15260, USA

^b National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236, USA

^c Department of Geology, University of Kansas, Lawrence, KS 66045, USA

^d U.S. Geological Survey, Reston, VA 20192, USA

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ABSTRACT

In this study, water and whole rock samples from hydraulically fractured wells in the Marcellus Shale (Middle Devonian), and water from conventional wells producing from Upper Devonian sandstones were analyzed for lithium concentrations and isotope ratios ($\delta^7\text{Li}$). The distribution of lithium concentrations in different mineral groups was determined using sequential extraction. Structurally bound Li, predominantly in clays, accounted for 75–91 wt.% of total Li, whereas exchangeable sites and carbonate cement contain negligible Li (<3%). Up to 20% of the Li is present in the oxidizable fraction (organic matter and sulfides). The $\delta^7\text{Li}$ values for whole rock shale in Greene Co., Pennsylvania, and Tioga Co., New York, ranged from -2.3 to $+4.3\%$, similar to values reported for other shales in the literature. The $\delta^7\text{Li}$ values in shale rocks with stratigraphic depth record progressive weathering of the source region; the most weathered and clay-rich strata with isotopically light Li are found closest to the top of the stratigraphic section. Diagenetic illite–smectite transition could also have partially affected the bulk Li content and isotope ratios of the Marcellus Shale.

In Greene Co., southwest Pennsylvania, the Upper Devonian sandstone formation waters have $\delta^7\text{Li}$ values of $+14.6 \pm 1.2$ (2SD, $n = 25$), and are distinct from Marcellus Shale formation waters which have $\delta^7\text{Li}$ of $+10.0 \pm 0.8$ (2SD, $n = 12$). These two formation waters also maintain distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting hydrologic separation between these units. Applying a temperature-dependent illitization model to Marcellus Shale, we found that Li concentration in clay minerals increased with Li concentration in pore fluid during diagenetic illite–smectite transition. Samples from north-central Pennsylvania show a much smaller range in both $\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ than those in southwest Pennsylvania. Spatial variations in Li and $\delta^7\text{Li}$ values show that Marcellus formation waters are not homogeneous across the Appalachian Basin. Marcellus formation waters in the north-eastern Pennsylvania portion of the basin show a much smaller range in both $\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, suggesting long term, cross-formational fluid migration in this region. Assessing the impact of potential mixing of fresh water with deep formation water requires establishment of a geochemical and isotopic baseline in the shallow, fresh water aquifers, and site specific characterization of formation water, followed by long-term monitoring, particularly in regions of future shale gas development.

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1. Introduction

Lithium (Li) isotopes have been widely used as a tracer for Earth surface processes, including origin and evolution of basinal brines (Bottomley et al., 1999; Macpherson et al., 2014) and weathering of silicate rocks (Millot et al., 2010b; Misra and Froelich, 2012; Pogge von Strandmann et al., 2013). Lithium is a fluid-mobile element whose concentration and isotopic composition vary widely among geologic

materials. The magnitude of Li isotope fractionation is found to be inversely related to the temperature during water–rock interactions (Millot et al., 2010a; Vigier et al., 2008). Clay formation induces Li isotope fractionation at both low and high temperatures, with the light isotope ^6Li preferentially incorporated into the structure of clay minerals leaving fluid enriched with the heavier isotope ^7Li . Silicate weathering and secondary mineral formation are two main processes thought to induce Li isotope fractionation (Rudnick et al., 2004; Pogge von Strandmann et al., 2006; Vigier et al., 2009) in geologic materials.

Laboratory experiments on Li isotope fractionation, including adsorption (Pistiner and Henderson, 2003; Millot and Girard, 2007), interaction of sea water with basalts (Millot et al., 2010a), precipitation of

* Corresponding author at: Department of Geology and Environmental Science, University of Pittsburgh, 4107 O'Hara St., 200 SRCC, Pittsburgh, PA 15260, USA.
E-mail addresses: thaiphann@pitt.edu, thai.phan@netl.doe.gov (T.T. Phan).

carbonate minerals (Marriott et al., 2004), and illitization (Williams and Hervig, 2005) have demonstrated the same fractionation direction in which ^6Li is preferentially incorporated into secondary minerals, even though the fractionation factors vary for each particular process. Lithium in calcite and aragonite is about 3‰ and 11‰ isotopically lighter, respectively, than Li in the initial (growth) solution (Marriott et al., 2004). On the other hand, dissolution of primary minerals does not significantly fractionate Li isotopes (Burton and Vigier, 2012). To date, processes controlling Li isotope fractionation from water and shale interactions are poorly understood. Teng et al. (2004) investigated shale samples in different cores from four basins in Australia; the samples' ages ranged from Proterozoic to Triassic. Li concentrations and isotope ratios, reported as $\delta^7\text{Li}$ relative to the LSVEC standard, ranged from 30 to 109 mg/kg and -3.1 to $+3.4\%$, respectively. A similar range of $\delta^7\text{Li}$ (-3.4 to $+0.4\%$) was reported for Paleozoic sedimentary rocks in Germany based on a more extensive data set (Romer and Meixner, 2014); however, these were primarily outcrop samples, which can be strongly affected by near-surface processes (e.g., Mosier, 1988). Lithium concentrations and isotope ratios of *in situ* basinal brines and Marcellus Shale core samples represent a stepping stone for understanding water–shale interactions.

In unconventional gas plays the reservoir rock is typically the same as the source rock. The Middle Devonian Marcellus Shale is an organic-rich, low permeability shale with a significant reservoir of gas that has been rapidly developed over the last decade. Previous studies have showed that the saline waters collected from Marcellus Shale gas wells are classified as Na–Ca–Cl type brine with median value of total dissolved solids (TDS) of 278,000 mg/L (Dresel and Rose, 2010; Rowan et al., 2015). Major cations and anions, strontium isotopes, and oxygen isotopes show that water produced from the Marcellus Shale is initially dominated by the fluid injected for hydraulic fracturing but shifts over time to the composition of the formation water (Chapman et al., 2012; Haluszczak et al., 2013; Capo et al., 2014; Rowan et al., 2015). Evaporation of sea water can explain the high TDS (Haluszczak et al., 2013; Rowan et al., 2015) but does not adequately explain the elevated Li concentrations in the Marcellus produced water (Macpherson et al., 2014). Diagenetic reactions with Li-bearing minerals in the shale could possibly account for anomalously high Li in Marcellus formation water (Macpherson et al., 2014). This study further investigates sources of Li by characterizing Li concentration and isotopic composition in both formation waters and rock samples of the Marcellus Shale. Sequential extraction experiments were conducted to determine the distribution of Li in shale minerals. We interpret the results in the context of rock–

water interaction at temperatures estimated for maximum burial and at present day in the reservoir. Both Li and Sr isotopes are shown to be useful geochemical tracers of the formation waters on a local scale.

2. Materials and methods

2.1. Sample description and geological setting

Water samples were collected from oil and gas wells producing from Upper and Middle Devonian, and Silurian reservoirs. The well locations ranged from southwestern to north-central Pennsylvania, USA (Fig. 1). Water samples were collected from a total of three conventional gas wells from multiple Upper Devonian units (UD-2, UD-5, UD-6) and five hydraulically fractured gas wells from the Middle Devonian Marcellus Shale (four horizontal wells: Well 7, 8, 9, 10; one vertical well: Well MW1). During hydraulic fracturing, fluid comprising fresh water, recycled produced water, chemical additives and sand (Soeder et al., 2014) is injected into the target formation under pressures high enough to create fractures along the length of the wellbore. As pressure is released, large amounts of the injected water return to the surface during the first few weeks; this is often termed “flowback water”. In this paper we use the term “produced water” to describe all water returned to the surface, regardless of timing. The chemistry of the produced water changes rapidly and reaches a stable composition over a short period, after which the *in situ* brine dominates the composition of the produced water. Therefore, the term “formation water” discussed in this study implies the *in situ* water from the hydraulically fractured formation that dominates the composition of produced water at the later stages of gas production (>45 days). Early produced water is likely a mixture of the injected water and formation water.

The vertical Marcellus well (MW-1) was hydraulically fractured in June 2008 and had been in operation for more than five years by the time of our sampling. Thus, all water samples from this well are derived from the *in situ* formation water and are not influenced by the injected fluid. On the other hand, time series water samples from four horizontal wells in three counties (Greene, Washington, and Westmoreland) in southwestern Pennsylvania, USA, were collected from day 1 to as long as 813 days after the beginning of water return. Additional grab samples reported in this study include a) two samples from wells tapping the Silurian Lockport Dolomite and Newburgh Sandstone; b) two samples from Marcellus Shale wells in Tioga County, PA (approximately 850 and 1060 days in production); and c) one sample from a gas well (approximately 1100 days in production) tapping the Upper Devonian

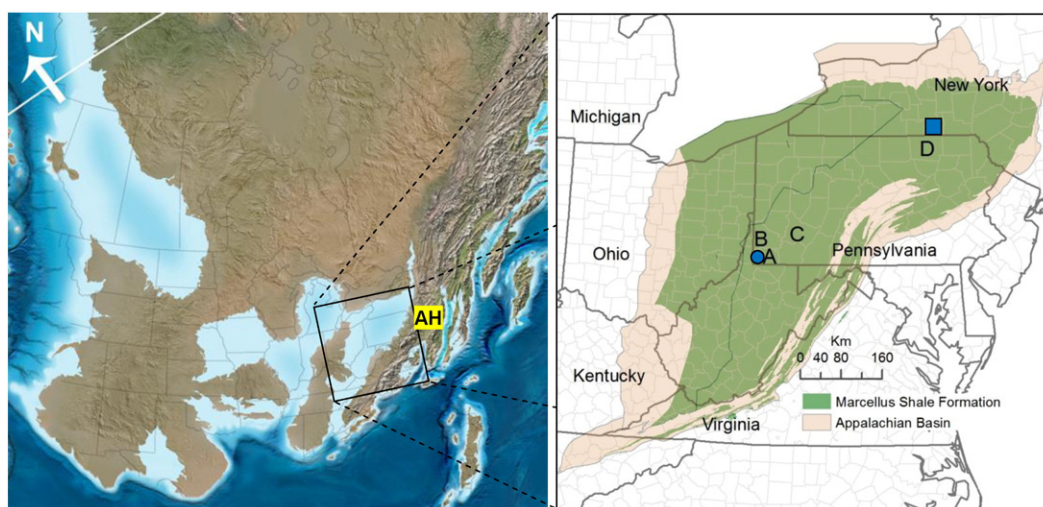


Fig. 1. Map showing part of North America Middle Devonian paleogeography modified after Blakey (2013). AH = Acadian Highlands. Inset shows the extent of the Middle Devonian Marcellus Shale in the present-day Appalachian Basin. Produced water samples are from Greene Co., (A), Washington Co. (B), Westmoreland Co. (C), and Tioga Co., PA (D). Core samples are from Greene Co, PA (blue circle); and dry-drilled rock cuttings from Tioga Co., NY (blue square). Base map is modified after Whitacre, 2014.

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