Lithium in Fluids from Paleozoic-aged Reservoirs, Appalachian Plateau Region, USA

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Abstract

This study presents the spatial distribution of a compilation of lithium (Li) and selected other dissolved species concentrations in saline fluids from oil and gas wells in western Pennsylvanian and eastern Ohio that are producing from Silurian- to Devonian-age formations. Li concentrations in the data set range from about 40 to 40,000 $\mu\text{mol kg}^{-1}$ indicating water-rock reactions that added Li to the saline fluids. Chloride (Cl) concentrations range from about 160 to 5,300 mmol kg^{-1} , likely the result of different burial fluids (seawater or evaporated seawater), variable dilution with meteoric water and variable interaction with marine evaporites. The Li/Cl in these fluids is not constant, potentially indicating multiple sources of Li in addition to multiple origins of Cl. Li and the Li/Cl ratio generally decrease from east to west across the study area in four or five bands of similar Li or Li/Cl. Li and Li/Cl are not correlated with petroleum-production formation and are only generally correlated with depth. A few of the fluid samples have anomalously high Li and Li/Cl. These anomalous samples coincide in location with northwesternly trending salients of high vitrinite reflectance, suggesting that Li in this segment of the Appalachian Plateau Province may provide insight into paleoflow pathways in the region, indicating where hot, chemically evolved, saline fluids might have been driven to the northwest, upwards and out of the basin, during tectonism.

Keywords: lithium, saline fluids, sedimentary basin, Appalachian Plateau, water-rock interaction, formation water, fluid expulsion

1. Introduction

1.1. Purpose and Scope

Saline fluids produced during oil and gas extraction from sedimentary basins contain minor amounts of dissolved lithium (Li). This study considers the spatial distribution of dissolved Li in saline fluids from part of the northern Appalachian Plateau region (eastern Ohio and western Pennsylvania, USA) of the Appalachian Basin. This area is undergoing renewed exploration and development for production of unconventional gas from tight shale (Engelder and Lash, 2008), and because of this, samples are now available in an area and in a depth range where samples had been absent.

Li exhibits fairly unusual geochemical behavior in basinal fluids in that, except during smectite formation in very early seafloor diagenesis, it is enriched in the fluid and depleted in the solid during progressive water-rock reactions (Tomascak, 2004; Decarreau et al., 2012), so that Li concentration is an aqueous indicator of progressive (salinity and temperature-driven) sedimentary basin diagenesis. In addition, it shows little change during cooling (Lui-Heung et al., 1994; James et al., 2003), making it a possible aqueous indicator of paleoflowpaths, if fluids are driven from deeper (warmer) parts of a basin to shallower (cooler) parts. In this study, the distribution of aqueous Li in the study area is compared to another indicator of fluid expulsion from the Appalachian Basin during tectonism, to test its potential use as a paleoflowpath indicator.

1.2. Background

Saline fluids in those sedimentary basins containing evaporites, such as the study area, are mostly seawater and evaporated seawater trapped during sediment deposition; the fluid chemistry has been highly modified by chemical reactions with the sediment or rock (Hanor, 1994) and potentially diluted by meteoric or mineral-dehydration water (Lowry et al., 1988). Li occurs in very low concentration in modern seawater ($27 \mu\text{mol kg}^{-1}$). During evaporation of ancient seawater, Li was probably conserved in the fluid, just as it is in modern

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30 seawater (McCaffrey et al., 1987); modern seawater evaporated to the stage of
10 halite deposition salinity contains about $250 \mu\text{mol kg}^{-1}$ Li. It follows that Li
11 is found in extremely low concentrations in marine evaporite salts, and that,
12 unlike bromide (Br), the Li/Cl ratio should remain steady during recrystalliza-
13 tion of halite and decrease during dissolution of halite (in the absence of other
14 mineral-water reactions).
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18 Clay minerals and shale (mudrocks) contain more Li, on average, than car-
19 bonates or sandstones (Parker et al., 1967). Shale (mudrock) has occupied the
20 highest volume percent of the Earth’s crust through the Phanerozoic (Macken-
21 zie, 2005), and this includes sedimentary basins (Sharp et al., 1988; Hanor and
22 McIntosh, 2007). For these reasons, shale (mudrock) is the largest reservoir of
23 Li in sedimentary basins, by having the combination of relatively high lithium
24 concentration and high volume (Macpherson, 1989), and so shale (mudrock) is
25 likely the most important source of Li in saline fluids in sedimentary basins.
40 Hanor and McIntosh (2007) demonstrated the important role that Cl has on
26 major and minor cation concentrations in saline fluids: Cl from dissolution of
27 NaCl is proportional to cations due to reactions with carbonate and silicate min-
28 erals exchanging aqueous Na stoichiometrically for mineral cations, to maintain
29 charge balance. Although not specifically discussed, it follows that Li should be
30 controlled similarly.
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40 Diagenesis and saline fluid composition are driven by Cl content (salinity),
41 but also by heat. Transformation of smectite to mixed-layer smectite-illite and
42 illite in sedimentary basins has been shown to be related to temperature, with
43 the transformation generally complete at a temperature of about 100°C (Eberl
44 and Hower, 1977). The intermediate minerals formed during the transforma-
45 tion depends upon the initial mineralogy (Lanson et al., 2002), but in general
46 smectite is consumed and illite is generated (Perry and Hower, 1970) as well as
47 chlorite (Hower et al., 1976). During metamorphism illite is then transformed
48 into muscovite (Gharrabi et al., 1998).
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54 The Appalachian Plateau is the westernmost province of the Appalachian
55 Basin, a Paleozoic foreland basin that was deformed during the Appalachian
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orogeny. Deformation in the Appalachian Plateau region was considerably less than in eastern provinces, and widespread permeable units such as the Oriskany Sandstone probably were conduits for fluid transport from the highly-deformed eastern portion to the less-deformed western portion during tectonism (Evans et al., 2012; Evans and Battles, 1999). Evaporites are concentrated near the middle of the basin fill, in the Upper Silurian Salina Group (Fig. 1), but are found in other formations as well (Lowry et al., 1988; Smosna et al., 2005) and most water produced from oil and gas wells has higher salinity than seawater (Osborn et al., 2012; Rowan et al., 2011; Dresel and Rose, 2010; Lowry et al., 1988; Breen et al., 1985). Fluid inclusions show that high salinity (up to about 25 weight percent NaCl equivalent) and high temperature (up to more than 220 °C) fluids moved in two temporally different pulses from east to west through the basin Evans and Battles (1999). Salinities and major element composition of fluids currently produced from oil and gas wells (Na-Ca-Cl) are similar to those found in fluid inclusions, but current temperatures are lower (Rowan, 2006) and reservoirs are in part underpressured, probably due to erosion of overburden (Bruner and Smosna, 2011; Ryder and Zagorski, 2003).

2. Methods

Chemical analyses of saline water produced from oil and gas wells in the study area were compiled from the literature (Breen et al., 1985; Lowry et al., 1988; Dresel and Rose, 2010; Macpherson et al., 2014). Some data sets were incomplete. Numbers of samples with reports of the parameters used in this study are shown in Table 1. Because choice of concentration units varied among the publications, all units were converted to be consistent. If density was provided, this was used to convert mass-per-volume units to mol-per mass units. If density was not provided, laboratory density was estimated (Phillips et al., 1983).

Some well locations were not available because the information is proprietary. In these cases, if county locations were known, wells were arbitrarily put at the county seat of the county in which they are located. Production depths

estimated for proprietary wells were based on geology and geographic location of county seat (Ryder et al., 2009).

Table 1: Sources and Completeness of Data

Data source	Depth	Location	Density	Li	Cl
Breen et al. (1985)	77/78	78/78	78/78	71/78	78/78
Lowry et al. (1988)	24/24	est.	0/24	0/24	24/24
Dresel and Rose (2010)	40/40	33/40	32/40	33/40	40/40
Macpherson et al. (2014)	0/8	0/8	0/8	8/8	8/8

3. Results and Discussion

Oil and gas productions reservoirs from which saline waters have been compiled for this study are hosted by Lower Silurian to Upper Devonian formations (Fig. 1, 2). The distribution of petroleum reservoirs follows the geologic structure of the area, with fields producing from the same age reservoirs trending mostly northeast-southwest except in the northeast, where the trend is east-west. The older units produce oil or gas in both the eastern and western parts of the study area, and the younger units dominate in the central part of the study area (Fig. 3). A few wells produce from depths shallower than 500 m and a few produce from deeper than 2,000 m, but the majority of the wells in this data set produce from depths of 500 to 2,000 m (Fig. 4). Shallow production is from Upper Devonian reservoirs, mostly in the north central part of the area. Deepest production is from Lower Silurian reservoirs in the eastern part of the study area.

The distribution of samples compiled for this study is uneven, with few wells in the eastern and northeastern parts of the study area (Fig. 2). Nevertheless, there are some patterns apparent in the spatial distribution of some components of the water chemistry.

Figure 2: Distribution of wells used in the four data sets compiled for this study. Axes are degrees west longitude (abscissa) and north latitude (ordinate).

110 Cl does not show systematic variations within the study area or with depth (Fig. 5a), and the highest Cl is found in some of the Lower Silurian-reservoir samples in the western part of the study area, farthest from the highly-deformed region. Most samples contain 2 to almost 10 times higher Cl than modern seawater, and only three samples contain less Cl than seawater. The majority of

115 samples from Upper Devonian reservoirs contain lower Cl than other reservoirs,
 116 but the total range in Cl in the Upper Devonian reservoir fluids is nearly as
 117 great as the Lower Silurian reservoir fluids. Because most Cl concentrations
 118 are greater than seawater Cl, dissolution of Silurian evaporites, as suggested
 119 previously (Breen et al., 1985; Lowry et al., 1988) and/or mixing of evaporatively
 120 concentrated seawater with lower salinity fluids (Dresel and Rose, 2010) is the
 likely explanation for the elevated Cl.

Li concentration in the fluids is highest in the east and northeast (Fig. 6)
 and generally increases with depth rather than age of the reservoir rock (Fig.
 5b). Three of the fluid samples from Lower Devonian reservoirs are enriched

Figure 3: Distribution of lithostratigraphic units of oil or gas reservoirs from which saline water samples were compiled for this study. Locations are approximate. Axes are degrees west longitude (abscissa) and north latitude (ordinate).

Figure 4: Depth of production of oil or gas and the saline water for samples used in this study. Locations are approximate. Axes are degrees west longitude (abscissa) and north latitude (ordinate). (Color, online; B and W, print)

in Li compared to the Li-depth trend, with more than 2-fold enrichment at a depth of 2,500 m. These Li-enriched samples have Li concentrations about 1.5 times higher than the deepest sample at about 3,400 m.

Li/Cl molar ratios are highest in the west and lowest in the east and north-east, similar to Li, and several of the samples from Middle Devonian reservoirs as well as the same Lower Devonian Li-rich samples are enriched in Li/Cl compared with the main trend (Fig. 5c). These observations suggest that, although Cl is a driver of fluid composition in sedimentary basin fluids (Hanor, 2001), another factor, such as heat, must enrich some of the samples in Li.

Bruner and Smosna (2011) show a compilation of vitrinite reflectance data

Figure 5: Dissolved species and species ratios versus depth in the study area. a) Cl (mmol kg^{-1}). b) Li ($\mu\text{mol kg}^{-1}$). c) Li/Cl ($\mu\text{mol/mmol}$).

135 distribution in Devonian shale in an area that includes the study area for this
 53 project (Fig. 7). Vitrinite reflectance is thought to reflect thermal maturity
 54 of the rock, with higher values indicating exposure to higher temperatures.

Figure 6: Li ($\mu\text{mol kg}^{-1}$) distribution in the study area. Locations are approximate. Axes are degrees west longitude (abscissa) and north latitude (ordinate). (Color, online; B and W, print)

The compilation suggests that, although thermal maturity increases fairly regularly from northwest to southeast across their study area, three northwestward-trending salients of higher vitrinite reflectance represent geologic features that may have permitted migration of hot, saline fluids further west than in other areas. Superposed on the map of vitrinite reflectance are the Li concentration data, showing that the Li (and Li/Cl, not shown) correspond nicely to thermal maturity indicator distribution. Although the Li fluid concentration data are sparse in the southeastern part of the area used in this study, the highest-Li samples in fall within or on the boundary of two of the high thermal-maturity salients. This suggests that Li in this region may act as a paleoflowpath indica-

Figure 7: Contours of vitrinite reflectance, modified from Bruner and Smosna (2011), with Li outliers (high Li and high Li/Cl) superposed.

tor, identifying the preferential loci of exit paths as fluids were driven out of the deeper basin to the east, because of tectonic thrusting during the Appalachian Orogeny.

Others have used geochemical data to identify fluid migration pathways. For example, Osborn et al. (2012) used iodine and strontium isotope ratios along with elemental geochemistry and clay mineral analysis to argue for large-scale fluid migration through part of the Devonian rock section in western New York, northwestern Pennsylvania and eastern Kentucky. They suggested that the uranium occurrences in the structural front of the Appalachian basin lie along the paleoflow paths they identified. Eccles and Berhane (2011) used geochemical analyses of saline formation waters to identify fluid migration paths of hot, Li-rich fluids from deep in the Alberta Basin to shallower formations. The fluid migration resulted in discrete areas of high Li (up to almost $15,000 \mu\text{mol kg}^{-1}$)

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9 in faulted reef deposits, the faults acting as conduits for deeper (hotter) saline
10 water to migrate upward into shallower formations.
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13 14 **4. Summary**

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16 This compilation of selected water chemistry and location information from
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18 165 saline water produced from Paleozoic reservoir oil and gas wells in the north-
19 ern Appalachian Plateau region shows that Li concentrations generally increase
20 from west to east and with depth, while Cl concentrations are more erratically
21 distributed. Li acts as an incompatible element during diagenesis, such that
22 progressive water-rock reactions enrich the fluid in Li. Although Cl is an im-
23 portant driver of diagenetic reactions of carbonate and silicate minerals, thereby
24 170 proportional to cation concentrations in Cl-rich fluids, in this setting tempera-
25 ture likely has such a large influence in restricted areas that some data appear
26 distinctly anomalous. The most enriched Li concentrations fall near or on top of
27 the trends of anomalously high vitrinite reflectance mapped in Devonian shale.
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29 These anomalies appear to mark the paleoflow paths of hot fluids being ex-
30 pulsed from the Appalachian Basin during orogenesis; expulsion of fluids in this
31 manner has been proposed before. The Li/Cl ratio is not always a useful indi-
32 cator of reaction progress in this setting, because of the variable sources of Cl,
33 but the highest Li/Cl ratios also coincide with vitrinite reflectance-suggested
34 175 pathways of fluid expulsion. The small number of data points with anomalous
35 Li and Li/Cl make it difficult to quantify the relationships among Li, Li/Cl
36 and vitrinite reflectance, but this study presents a hypothesis that could be fur-
37 ther tested if more data become available in this region of rapid exploration for
38 unconventional hydrocarbons.
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