



# Tracing hydrocarbons in gas shale using lithium and boron isotopes: Denver Basin USA, Wattenberg Gas Field



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## ABSTRACT

Bentonites are altered volcanic ash layers commonly used as marker beds in sedimentary basins. The ash (glass) alters to diagenetic mixed-layered illite–smectite (I–S), and the illite incorporates trace elements from the interacting porefluid, recording paleofluid changes over time. Among these trace elements, lithium and boron are common heteroatoms of organic macerals released during thermal maturation into the porefluids, and are incorporated by the diagenetic illite, potentially becoming useful tracers of hydrocarbon-related fluids.

This study examines Li and B in bentonite samples from the Wattenberg Gas Field, Denver Basin, Colorado (USA). Using secondary ion mass spectrometry, different crystal size fractions of I–S extracted from the bentonite were measured. Illite incorporates Li in octahedral sites and B in tetrahedral sites of the framework during diagenetic crystallization, recording distinctly light isotopic signatures of the organic source.

The  $\delta^7\text{Li}$  of I–S in outcrops outside of the gas field ranges from  $-7$  to  $+4\%$ , compared to samples within the gas field, which generally range from  $-18$  to  $-4\%$ . One exception is in the highly mature region, where vitrinite reflectance values (%Ro) reach 1.3. The  $\delta^7\text{Li}$  is  $+12\%$  in the finer clay fraction ( $<0.1\ \mu\text{m}$ ) containing first nucleated illite while the coarser size fraction ( $0.1\text{--}2.0\ \mu\text{m}$ ) of the same sample shows the lowest  $\delta^7\text{Li}$  value of  $-18\%$ . This 30% decrease in  $\delta^7\text{Li}$  within the same sample suggests the influx of  $^6\text{Li}$  dominated fluid coinciding with gas generation during illitization. K–Ar dating of the illite in this sample indicates that influx of the  $^6\text{Li}$ -rich fluid occurred at  $60 \pm 3$  Ma, before local igneous activity ( $\sim 40$  Ma) related to the Laramide Orogeny (Colorado Mineral Belt) increased vitrinite %Ro.

B-isotopes ranged from  $-15$  to  $-7\%$ , showing no significant change between different size fractions, but the B-content in the gas field reaches 180 ppm, and decreases radially away from the thermally mature region. We conclude that isotopically light B influx coincides with generation of oil and isotopically light Li is associated with influx of gas related fluids, and therefore the age of the illites record the timing of oil and gas generation.

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## 1. Introduction

The Denver Basin has a long record of oil and gas exploration and production (see Higley and Cox, 2007 and the references therein). This well-known time–temperature and geologic context provides an excellent area for studies concerning diagenesis and fluid flow during oil and gas generation. Therefore, this study area was chosen to explore variations in the light trace element isotopes (Li, B) that link the processes of hydrocarbon generation and illitization, and may be useful exploration tools for oil and gas.

Li and B are soluble in hydrous fluids relative to magmas (London et al., 1988; Webster et al., 1989). They are also incompatible in most silicate minerals and are thus concentrated in fluids over a large range

in temperature. They display a large isotopic variation in nature (nearly 100‰) and do not undergo redox reactions that could complicate isotopic interpretations (Palmer and Swihart, 1996; Tomascak, 2004). Collins (1975) found that these elements are concentrated in many oilfield brines (10–100s ppm), which suggests that they are released from hydrocarbon source rock along with oil and gas. Because Li and B can substitute in octahedral and tetrahedral sites (respectively) of illite during diagenesis (Palmer and Swihart, 1996; Starkey, 1982; Williams et al., 2012) the growth of diagenetic illite over time provides a record of the composition of paleofluids that transported these elements.

### 1.1. Evidence for organic Li and B in kerogen

Boron is a trace heteroatom in kerogen, derived from primary terrestrial and marine organisms (Douthitt, 1985; Goodarzi and Swain, 1994; Takahashi et al., 2011), however the bonding of Li in kerogen organic macerals has not been studied. One of the most compelling lines of

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evidence for a kerogen source of these trace elements is their high concentration in oilfield brines (Collins, 1975) with Li reaching 10–100 mg/L and B up to 700 mg/L; orders of magnitude greater than in seawater, meteoric or natural ground waters (Vengosh et al., 1994; Hogan and Blum, 2003; Tomascak, 2004). Swain (1990) documented the Li and B contents of coal (bituminous to anthracite) up to 300 ppm, consistent with concentrations measured in oilfield brines. High concentrations of Li measured in hydrocarbon source rock (Alum shale) from the Baltic Basin (Williams et al., 2013) and East Slovak Basin (Clauer et al., 2014b) also support that Li is a trace heteroatom in organic macerals. The biological use of Li in plants is negligible (Hogan and Blum, 2003; Marschner, 2012), however it is a trace element in marine plankton (Misra and Froelich, 2012), which are a major constituent of Type II kerogen (Tissot et al., 1974). The stability of Li-C straight and branched chain alkanes and amines has been studied in hydrocarbon solutions (Kamienski and Lewis, 1965) showing that Li-alkoxides are stable at temperatures of hydrocarbon generation (to 80 °C).

The evidence for release of trace B and Li from organic macerals as oil and gas are generated from the kerogen is empirical. Isotopically light B was found associated with hydrocarbons in the U.S. Gulf Coast Sedimentary Basin (Williams et al., 2001a), the Alberta Basin (Williams et al., 2001b), the Baltic Basin (Środoń et al., 2009; Williams et al., 2013) and East Slovak Basin (Clauer et al., 2014b). Using solid-state magic angle spinning <sup>11</sup>B NMR, Lemarchand et al. (2005) found a large pH dependent isotopic fractionation during adsorption of B onto humic acid (–25% at pH between 5 and 9), indicating <sup>10</sup>B enrichment in tetrahedral coordination on the organic compounds. Takahashi et al. (2011) similarly showed tetrahedral bonding and <sup>10</sup>B-enrichment of B in kerogen using solid-state NMR. This is consistent with the earlier results of Williams and Hervig (2004) showing that kerogen from petroleum source rocks and coal deposits typically contains hundreds of ppm B that is isotopically light (0% to –70%) and is a likely source of the B in oilfield brines. Fewer measurements of Li-isotope compositions of kerogen have been reported, but the existing data from measurements of the Alum shale, a source rock for Baltic basin oilfields (Williams et al., 2013; Clauer et al., 2014b) indicate that Li-isotopes of kerogen are also isotopically light, in the range of +4 to –32%. In general, organic sources of both B and Li are isotopically lighter than most natural waters and minerals (Williams et al., 2001a, 2001b; Hogan and Blum, 2003; Tang et al., 2007). In the Alum shale study (Williams et al., 2013), changes in both Li and B isotopes in the source rock correlated with thermal maturity. The clays and kerogen in the bulk shale were assumed to be in equilibrium, therefore trends in the clay isotopes were thought to reflect trends in the organic matter (fractionation unknown). With increasing thermal maturity the shale  $\delta^7\text{Li}$  became progressively heavier (–20.2 to –5.3%), therefore by mass balance the fluids released from the source rock when hydrocarbons were generated were <sup>6</sup>Li enriched at highest maturity (gas generation). The isotopically light  $\delta^7\text{Li}$  fluids infiltrated bentonites near the oilfields in Poland where diagenetic illite recorded the light  $\delta^7\text{Li}$ . It is likely that the B and Li trends observed with temperature depend on the type of organic matter (terrestrial or marine) that hosts the trace elements.

The relative timing (temperature) of the light element release from kerogen during burial depends on the stability of the B–C or Li–C bonds in the organic maceral. Release of B or Li from a mineral host (igneous or detrital sedimentary minerals) would require much higher temperatures than diagenesis (>400 °C for dehydroxylation of clays) capable of breaking M–OH and ultimately M–O bonds in the mineral framework. Once released to the porefluid, kinetic isotopic fractionation of these mobile elements may occur during fluid migration because the light isotope of each element is preferentially incorporated in diagenetic illite forming at temperatures of oil generation. Thus, the migrating fluids will be gradually enriched in the heavier isotope with distance of migration through clay-rich sediments.

## 1.2. Illite crystal growth in Wattenberg bentonites

We focus on the chemistry of I–S in bentonite layers enclosed within Cretaceous black shale and limestones because bentonites (deposited as volcanic ash layers) are theoretically devoid of detrital minerals that may represent different ages and geochemical histories. Furthermore, if there were detrital contaminants they have been shown to diminish in abundance in the progressively smaller size fractions of clay (Pevear, 1999). The bentonite, while fairly impermeable relative to sandstones, is infiltrated by porefluids from the surrounding shale, allowing alteration of the volcanic glass (ash) to smectite first, then illite with increasing temperature and K supply (Altaner et al., 1984; Elliott and Aronson, 1987; Altaner, 1989; Williams and Ferrell, 1991; Clauer et al., 2014a; Osborn et al., 2014). Crystallization of illite in bentonites occurs at 60–150 °C; temperatures of hydrocarbon generation (Tissot and Welte, 1984; Hower et al., 1976) when B and Li are released from source rocks (Williams et al., 2001a, 2001b, 2012).

The growth of illite produces a crystal size distribution that is either asymptotic, where there is constant nucleation from a supersaturated fluid, or log normal where there is an initial nucleation event followed by supply/surface controlled growth (Eberl et al., 1998, 2002). Nucleation followed by surface controlled growth generally applies to an open system during burial, where the first nucleated illite is concentrated in the smallest size fractions and forms in equilibrium with the paleofluid (Williams and Hervig, 2005, 2006). As crystals grow they must incorporate new material, thus larger crystals are generally younger and their chemistry reflects the chemistry of the most recent fluid (Williams et al., 2012; Clauer et al., 2014b). It is possible to have several episodes of nucleating small crystals in open systems where fluid flow is rapid and supersaturation occurs episodically. However, bentonites that have low permeability normally do not experience multiple fluid cycles during diagenesis. Many bentonites have been studied that document the oldest K–Ar age given by the smallest size fraction of illite (Środoń et al., 2002, 2009; Clauer et al., 1997, 2014b), and the isotopic composition of that size fraction represents equilibrium with the fluids present at that time (Williams and Hervig, 2005).

Our hypothesis is that isotopically light Li and B, released from organic matter coincident with the generation of oil and gas are incorporated by the diagenetic illite in bentonites. Therefore, the ages of illite with these isotopic signatures record the timing of oil and gas migration. Kerogen-derived Li and B alter the isotopic composition of porewater to values distinctly lower than most groundwaters (Hogan and Blum, 2003; Clauer et al., 2014b). Therefore, changes in the porewater composition related to hydrocarbon generation can be tracked through changes in the Li and B isotopic compositions of different size fractions of diagenetic illite because the isotopic fractionation of these elements between illite and water as a function of temperature is known. In this study we examine changes in the Li and B contents and isotope ratios of I–S in bentonites from the Denver basin (Colorado, USA), in order to evaluate the relationship with oil and gas generation as a function of diagenetic illite crystal size and distance from the source rock.

## 1.3. Geologic setting

The Denver Basin is one of several Tertiary foreland basins formed from a larger western Interior Basin during the Laramide Orogeny. The resulting basin is an asymmetric N–S trending basin whose axis is located close to the western basin margin. Thermal maturation of Cretaceous source rocks along the Denver Basin axis occurred by the middle Eocene (Tainter, 1984). Cretaceous and early Tertiary (Paleocene–Eocene) sediments were buried progressively until about 50 Ma ago (Soister, 1978; Trimble, 1980).

The Wattenberg Gas Field (WGF) is located north of Denver along the basin axis. The natural gas within the WGF is produced from the Cretaceous Dakota, Muddy J, and Planview sandstones (Higley et al., 2003). An anomalously high area of thermal maturity is found in the

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