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5 **Tracing hydrocarbons in gas shale using lithium and boron isotopes:**
6 **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 in 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 range from -7 to $+4\text{‰}$, 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 ($\%R_o$) reach 1.3. The $\delta^7\text{Li}$ is $+12\text{‰}$ in the finer clay fraction ($<0.1\text{ }\mu\text{m}$) containing first nucleated illite while the coarser size fraction ($0.1 - 2.0\text{ }\mu\text{m}$) 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 influx of ^6Li dominated fluid coinciding with gas generation during illitization. K-Ar dating of the illite in this sample indicates that influx of the ^6Li -rich fluid occurred at $60 \pm 3\text{Ma}$, before local igneous activity ($\sim 40\text{Ma}$) related to the Laramide Orogeny (Colorado Mineral Belt) increased vitrinite $\%R_o$.

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.

Keywords: illite, K-Ar dating, Li-isotopes, B-isotopes, hydrocarbon, diagenesis, gas generation

1.0 INTRODUCTION

The Denver Basin has a long record of oil and gas exploration and production (see Higley and Cox, 2007 and 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 (1974) 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 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 ^{11}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 ^{10}B enrichment in tetrahedral coordination on the organic compounds. Takahashi et al. (2011) similarly showed tetrahedral bonding and ^{10}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., 2001; 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 ^6Li 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 et al., 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., 2001; 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 WGF within the Denver Basin. Vitrinite reflectance (%Ro) values of the Cretaceous sediments range from 0.8 to as high as 1.3 within the WGF (Higley and Cox, 2007). Current geothermal gradients range from 36°C/km to as high as 51°C/km (Meyer and McGee, 1985). The superposition of the highest %Ro along the basin axis and highest geothermal gradient in the WGF over the regionally high %Ro led to the interpretation that a secondary thermal event occurred after burial-related diagenesis to produce the observed high level of thermal maturity (Higley et al., 1985; Higley and Cox, 2007).

The southern part of the WGF overlies an area of relatively high residual magnetic intensity bounded by the Johnstown and Lafayette wrench faults that relate to the NE extension of the Colorado Mineral Belt (Higley et al., 2003); it is also an area of high gas productivity. The magnetic intensities are suggestive of the presence of a deep seated pluton or batholith that may have induced a late thermal episode in the WGF. The enhanced levels of thermal maturation resulted from combined effects of burial and later emplacement of the pluton, both producing heat and migration of hot fluids (Higley and Cox, 2007). Based on the percentage of illite layers in I-S, Elliott et al. (1991) found the extent of illitization was highest in two Cretaceous bentonites within the WGF (Mowry shale and Niobrara Formation). The measured K-Ar ages of I-S collected from bentonites within the WGF range from 60-63 Ma (Elliott et al, 1991).

Outside of the WGF, the ages of illite in outcrop exposures of bentonite vary (65-85 Ma) and samples contain less diagenetic illite (<10%; Elliott et al., 1991). These samples were apparently not affected by the rapid burial that produced thermally mature rocks in the WGF and

along the basin axis. The outcrop samples reflect a more normal burial rate and temperatures that produced slower reaction kinetics allowing diagenetic illite to equilibrate with local pore fluids, with no evidence of hydrothermal inputs.

1.4 Sample locations

Cretaceous bentonites were collected from shale (Mowry Shale, Skull Creek Shale) and limestone formations in the Niobrara Formation (Elliott et al., 1991). The locations of six bentonites sampled are shown in Figure 1. Three bentonites (Horse Creek WY, Colorado Springs, CO, and Marathon 2 Holt Core 510, Morrill Co, NB) were collected from areas of the basin that did not experience significant burial, based on the low percentages of illite layers in I-S in these bentonites and their lower %Ro values (Higley and Cox, 2007). One bentonite was collected from the Mowry Shale in core S-069 located close to the basin axis in SE Wyoming. The remaining two bentonites were collected from USGS cores in the WGF; core R142 (Cretaceous Mowry Shale) and core S911 (Cretaceous Niobrara Limestone), both from Weld County, CO.

2.0 METHODS

2.1 Sample Preparation

The clay fractions of cores R142 and S911 were separated by centrifugation to select the <0.1 μm and 0.1 – 0.2 μm size fractions following methods in Jackson (1969). All other samples were prepared as <2 μm fractions for a total of eight samples. The purity of the I-S samples was determined by X-ray diffraction (Cu $k\alpha$ radiation) using standard clay mineralogy methods (Moore and Reynolds, 1997), as presented in Elliott et al., (1991). An aliquot of these same

samples was then prepared for trace element and isotope ratio analysis by secondary ion mass spectrometry (SIMS).

At pH <7, common in hydrocarbon bearing sediments, boric acid [B(OH)₃] is the dominant aqueous B-species and Li occurs as LiOH. These neutral compounds may enter the interlayer of expandable clays (I-S) and may be adsorbed to exterior surfaces of the clay crystals at OH sites (Couch and Grim, 1968). The I-S samples are easily contaminated when exposed to laboratory chemicals that often have trace levels of Li and B, therefore it is essential to remove external surface contaminants. Mannitol is a polyhydric alcohol that complexes both Li and B and can be used to remove surface adsorbed contaminants (Hingston, 1964). However, removing any interlayer Li and B requires cation exchange (Williams et al., 2012).

It is important to realize that all adsorbed Li and B are removed from the interlayers of smectite and external surfaces before isotopic analysis because it was shown that the exchangeable cations in I-S are not necessarily in equilibrium with the silicate framework (Williams et al., 2007). The Denver basin samples studied here were Na-saturated for XRD and K-Ar analyses (Elliott et al., 1991), which removes interlayer B, and were subsequently treated with mannitol (0.1N solution shaken 24 hrs) and rinsed in Amberlite resin filtered water, in triplicate to remove exterior surface adsorbed-B. A 5µl suspension of clay in water (~10mg clay/ml) was dropped onto a one inch round glass slide (nominally Li and B free) where the water surface tension orients the clays flat when dried. The samples were then gold-coated for conductivity before placing under vacuum (<10⁻⁷ Torr) in the mass spectrometer. The SIMS analysis of these exchanged and cleaned clay fractions measures only the Li and B that is structurally bound in the silicate sheets (i.e. tetrahedral B and octahedral Li).

2.2 Secondary Ion Mass Spectrometry

A Cameca IMS 6F secondary ion mass spectrometer (SIMS) was used to analyze Li and B in the different size fractions of I-S samples. The method followed earlier applications (Hervig, 1996; Williams et al., 2012). Briefly, a primary beam of O^- ions was defocussed to $\sim 30 \mu m$ diameter and used to sputter secondary ions from clays prepared as described above. Positive secondary ions were detected. Two analysis routines were used: one for concentration and one for isotope ratios. The analyses for Li and B concentrations only allowed secondary ions with 75 ± 20 eV initial kinetic energy into the mass spectrometer. A calibration curve was created from bulk-analyzed clay and glass standards (Williams et al., 2012). The typical precision is $<3\%$ for Li and B contents. Isotope ratio analyses were conducted at similar conditions except that secondary ions with 0 ± 20 eV initial kinetic energy were detected. In both cases, the instrument was operated at a mass resolving power (MRP ~ 1200) sufficient to separate ^{11}B from interfering ^{10}BH and 7Li from 6LiH . For Li and B. Where natural isotopic ranges vary by $>100\%$, errors on the order of 1-2‰ are acceptable. Analytical errors were compared to predicted errors based on counting statistics, and if the result was >2 times predicted the analysis was rejected. This usually indicates a problem with sample charging or a non-flat surface. See Williams et al. (2012) for more details.

Isotope ratios are reported in the standard delta notation in parts per thousand (‰):

$$\delta^{\text{heavy}}M = \{[(^{\text{heavy}}M/^{\text{light}}M)_{\text{sample}} / (^{\text{heavy}}M/^{\text{light}}M)_{\text{reference}}] - 1\} * 1000; \text{ where } M = \text{element}$$

The reference value for Li isotopes is NIST LSVEC Li carbonate with $^7Li/^6Li$ ratio of 12.0392 (Chan et al., 1992) and for B isotopes it is NIST NBS 951 boric acid with a certified $^{11}B/^10B$ ratio of 4.0437 (Catanzaro et al., 1970). The SIMS analyses were calibrated against internal reference

material IMt-1 illite (Clay Repository, Purdue IN) with bulk analyses for $\delta^{11}\text{B}$ and $\delta^7\text{Li}$ of $-9 \pm 1\text{‰}$ (Williams et al, 2012).

3.0 RESULTS

The analyses of I-S samples in the Wattenberg gas field (WGF) are given in Table 1. The %illite in I-S reflects the thermal maturity indicated by %Ro (Elliott et al., 1991), and the K-Ar dates measure the time of illite crystallization. The results show that generally light $\delta^{11}\text{B}$ values (-15‰ to -7‰) are observed in the I-S separates from the bentonite samples. Three outcrop samples in the distal margins of the basin (Horse Creek, WY, Colorado Springs, CO and core 510, NE; Fig. 1) showed the lightest $\delta^{11}\text{B}$ values (-15‰ to -10‰). Heavier $\delta^{11}\text{B}$ values (-10‰ to -7‰) were found in the thermally mature samples from the basin axis and WGF. The $\delta^7\text{Li}$ values range from -18‰ to -4‰ in the WGF with the exception of one heavy value of $\delta^7\text{Li}$ ($+12\text{‰}$; R142F). The $\delta^7\text{Li}$ of the coarser fraction of that same sample is -18‰ . Outside of the WGF, the $\delta^7\text{Li}$ values range from -7‰ to $+4\text{‰}$. Overall, the Li-isotopes display a larger range than the B-isotope values.

The B-contents are mostly high (110-180 ppm) in the WGF (with the exception of one analysis), and the basin axis (core S-069) compared to lower values in the distal basin margins well outside the WGF and the basin axis (64-105 ppm). While Li concentrations range from 2-60 ppm, most of the measured Li concentrations are low (<10 ppm). The two highest concentrations (37 and 60 ppm) are from the I-S in the Niobrara bentonite from core S911 in the WGF.

4.0 DISCUSSION

In this study, we test the hypothesis that thermally mature kerogen releases isotopically light Li and B to diagenetic pore fluids in sedimentary basins, and that the light isotopic signature is reflected in the isotopic composition of the associated diagenetic illite. The discussion below presents an interpretation of the isotopic results for Li and B, assuming kerogen is the source, then explores the possibility of alternative sources of these tracers given the geologic history of the Denver basin.

4.1 Lithium isotopes in illite

Within the WGF, there are large differences in the $\delta^7\text{Li}$ between the finer and coarser fractions of the two bentonite core samples (R142, S911). These two bentonites were collected within the zone of highest thermal maturity (Fig. 2) where high geothermal gradients correlate with highest vitrinite %Ro values (Elliott, 1988; Elliott et al., 1991). The Li-content of the illite increases with increasing size fraction (Table 1) with a 30‰ decrease in the $\delta^7\text{Li}$ from fine to coarse fractions of core R142 and a 12‰ decrease in core S911. This difference indicates uptake of isotopically light Li some time after the onset of illitization at ~60 Ma (Elliott et al., 1991). The first nucleated illite, contained in the finest size fraction, was enriched in ^7Li (+12‰), however as these crystals grew, they incorporated elements from new fluids enriched in ^6Li . We interpret the dramatic shift in $\delta^7\text{Li}$ between fine and coarse fractions of illite in the WGF bentonites as a record of the influx of isotopically light, gas-related fluids (see Section 4.2). The measured K-Ar ages of the two size fractions of I-S are not significantly different ($\pm 3\text{Ma}$), indicating that the change in fluid composition reflected in the different size fractions had to occur rapidly, within this 6Ma interval. These ages correlate with the formation of the WGF as a structural foreland basin.

Outside of the WGF, the percentages of illite in I-S, and projected burial depth both decrease with distance from the WGF (Elliott et al., 1991) and the %Ro values (<0.8) indicate a lower thermal maturity (Tainter, 1984). The Li-isotopic compositions of I-S from bentonites generally increase with distance from the WGF, and the ages of the bentonites vary (Table 1). The oldest illite formed to the south (Colorado Springs) and the youngest to the northeast (510), confirming that illite in those samples did not result from the thermal events within the WGF. Outcrop samples were only buried deep enough to produce <10% illite, and using the present day geothermal gradient (30.6°C/km; Higley and Cox, 2007) temperatures only reached ~60°C, where illitization begins during burial (Burst, 1969; Perry and Hower, 1970; Hower et al., 1976; Sucha et al., 1993). The heavier $\delta^7\text{Li}$ compositions (–7 to +4‰) of the outcrop samples may represent the isotopic composition of normally buried sediments, influenced by local organic sources and groundwater. The enrichment of ^6Li within the WGF by tens of per mil over nearby correlated bentonites outside the depocenter, clearly indicates different paleofluids within the WGF than in the shallower buried sediments.

4.2 Paleofluid Li-isotopes

The experimentally determined fractionation equation for Li between illite and water (Williams and Hervig, 2005; Williams et al., 2012)

$$1000 \ln \left(\frac{^{6}\text{Li}}{^{7}\text{Li}} \right)_{\text{illite-water}} = 6.15 - 9.07 (1000/T \text{ (K)})$$

corresponds well with theoretical (Oi et al., 1991) and empirical (Chan et al., 1992) calibrations. This fractionation is in close agreement with experiments recently performed at low temperature (<250°C) by Millot et al. (2010) and experimental fraction curves published for smectite (Vigier et al., 2008). The above studies show significantly higher sensitivity to temperature than experiments on micas (Wunder et al., 2007).

Thus, the isotopic composition of the WGF paleofluid can be estimated if the temperature of illitization can be constrained. Table 2 presents a range of burial temperatures supported by %Ro measurements to evaluate the potential range of water $\delta^7\text{Li}$ compositions in equilibrium with illite. The high vitrinite reflectance measurements (%Ro >1.2) in the WGF suggest that maximum temperatures reached over 120°C (e.g., Jiang, 2012) in the locality of sample R142, ~100°C (%Ro ~1.0) for that of sample S911, and ~80°C (%Ro ~0.8) at the limits of the hot spot. However, illitization may have started at temperatures as low as ~60°C when burial diagenesis begins (e.g., Hower et al., 1976).

Given this range of temperatures and the isotopic compositions measured in illite, Table 2 summarizes calculated paleofluid compositions for hypothetical temperatures ranging from 60°C (onset of illitization) to 150°C (dry gas stage). We deduce that the first nucleated illite formed when the basin was rapidly buried, as temperatures approached 60°C, producing the illite $\delta^7\text{Li}$ of $+12 \pm 0.8\text{‰}$ (sample R142F). This illite reflects equilibrium with a $+33\text{‰}$ $\delta^7\text{Li}$ paleofluid, which is approximately the composition of seawater (Chan and Edmond, 1988). This is consistent with the marine deposition of the Cretaceous Mowry and Graneros shales that are the source rocks for the WGF (Higley et al., 2003). The rapid burial of the WGF at $\sim 60 \pm 3\text{Ma}$ (Elliott et al., 1991; Higley and Cox, 2007) produced more extensive illitization in the bentonite (up to 73% in R142C). Using estimates of the geothermal gradient inside the WGF during initial burial (32.6°C/km; Elliott et al., 1991), and the maximum burial depth (3.2km), the illite in R142C formed at temperatures closer to 100°C, however the vitrinite %Ro indicates a maximum temperature of 120°C. Using these temperature estimates of 100° to 120°C, the R142C illite with a $\delta^7\text{Li}$ value of $-18 \pm 0.5\text{‰}$ suggests a paleofluid composition between 0‰ and -1‰ (Table 2). Notice that the 20°C temperature range has negligible effect on the estimated water composition.

Similar isotopically light $\delta^7\text{Li}$ compositions have been measured in hydrothermal waters from Yellowstone (Sturchio and Chan, 2003) and marine hydrothermal fluids (Tomascak, 2004). Such low $\delta^7\text{Li}$ values were also estimated for porefluids that precipitated illite in bentonites of the southeast Baltic basin near Poland oilfields (Williams et al., 2013).

Sample S911 shows a -12‰ change in $\delta^7\text{Li}$ between the fine and coarse I-S fractions. Assuming again that illitization began at $\sim 60^\circ\text{C}$, we calculate that the fine illite (-1‰) nucleated from porefluid with $\delta^7\text{Li}$ values near $+20\text{‰}$, a value that is common for ground waters (You et al., 1995, Zhang et al., 1998, James and Palmer, 1999), however it could also represent mixing of the 0‰ water indicated for R142C with original marine pore fluids. Given the burial depth (2.9km) and geothermal gradient estimated for the WGF at that time (Elliott et al, 1991), the coarser illite fraction (-13‰) precipitated from porefluid with $\delta^7\text{Li}$ near $+5\text{‰}$ at 100°C . The lower %Ro around sample S911C is reflected by lower illitization (71%) compared to R142C (73%), however the Li-content is much higher (60 ppm) suggesting increased substitution of Li in the coarse fraction I-S, and supporting localized influx of ^6Li (rather than loss of ^7Li) in the bentonite.

Sample S-069 taken from core outside of the WGF hot spot, but along the Denver basin axis, is less illitized than the WGF samples, and has a $\delta^7\text{Li}$ of -1‰ , like S911F. The vitrinite %Ro values are 0.8 - 1.0% in this region (Higley et al., 2003). The age of this sample (56 ± 3 Ma) is slightly younger than I-S in the WGF, suggesting cooling with time. At $80 - 100^\circ\text{C}$ the illite in this sample would have precipitated from a fluid with $\delta^7\text{Li}$ of 17-19‰ reflecting mixing of the WGF hydrothermal fluid (0 to $+5\text{‰}$) with the isotopically heavier porewaters in the distal basin.

Sample 510 (<2 μ m) taken from shallow core at the northeast border of the Denver basin, formed at ~49Ma and has the highest $\delta^7\text{Li}$ value of $+4 \pm 0.7\text{‰}$. If the illite precipitated at ~60°C (based on regional %Ro) then the composition of the regional pore fluid was +25‰. This value is within the range of $\delta^7\text{Li}$ values reported for ground waters (Huh et al., 1998; Tang et al., 2007) or seawater that has been diagenetically modified during burial. The outcrop samples (Horse Creek and Colorado Springs) have $\delta^7\text{Li}$ values reflecting paleofluid compositions of +14 to +20‰ if the bentonites were shallowly buried (<60°C) as indicated by their low %illite in I-S (Table 1). The isotopic variations reflect local diagenetic conditions with no hydrothermal inputs.

4.3 Boron isotopes in illite

At the distal margins of the WGF (core 510, Colorado Springs, and Horse Creek, WY), where illitization is <10%, the B-content of the bentonites is <105 ppm and the B-isotope composition of I-S in bentonite ranges from -12 to -15‰ (Fig. 3). These values are lighter than the $\delta^{11}\text{B}$ measured in the more thermally altered and more illitized core samples from the WGF and basin axis core where B contents are highest (S-069, S-911). In contrast to the observations for Li isotopes, there are no large changes in the isotopic composition of B between the fine and coarser fractions of the core samples (R142 and S911). This can be explained by the timing of illitization relative to the timing of B and Li release from kerogen. If B was released at a low temperature (e.g., early oil generation) during normal burial, but rapid illitization occurred during basin down warping and hydrothermal flow (e.g. gas generation) then the isotopic signal from the rapid illitization would dominate. In other words the illitization coincided with the higher temperature fluids associated with the influx of ^6Li , after ^{10}B release.

4.4 Paleofluid B-isotopes

Given the temperatures estimated for illitization in the WGF, we calculated the B-isotopic composition of the water using the illite-water fractionation equation for B at pH < 7:

$$1000 \ln \alpha_{B_{\text{min-water}}} = 3.28 - 10.35 (1000/T \text{ (K)}) \quad (\text{Williams et al., 2012})$$

Calculated values of $\delta^{11}\text{B}$ in water associated with R142 ranged from +18‰ at 60°C to +16‰ at 120 °C (Table 2), lighter than average values of uncontaminated groundwater (+22 to +30‰; Vengosh et al., 1994). In fact, all of the estimates of $\delta^{11}\text{B}$ in water are lighter than these average values, as this is generally the case for kerogen-rich sediments (Williams and Hervig, 2004).

The temperatures estimated for peak illitization in the WGF were possibly as high as 150°C using a deep burial model (Elliott et al., 1991). The estimated temperatures are based on reconstructed burial curves and available geothermal gradients (Higley and Schmoker, 1989) and they correspond to peak hydrocarbon generation from mature source rocks (Durand, 1980). Considering evidence from the $\delta^7\text{Li}$ of the fine illite fractions in the WGF, indicating that initial paleofluids had approximately a seawater composition, we infer that the original porefluids had a $\delta^{11}\text{B}$ near +39‰ (modern seawater; Barth, 1993). However, the paleofluid $\delta^{11}\text{B}$ composition recorded by the fine size fraction illite in the WGF was +18 to +20‰ (Table 2), at the onset of illitization (60°C). This indicates that ^{10}B influx had already occurred and mixed with the original pore fluid by the time rapid illitization began. The similar paleofluid $\delta^{11}\text{B}$ calculated for the coarse illite fractions in the WGF and S-069 supports that B (^{10}B -enriched) was released before Li (^6Li -enriched), close to the onset of illitization.

If B is predominantly released from kerogen coincident with the ‘oil window’, and Li is predominantly released at the higher temperature of gas generation, then the dramatic isotopic

change in Li between fine and coarse illite fractions is a ‘snapshot’ in geologic time recording the influx of gas-related, ^6Li -rich water (Fig.4). The ~5‰ enrichment of ^{11}B in illite samples from the WGF, compared to shallower outcrop samples outside the WGF results from the different geothermal gradients, where burial under normal geothermal gradients did not preserve the later ‘fluid mixing’ demonstrated by the rapidly buried sediment under high geothermal gradient.

4.5 Alternative sources of lithium and boron

As discussed in the introduction (Section 1.3), there is evidence for a second thermal event in the WGF occurring at 40 - 20Ma (Higley and Schmoker, 1989) that potentially increased the organic maturity to the maximum %Ro measured (1.3%). Based on residual magnetic mapping, an anomaly beneath the WGF indicates the emplacement of a deep-seated batholith containing ultramafic minerals (Higley et al., 2003). This magnetic anomaly is consistent with observations of a northeast extension of the magmatic emplacement along the Colorado mineral belt within the Denver basin (Rice and Gautier, 1983). The igneous intrusion produced a thermal anomaly in the WGF estimated at 51.1° to 52.9°C/km (Higley et al., 2003) compared to surrounding areas (29° to 32.8°C/km; Meyer and McGee, 1985) and it was proposed that gas generation began at this more recent time. In light of this evidence, alternative sources of Li and B must be considered.

Elliott et al. (1991) examined the rates of burial in the WGF samples studied here, using K-Ar dating of illite, and concluded that rapid down-warping of the WGF, associated with the Laramide orogeny and development of the foreland Denver Basin, caused the high percentages of illite in the bentonites. The later thermal anomaly related to igneous intrusions may have driven hydrothermal fluid migration upward along faults (Higley et al. 2003), introducing

magma-related Li and B, so the question is how much of these elements were brought up and what was their likely isotopic signature?

While a magmatic heating event at ~40Ma could have affected vitrinite reflectance, it clearly did not affect the K-Ar dates of the illites, which show consistent ages (60 ± 3 Ma) for the fine and coarse size fractions studied in the R142 and S911 bentonites (Elliott et al, 1991). These ages are also consistent with the burial history in this area of the Denver Basin (Elliott et al., 1991). Any thermal event following that of the first generation of illite at ~60 Ma is expected to potentially alter the K-Ar signature of the older illite in two ways: (1) If the temperature of the gas generation at 40 Ma was higher than that of the first illite generation, then the available K-Ar data of the first-generation illite should have been altered or completely erased (e.g., Clauer et al., 2014a; Hamilton et al., 1989), and the illite dates would be 40-20Ma reflecting the age of igneous intrusion. (2) The second thermal event could have induced crystallization of a new generation of illite at a lower temperature than that of the first illitization. In this case, the K-Ar system of the older illite would have remained unaffected but a second generation of illite should be detected in the K-Ar date of the finer separates, which should contain this hypothetical new generation of illite. This is also not observed because the fine fractions of illite in the WGF samples do not show dates younger than 60Ma. Fluids derived from an ultramafic magma (Higley et al., 2003) could also have contributed to the Li and B composition of the WGF fluids after illitization. However, this late emplacement of a deep ultramafic pluton apparently did not produce temperatures that altered the K-Ar system of the first generation of illite, nor favored crystallization of a second generation of illite at a lower temperature for the same reasons as above (no perturbation of the K-Ar ages). The influx of fluids from the mafic intrusion would only be reflected in the Li and B-isotope ratios of the I-S if these minerals dissolved and re-

precipitated with an age of 40-20Ma. As noted previously, we carefully removed all adsorbed-Li and B (interlayer and external surfaces) from the clays that might have represented later fluids that diffused into bentonites post-illitization (Section 2.1).

Furthermore, the isotopic composition of Li and B measured in the different illite size fractions from bentonites is not consistent with the potential influence of a magmatic influx of hydrothermal fluid. For Li, the isotopic composition of ultramafic minerals range from +2 to +5‰, with concentrations <10ppm (Tomascak, 2004; Halama et al., 2009). While ultramafic minerals can be particularly rich in ^6Li (Tang et al., 2007), their associated waters are enriched in the heavy isotope, with $\delta^7\text{Li}$ compositions ranging from +23 to +40‰ (Boschetti et al., 2013; Rudnick et al., 2004; Pistiner and Henderson, 2003), which is not consistent with the 0 ‰ isotopic composition of waters indicated for paleofluids in the WGF.

Similarly, the interaction of hydrothermal fluids with B-bearing minerals from mafic intrusives will produce a fluid enriched in the heavy isotope compared to the mineral, and with low B-contents (Palmer and Swihart, 1996; Hervig et al. 2002, Wunder et al. 2005). Assuming fluids evolved from a mafic intrusion at sub-solidus conditions (mafic rock $\delta^{11}\text{B}$ typically range from -5 to +5 ‰), we estimate isotopically heavy hydrothermal fluids (>20‰), as temperatures decrease and the fluid interacts with marine deposited sediments. We conclude that it is difficult to get the observed B-content and isotopic signatures from a non-convective hydrothermal system, and there is no evidence of a convective hydrothermal system, which would homogenize the trace element content of the fluids across the WGF.

While it is possible that a magmatic geothermal anomaly occurring at 40-20Ma affected the maximum organic maturity, it apparently did not alter the first illite generation, nor did it cause additional illitization, on the basis of the available K-Ar ages, and it is not reflected in the

Li and B isotopic signatures in the diagenetic illite. On the contrary, the large Li-isotopic change between fine and coarse fractions of 60 ± 3 Ma illite in the WGF suggests gas generation within that time frame, enriching pore fluid in ^6Li generated from kerogen, not from magmatic fluids.

5.0 CONCLUSION

Rapid down-warping of the Wattenberg basin coincident with the Laramide orogeny accounts for the Early Tertiary ages (60 ± 3 Ma) of illite in the WGF bentonites compared to older bentonites along the Front Range at Colorado Springs, Colorado and Horse Creek, Wyoming and a much younger bentonite in Nebraska (510) at the northeast basin margin (Elliott et al., 1991). The structural down warping increased the thermal gradient; generating oil and releasing B from organic-rich source rock that enriched pore fluid in ^{10}B , mixing with the initial marine porefluid to produce a fluid composition around +16 to +20‰. This down warping extended along the basin axis to Wyoming (Tainter, 1984), affecting core S-069. In contrast, the bentonites from outside the WGF (Colorado Springs, Horse Creek, 510) reflect sediments buried at a normal rate under a lower geothermal gradient, where the pore fluids gradually equilibrated with the organic-rich sediments.

Within the WGF, the two core samples have variable Li-content, and they show a two-fold increase in Li between fine and coarse fractions of illite corresponding to a $\delta^7\text{Li}$ shift of -12 to -30‰. This requires influx of ^6Li -enriched fluid with a $\delta^7\text{Li}$ composition near 0‰. Similar isotopically light $\delta^7\text{Li}$ values have been measured in other source rocks (Williams et al., 2013) at thermal grades associated with thermogenic gas generation. Therefore, we conclude that the WGF isotopic shift marks the first generation of gas. This does not rule out the possibility of a

second episode of gas generation during later magmatic heating at ~40 Ma, but it was not recorded by the diagenetic illite according to their K-Ar dates and isotopic signatures.

The implications of this work are that light trace elements, Li and B, are associated with organic matter and can trace the generation and migration of hydrocarbon related fluids. Isotopically light B appears to be released at temperatures marking the onset of oil generation, while isotopically light Li appears to be released at higher temperatures associated with gas generation. While the light isotopes of B and Li partition preferentially into pore fluid during hydrocarbon maturation, the snapshot of that fluid composition depends on the timing of diagenetic illite growth relative to trace element release. For the WGF we conclude that illite with significantly light $\delta^7\text{Li}$ marks the influx of gas and the illite K-Ar ages record the timing of gas generation during the evolution of this foreland basin.

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721

Figure Captions

Fig. 1. Denver Basin map showing sample locations. The shaded areas indicate range of vitrinite reflectance values (R_o %) in the WGF (from Higley et al., 1985). Approximate trace of the basin axis is shown.

Fig. 2. Lithium isotope composition of I-S from bentonites in the WGF and surrounding region. F = fine fraction ($<0.1\mu\text{m}$); C = coarse fraction ($0.1 - 2.0\mu\text{m}$), otherwise samples were $<2\mu\text{m}$ fractions.

Fig. 3. Boron isotope composition of I-S from bentonites in the WGF and surrounding region. F = fine fraction ($<0.1\mu\text{m}$); C = coarse fraction ($0.1 - 2.0\mu\text{m}$), otherwise samples were $<2\mu\text{m}$ fractions.

Fig. 4. Schematic diagram showing the diagenetic zones of hydrocarbon generation, percent illitization, and inferred temperature of B and Li release from organic compounds with thermal maturity, based on results presented here. The crystal sizes represent authigenic illite in I-S showing the initial nucleation of small crystals, and continued growth during burial. The most common crystal size distribution is log-normal in buried bentonites (Eberl et al., 2002).

Figure 1

Figure 2

Figure 3

Figure 4

Table 1

Table 1. Denver Basin (Wattenberg Gas field) B and Li-content and isotopic compositions of I-S isolated from bentonites in cores and outcrops. Number of analyses (n) is given for the averaged and 1s standard errors reported for isotope values. F = fine, C = coarse size fractions.

Sample ID	B ppm	B (n)	$\delta^{11}\text{B}$ ‰	$\pm 1\sigma$ ‰	Li ppm	Li (n)	$\delta^7\text{Li}$ ‰	$\pm 1\sigma$ ‰	‰I (I-S)	* Age (Ma)
<u>cores</u>										
R142F (<0.1 μm)	51	19	-10	1.0	2	5	12	0.8	66	59 ± 3
R142C (0.1-2.0 μm)	110	7	-7	0.6	6	17	-18	0.5	73	60 ± 3
S911F (<0.1 μm)	173	10	-8	0.3	37	5	-1	0.6	73	61 ± 3
S911C (0.1-2.0 μm)	180	6	-9	0.5	60	10	-13	0.6	71	63 ± 3
S-069 (<2.0 μm)	143	6	-7	0.6	2	3	-1	0.1	46	56 ± 3
<u>outcrops</u>										
510 (<2.0 μm)	97	5	-13	0.6	9	5	4	0.7	7	49 ± 4
Horse Creek (<2.0 μm)	105	14	-12	0.7	5	19	-7	0.4	6	65 ± 3
CO Springs (<2.0 μm)	64	6	-15	0.9	4	4	-1	0.5	4	85 ± 4

* Data from Elliott et al., 1991, Age determined by K-Ar dating

Table 2. Paleofluid isotopic compositions (‰) calculated from fractionation equations and the measured isotope ratios in I-S, for a range of potential diagenetic temperatures.

Sample	Temp (°C)	$\delta^7\text{Li}$ illite	$\delta^7\text{Li}$ water	$\delta^{11}\text{B}$ illite	$\delta^{11}\text{B}$ water
<u>cores</u>					
WGF R142F	60	12	33	-10	18
WGF R142C	100	-18	0	-7	18
	120	-18	-1	-7	16
	150	-18	-3	-7	14
WGF S911F	60	-1	20	-8	20
WGF S911C	100	-13	5	-9	16
	120	-13	4	-9	14
	150	-13	2	-9	12
S-069	60	-1	20	-7	21
	100	-1	17	-7	18
	120	-1	16	-7	16
	150	-1	14	-7	14
<u>outcrops</u>					
510	60	4	25	-13	15
Horse Creek	60	-7	14	-12	16
CO Springs	60	-1	20	-15	13

(Modified from Tissot and Welte, 1984)