The influence of organic matter on the boron isotope geochemistry of the gulf coast sedimentary basin, USA

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Abstract

Large variations in the boron isotopic composition of sedimentary environments make boron an attractive monitor of fluid/rock interactions during diagenesis. Studies of B in marine sediments have shown that preferential adsorption of ^{10}B on clay minerals leaves pore waters enriched in ^{11}B. During diagenesis, clay minerals recrystallize and incorporate ^{10}B into the mineral structure (Spivack, A.J., Palmer, M.R., Edmond, J.M., 1987. The sedimentary cycle of the boron isotopes. Geochim. Cosmochim. Acta 51, 1939–1949). This process should cause a depletion of B in the pore water with an increase in the δ^{11}B. In the Gulf Coast sedimentary basin (USA), however, there is a general increase in B-content of formation waters (Land, L.S., Macpherson, G.L., 1992. Origin of saline formation waters. Cenozoic Section, Gulf of Mexico Sedimentary Basin. Geochim. Cosmochim. Acta 76, 1344–1362; Moldovanyi, E.P., Walter, L.M., 1992. Regional trends in water chemistry, Smackover Formation, Southwest Arkansas: Geochemical and physical controls. AAPG Bull. 76, 864–894.) and a decrease in δ^{11}B with depth. This suggests that another source of ^{10}B exists in deep basinal environments. We know that oil reservoir brines are commonly enriched in boron (Collins, A.G., 1975. Geochemistry of Oilfield Waters. Elsevier, New York, p. 496.), therefore this study examines organic matter as a possible source of boron during thermal maturation.

Samples of water, oil, and cored sediments were collected from three stacked hydrocarbon reservoirs in the Gulf of Mexico sedimentary basin at a depth of 3500–4350 m. Extraction of boron from organic matter (oil and kerogen) was done by Parr Bomb volatilization, with mannitol used as a B-complexing agent. The isotope ratios were measured using negative thermal ionization and compared to in situ analyses using secondary ion mass spectrometry.

The δ^{11}B values of pore filling clays in sandstone reservoirs is -2 ± 2‰. The B-content of the clay averages 144 ppm. Oil field waters show a range in B-content from 8–85 ppm and δ^{11}B values from $+28$ to $+37$‰, increasing from the lowest to the uppermost reservoir. There is an apparent ^{11}B-enrichment of fluids with progressive migration through clay-rich sediments. Very little B (ppb) was found in the oil, but kerogen extracted from the oil source rock (Sassen, R., 1990. Lower Tertiary and Upper Cretaceous source rocks in Lousiana and Mississippi: implications to Gulf of Mexico crude

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oil. AAPG Bull. 74, 857–878.) contains significant B (140 ppm) with a $\delta^{11}B$ of -2 ± 2‰, similar to the pore filling clay minerals in the sandstones. While kerogen comprises only $\sim 2\%$ of the sedimentary basin, its influence can be significant if B with distinctly low $\delta^{11}B$ is released over a specific temperature interval during thermal maturation. The release of B from organic compounds could cause the observed regional [10]B enrichment in waters deep in the Gulf Coast basin. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to evaluate the B-isotope systematics of sedimentary basins, we need to know the relative amount of B derived from organic matter during thermal maturation and its isotopic composition. The objective of this study is to determine the contribution of boron from oil and kerogen in a hydrocarbon-producing region of the Gulf Coast sedimentary basin and to evaluate its effect on the isotopic composition of associated water and minerals.

Boron is an important constituent of clastic sedimentary basins because it is concentrated in clay minerals, causing shales to contain one to two orders of magnitude more boron than other crustal or mantle silicates (Goldschmidt and Peters, 1932). Detrital clay minerals initially adsorb boron onto the mineral surface, but with increasing burial, boron is substituted in tetrahedral sites of the clay structure, replacing Si (Couch and Grim, 1968). This B is non-desorbable or 'fixed-B'. Perry (1972) studied boron fixation in clay minerals from natural sediments by isolating < 1 μm size fraction clays from samples of the Gulf of Mexico sedimentary basin (USA). He showed that fixed-B concentrations increase with increasing quantity of authigenic illite (Fig. 1a), and proposed that the source for B in authigenic illite was the adsorbed-B from detrital minerals, perhaps redistributed during breakdown of detrital illite (also a supply of K^+). Boron isotope systematics during progressive burial and illitization were not examined.

Recent B-isotope studies have focused on B in shallow marine sediments (< 2 km) where adsorption on clay-rich sediments has a significant effect on the isotopic composition of the associated pore fluids (Vengosh et al., 1991; Brumsack and Zulegar, 1992; You et al., 1995). Generally, high $\delta^{11}B$ waters are thought to result from preferential adsorption of [10]B onto clay mineral surfaces, causing a reduction

of the B-content of the water as well (Brumsack and Zulegar, 1992). Therefore, in shallow marine sediments the B-content of pore waters commonly decreases with depth while the $\delta^{11}B$ increases.

In the deep Gulf of Mexico basin, however, this variation of B and $\delta^{11}B$ with depth is not observed. Boron increases from 20 to 300 ppm and $\delta^{11}B$ decreases from a maximum of 40‰ to a minimum near 12‰ (Fig. 1; Land and Macpherson, 1992; Moldovanyi and Walter, 1992). There is considerable scatter in Fig. 1 which combines analyses from a number of localities. Such variations presumably indicate local differences in the chemistry of the sediments. However, the regional trend indicates the existence of an additional, isotopically light source of B in deep sedimentary basins which is not observed in shallow marine sediments.

Organic matter in the Gulf of Mexico sedimentary basin is a potential source of boron that has not been previously investigated. Available literature on the B content of organic matter is sparse, but B is often mentioned as a substantial component of organic
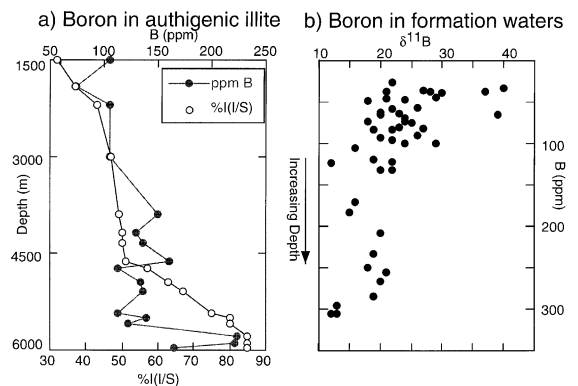

Fig. 1. (a) Variation in the B-content of authigenic illite with depth of burial in the Gulf Coast sedimentary basin, USA (Perry 1972) and (b) concurrent changes in B-content and $\delta^{11}B$ of formation waters from clastic reservoirs in the Gulf Coast sedimentary basin (Land and Macpherson, 1992).

compounds. Boron in oil has been found in concentrations up to 70 ppm B (Gulyayeva et al., 1966) and coals have been found with as much as 500 ppm B (Goodarzi and Swain, 1994). Gulyayeva et al. (1966) studied boron in various fractions of oil and found boron primarily associated with napthenic acids in the resinous oil components. Elevated concentrations of boron are common in oil field waters (Collins, 1975) suggestive of organically derived B. No data are available on the isotopic composition of boron in hydrocarbons and kerogen, therefore, the objective of this research was to explore the potential influence of organically derived B on the B-isotopic composition of basin waters.

2. Field area

Samples of water, oil and cored sediments were collected from drill holes that intersected three stacked hydrocarbon reservoirs in Fordoche Field, located in the Eocene Wilcox Fm of south-central Louisiana (Fig. 2). These samples allowed examination of the role of B in clays, organic matter and pore water during thermal maturation. The samples collected are from a locality where the structural, stratigraphic and mineralogic details as well as the thermal maturity of organic matter are known (Williams et al., 1995). The source region for the oils has been identified using biomarkers and oil–source rock correlations (Sassen, 1990), and thermal maturity in-

Fig. 3. Cross section of Fordoche field showing the structural and stratigraphic relationships of the three sandstone reservoirs sampled. Black denotes oil-saturated zones of the sandstone.

dices (Rock Eval pyrolysis) show the source rock to contain mixed type II and III organic matter with a moderate generative potential and averaging 2% total organic carbon (TOC). The ratio of H/C is approximately twice that of O/C indicative of a mature source (Williams et al., 1992; Williams et al., 1995).

The Wilcox Fm is comprised of a thick sequence of organic-rich mudstone with interbedded sandstones that were deposited along a prograding delta. Fordoche Field reservoirs are located just above the source region for the oils (Sassen, 1990). Previous investigations of this field (Williams et al., 1995) indicated that hydrocarbons were introduced into the three reservoirs along a normal growth fault that bounds the field to the northwest. The direction of hydrocarbon migration is up dip, away from the fault. The API gravity of the hydrocarbons increases from the deepest (46.9° API) to the middle reservoir (44.9° API) and uppermost reservoir (40° API).
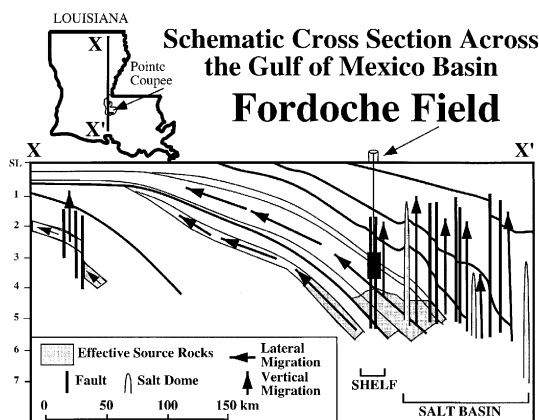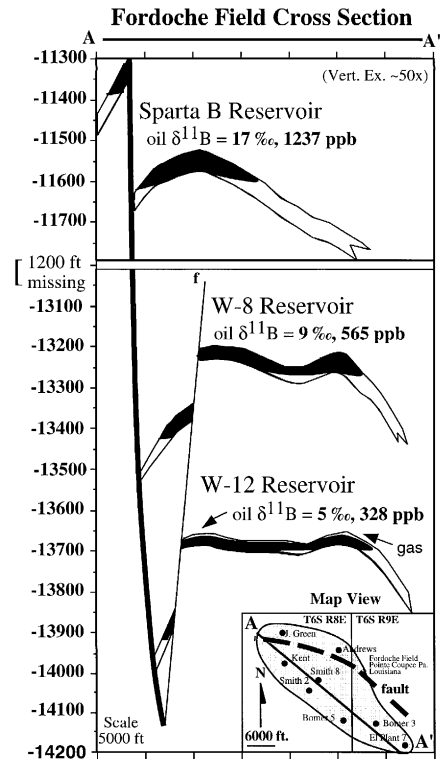

Fig. 2. Stratigraphic cross section across central Louisiana (N–S). The Fordoche field is located in the Eocene Wilcox Fm, directly above the inferred hydrocarbon source rock (Sassen, 1990).

A cross-section of Fordoche Field from the major growth fault toward the southeast (Fig. 3) shows the structural relationship of the three reservoirs sampled (W-12, W-8 and Sparta B reservoirs). Kerogen was extracted from mudstones located below the reservoirs at 14,200 ft (4.3 km). This region is slightly above the depth of source rocks, but the thermal maturity is very close to the threshold for hydrocarbon generation (Williams et al., 1995). The distance of fluid migration from the source region increases from the deepest toward the shallowest reservoir, and from the fault toward the southeast end of each reservoir in the field. The oil and water samples were taken from wells where cores were retrieved from the same production intervals. It was not possible to sample oil and water from each cored well across the field because some were out of production, but samples were taken across the deepest reservoir (W-12) along the section line and near the fault in the two shallower reservoirs (W-8 and Sparta B).

3. Methods

Two different mass spectrometric techniques were used in this study: Thermal Ionization Mass Spectrometry utilizing negative BO_2^- ion emission (NTIMS; Heumann and Zeininger, 1985; Vengosh et al., 1989; Klötzli, 1992; Hemming and Hanson, 1994), and Secondary Ion Mass Spectrometry (SIMS) (Chaussidon et al., 1997) which analyzes positive ions of B. The isotopic abundance ratio, $^{11}B/^{10}B$, is expressed in delta notation as $\delta^{11}B = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard} - 1] \times 1000$ (‰). The standard is NBS SRM-951 (boric acid) with $^{11}B/^{10}B$ ratio of 4.0437.

3.1. Analytical techniques

3.1.1. Thermal Ionization Mass Spectrometry

Negative Thermal Ionization Mass Spectrometry (NTIMS) is a conventional technique for analysis of solutions with very small amounts of B (Heumann and Zeininger, 1985; Vengosh et al., 1989; Klötzli, 1992). The ionization efficiency for negative ions is greater than for positive ions, therefore analyses can be made on samples containing as little as 10 ng of B (Hemming and Hanson, 1994). Typically 1–3 μl of sample solution is loaded on an outgassed rhenium filament, along with 3 μl of a Ba(OH)$_2$ solution (10 μg Ba) as an emission activator. The filament is introduced into the spectrometer with a vacuum of $\sim 2 \times 10^{-7}$ Torr, floated to -5 kV, and heated by a current of ~ 1800 mA. A stable emission current was normally generated at temperatures of 850–900°C.

Analyses yielded errors on the order of ± 2‰. These errors are greater than those obtained by PTIMS techniques using cesium metaborate (Swihart, 1996), however, given the large variations in $\delta^{11}B$ observed in the diagenetic environment (> 60‰), the errors should not preclude interpretation of the data. Measurements of the boron isotope standard NBS SRM 951 (Catanzaro et al., 1970) yielded a $^{11}B/^{10}B$ ratio of 4.0337 ± 0.0041, which is slightly higher than that reported by other labs using NTIMS (Vengosh et al., 1991; Hemming and Hanson, 1994). However, repeated analysis of seawater collected from the Pacific ocean yielded a $\delta^{11}B$ value of $+39.8 \pm 3$‰, which is in excellent agreement with that measured in other laboratories (Hemming and Hanson, 1994).

3.1.2. Secondary Ion Mass Spectrometry

SIMS analyses do not yield the high precision results of TIMS (Tonarini et al., 1997), but they allow better spatial resolution and control of the analyzed area based on textural observation. This can be essential for the analysis of authigenic pore-filling clay minerals that are impossible to separate from detrital clays during extraction from a core. It is sometimes possible to focus an analysis on a thick cement of a particular clay mineral, thus avoiding the complexity of analyzing multiple types of clay minerals. The general method for analysis of B-isotope ratios in silicates by SIMS is described by Chaussidon et al. (1997).

The SIMS was calibrated for analysis of clay minerals by comparing results of analyses on standards to analyses done by TIMS. A standard illite (IMt-1) was rinsed three times in B-free water, and centrifuged to select the < 2 μm fraction. Aliquots of this standard were analyzed (by W.P. Leeman, Rice University) by the method of Tonarini et al. (1997) using alkali carbonate fusion and ion-exchange separation for boron purification, and PTIMS using $Cs_2BO_2^+$. Three replicate analyses average -8.66 ± 0.23‰. Another aliquot was analyzed by

NTIMS (built in-house at Univ. of Calgary) with an average of two analyses of -9.86 ± 0.65 ‰. Using an average $\delta^{11}B$ value of -9‰ for the IMt-1 illite standard, we determine the instrumental mass fractionation (IMF) for the SIMS during each analytical session by measuring the B-isotope ratio on an aliquot of standard. Among the analytical sessions, the IMF varied between -44 and -51‰, depending on the instrumental set up. However, the IMF remained constant (within error) during each analytical session, allowing the correction for $\delta^{11}B$ relative to NBS 951. As noted by Chaussidon et al. (1997), there is not a significant matrix effect on B-isotope analyses, therefore, we assume no significant differences in the IMF for different clay minerals.

3.2. Sample preparation

3.2.1. Formation water

Eight water samples were filtered and acidified to pH ~ 2 when collected, in order to prevent bacterial alteration of the samples. The samples were never in contact with borosilicate glass, and were stored in polypropylene bottles. The B-contents of waters were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The levels of boron in the waters were high enough that no ion exchange was necessary in order to concentrate the B in solution for $\delta^{11}B$ analysis. The isotope ratios were measured by NTIMS.

3.2.2. Organic matter

Oils were collected from the same wells as waters and stored in polypropylene containers. Attempts to extract bitumen from powdered core samples failed because the core samples had been stored for several years so bitumen was lost. However, kerogen was extracted from mudstones by dissolution of the silicates in HF (Durand, 1980). The undigested kerogen was filtered out and dried. We found no published method for extracting and analyzing B-isotopes in organic matter, therefore, the sample preparation was tested and is described in detail.

Gulyayeva et al. (1966) used a Parr Bomb technique to extract B from oils for analysis of B-content. The Parr bomb is a steel cylinder in which a stainless steel vessel containing ~ 1 g of sample is suspended (Fig. 4). A nickel alloy ignition wire is
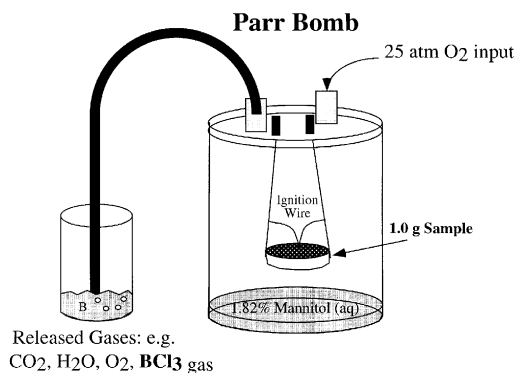

Fig. 4. Schematic diagram of the Parr bomb apparatus for extraction of B from organic matter.

placed just above the sample and about 4 ml of an absorbent (NaOH or water) is placed in the bottom of the cylinder. We used 'B-free' water defined as deionized water filtered through Amberlite resin to remove B. ICP analysis indicates a B-content of the treated water below the detection limit of 4 ppb. The bomb was then sealed, loaded with $25-30$ atm oxygen, and submerged in water. The bomb was ignited by a current supplied to the ignition wire, and the organic matter was volatilized.

There was minimal boron recovery in the aqueous solution within the bomb, perhaps due to loss of certain volatile forms of B, such as BCl_3 which is gaseous at $12.5°C$, and therefore might not have been trapped in solution. The relatively high salinity of oil field brines suggests an abundance of Cl^-, therefore, there is a likelihood of BCl_3 being lost along with CO_2 and other gases released when the bomb is opened. To remedy this, a boron complexing agent, mannitol, was used in the Parr Bomb. Mannitol is a polyhydric alcohol ($CH_2OH\ (CHOH)_4CH_2OH$), that is used to eliminate significant B loss from acidic solutions during silicate digestion (Ishikawa and Nakamura, 1990; Nakamura et al., 1992). A solution of 1.82% mannitol (Leeman et al., 1991) was added to the Parr Bomb. BCl_3 in the released gas was trapped by purging the gas through an external container of the mannitol solution (Fig. 4). The B-contents of solutions collected from inside the Parr Bomb were compared to the external solution and it was discovered that 90–95% of the total-B extracted was in the external solution. Tests were made for the

appropriate purge flow rate to yield the highest boron recovery. Initial purge rates took 20 min to empty the ∼ 1-l volume of gas in the cylinder (∼ 50 ml/min). The highest yields were obtained at a flow rate of ∼ 15 ml/min, however, this does not guarantee complete recovery. A double trap (two external solutions) is recommended as the most effective method for trapping the volatile boron.

Kerogen was initially extracted from six powdered mudstone samples by dissolution of silicates in hot (70–80°C) 5 N HF–1 N HCl. The undigested kerogen and amorphous silica residue were filtered out of the acid solution. This filtrate was Parr bombed to remove B from kerogen. Because of the variable content of undissolved silica in the organic concentrate (referred to as "ash" by coal petrologists), a small amount of ethanol was added to the sample to enhance ignition (just enough alcohol to dampen the sample). When pure organic compounds (e.g., oil) are Parr bombed there is no residue as volatilization is nearly complete, however silicate material trapped in the kerogen leaves considerable residue in the form of ash or glass beads. These residues were weighed in order to estimate the amount of kerogen volatilized during the Parr bomb procedure. In each sample, the ratio of organic matter to ash was ∼ 0.3. Insufficient B was recovered from 1-g samples of shale; however, a 50 g sample of organic-rich shale from beneath the Fordoche reservoirs yielded ∼ 18 g of kerogen (plus silica). The Parr bomb ignition was performed in batches since the capacity of each bomb is approximately 1 g of sample. The total ash recovered was 13 g, indicating that only about one third of this residue was organic matter (∼ 5 g, consistent with the ratio of organic matter to ash found previously). This kerogen provided enough B for ICP and TIMS analyses.

3.2.3. Clay minerals

SIMS analyses of $\delta^{11}B$ were done on thin sections of sandstone and mudstone from the Fordoche cores. B-contamination of minerals in thin section can occur during processing by polishing materials and epoxy. Experiments indicate that ultrasonic cleaning of the thin section with B-free water, and pre-sputtering of the analyzed area decreases B contamination to the level of 0.01 ppm (Chaussidon et al., 1997). However, clay minerals are sponges for

boron. The adsorbed-B can exchange in a few hours depending on the clay type (Bassett, 1976). Boron introduced with drilling fluids might significantly affect the isotopic composition of the adsorbed-B in core samples. Clay minerals are generally < 2 μm in size so the primary ion beam with a diameter of 20–50 μm may sputter many clay surfaces at various orientations during a single SIMS analysis. The resulting analysis would be some combination of adsorbed plus fixed-B. Therefore, it is very important to remove adsorbed-B from the thin-sectioned clays before analysis.

Removal of adsorbed-B from clay minerals was tested on clay mineral separates and compared to pore-filling and mudstone clay minerals in thin section from the same cored interval. Many authors (e.g., Keren and Mezuman, 1981; Palmer et al., 1987; Spivack et al., 1987) have removed adsorbed-B by rinsing the sample several times in deionized water. This is a standard procedure for separating out < 2 μm size fractions because Cl must be removed from the sample in order to prevent clay mineral flocculation. We found, however, that this does not consistently remove the adsorbed-B, especially if the clay sample is enriched in smectite. We compared B-isotope ratios of a standard smectite (SWy-1) rinsed five times in deionized (B-free) water and centrifuged to separate the < 2 μm size fraction, with an aliquot of that same sample that was K-saturated (shaken in 1 N KCl for 24 h then rinsed to remove Cl), and another aliquot that was washed in 1.82% mannitol solution for 2 h. A few drops of clay slurry was dried (60°C) on a B-free glass slide or silicon wafer and Au-coated for SIMS analysis. The results showed that the water-washed smectite has a $\delta^{11}B$ of + 12.1 ± 1.3‰, while the $\delta^{11}B$ of the K-saturated sample is − 3.0 ± 1.0‰, and the mannitol-washed sample similarly has a negative $\delta^{11}B$ of − 1.1 ± 0.6‰. Removal of adsorbed-B on kaolinite, smectite and illite by washing in mannitol has been tested (Hingston, 1963) and shown to be the most effective treatment. Mannitol also prevents B-isotope fractionation during evaporation (Xiao et al., 1997).

Since mannitol is an effective B-complexing agent we tried soaking a thin section in 1.82% mannitol solution and compared the $\delta^{11}B$ of clays before and after soaking. The sample was a mudstone sampled

Table 1
Boron contents of oil field waters and oils from the Fordoche Field

Waters

Sample	Reservoir	AA (ppm) S.D.	$^{11}B/^{10}B$ S.D.	$\delta^{11}B$ (‰)
John Green 1	Sparta B	85.1 ± 0.7	4.1787 ± 0.0093	36 ± 2.2
Andrews 2	Sparta B	29.3 ± 1.5	4.1804 ± 0.0190	36 ± 4.5
Kent 1	W-8	14.6 ± 0.9	4.1844 ± 0.0057	37 ± 1.4
Smith 2	W-8	15.6 ± 0.1	4.1514 ± 0.0087	33 ± 2.1
Kent 1D	W-12	13.1 ± 0.3	4.1479 ± 0.0160	28 ± 3.9
Smith 2D	W-12	8.3 ± 1.8	4.1688 ± 0.0081	29 ± 1.9
Bomer 3	W-12	18.6 ± 1.5	4.1480 ± 0.0068	28 ± 1.6
El Plant 5	W-12	30.2 ± 2.4	4.1817 ± 0.0084	37 ± 2.0

Oils

Sample	Reservoir	ICP (ppb) S.D.	$^{11}B/^{10}B$ S.D.	$\delta^{11}B$ (‰)
Andrews 2	Sparta B	1527 ± 3.7	4.1035 ± 0.0052	17 ± 1.3
Andrews 2D	Sparta B	947 ± 2.4		
Kent 1	W-8	433 ± 3.5		
Smith 2	W-8	696 ± 1.3	4.0702 ± 0.0089	9 ± 2.2
Kent 1D	W-12	228 ± 2.6		
Smith 2D	W-12	452 ± 1.8	4.0532 ± 0.0130	5 ± 3.2
Bomer 3	W-12	341 ± 1.5		
El Plant 5	W-12	289 ± 0.4		

Kerogen

		ICP (ppm) S.D.	$^{11}B/^{10}B$ S.D.	$\delta^{11}B$ (‰)
Kimball	Sample Rock	140 ± 1.4	4.0268 ± 0.0085	− 2 ± 2.1

Waters measured by atomic absorption (AA) spectroscopy with a detection limit of 2 ppm.
Oils measured by induced coupled plasma (ICP) spectroscopy with a 4 ppb detection limit.
S.D. is standard deviation. ICP and AA analyses are averages of four analyses per sample.

just below the uppermost reservoir (3535 m). The clays were a mixture of detrital and authigenic material, but the texture, grain size and mineralogy appeared homogeneous. The clay fraction of the mud- stone was composed of 44% kaolinite, 30% smectite, 15% chlorite and 11% illite/smectite. The initial analysis of clays in the untreated sample (sonicated in de-ionized water) gave a $\delta^{11}B$ value of + 6.6 ±
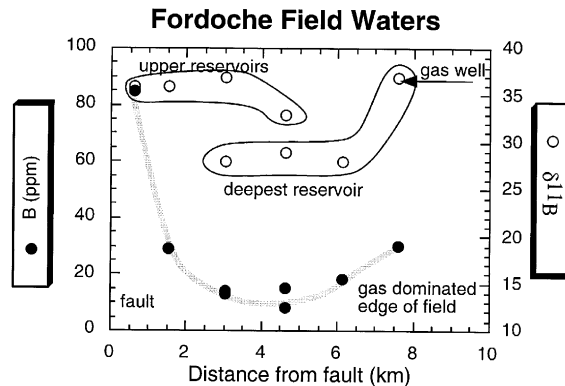

Fig. 5. Variations in B-content and $\delta^{11}B$ of formation waters across Fordoche Field.

Table 2
B-isotope analyses of clay minerals in (A) sandstone and (B) mudstone thin sections soaked in mannitol

Session date	Sample	Mass 11/10	S.D.	Error ‰	Pred. error ‰	IMF	S.E.
(A) Sandstone analyses							
August 27, 1998	IMt-1 standard, 240 ppm B	3.8084	0.0042	0.6	0.4	−49.2[a]	
		3.8135	0.0046	0.7	0.5	−47.9[a]	
		3.8139	0.0047	0.7	0.5	−47.8[a]	
	Average					−48[a]	0.8
	LNB 11614 SS, mannitol	3.8396	0.0126	1.8	1.0	−2.2[b]	
	washed, 228 ppm B	3.8374	0.0112	1.6	1.0	−2.7[b]	
		3.8395	0.0119	1.7	1.0	−2.2[b]	
		3.8366	0.0205	2.9	1.5	−2.9[b]	
		3.8394	0.0180	2.6	1.9	−2.2[b]	
		3.8345	0.0171	2.4	1.1	−3.4[b]	
		3.8431	0.0218	3.1	1.9	−1.3[b]	
		3.8350	0.0263	3.8	2.1	−3.3[b]	
	Average					−2.5[b]	0.2
	Holloway, 13820 SS, manitol	3.8464	0.0101	1.4	0.7	−0.5[b]	
	washed, 157 ppm B	3.8432	0.0241	3.4	2.3	−1.3[b]	
		3.8221	0.0051	0.7	0.7	−6.5[b]	
		3.8155	0.0128	1.8	1.4	−8.1[b]	
	new pore	3.8522	0.0163	2.3	1.6	0.9[b]	
	new pore	3.8589	0.0132	2.2	1.9	2.6[b]	
	Average					−2.1[b]	1.7
(B) Mudstone analyses							
August 24, 1998	IMt-1 standard, 240 ppm B	3.7947	0.0034	0.5	0.4	−52.6[a]	
		3.7989	0.0052	0.7	0.4	−51.5[a]	
		3.8065	0.0050	0.7	0.4	−49.7[a]	
	Average					−51.3[a]	0.9
	LNB 11607, mudstone, 258 ppm B	3.7584	0.0173	2.5	1.8	−19.3[b]	
		3.7646	0.0157	2.2	1.8	−17.7[b]	
		3.7517	0.0185	2.6	1.8	−20.9[b]	
		3.7649	0.0175	2.5	1.8	−17.6[b]	
		3.7696	0.0214	3.1	1.6	−16.5[b]	
		3.7565	0.0185	2.6	1.8	−19.7[b]	
		3.7609	0.0193	2.8	1.9	−18.6[b]	
		3.7985	0.0175	2.5	2.0	−9.3[b]	
		3.7516	0.0173	2.5	2.0	−20.9[b]	
		3.7659	0.0205	2.9	1.9	−17.4[b]	
		3.7459	0.0217	3.1	1.9	−22.3[b]	
		3.7417	0.0186	2.7	2.1	−23.4[b]	
		3.7500	0.0230	3.3	1.9	−21.3[b]	
	Average					−18.9[b]	1.0
Re-test of mannitol washed mudstone clay							
September 16, 1998	IMt-1 standard, 240 ppm B	3.8265	0.0043	0.6	0.4	−44.7[a]	
		3.8387	0.0039	0.6	0.5	−41.7[a]	
		3.8301	0.0054	0.8	0.5	−43.8[a]	
		3.8197	0.0049	0.7	0.4	−46.4[a]	
	Average					−44.2[a]	1.0
	LNB 11607 MS, re-polished, no	3.7951	0.0110	1.6	1.5	−17.3[b]	
	additional mannitol wash	3.7876	0.0119	1.2	1.2	−19.1[b]	
		3.7848	0.0111	1.6	1.6	−19.8[b]	
	Average					−18.7[b]	0.8

Table 2 (*continued*)

Session date	Sample	Mass 11/10	S.D.	Error ‰	Pred. error ‰	IMF	S.E.
(B) Mudstone analyses							
April 23, 1998	Kimball 14220 MS, mannitol	3.8041	0.0081	2.1	1.7	−16.8[b]	
	washed, 196 ppm B	3.7776	0.0129	3.4	2.8	−23.7[b]	
		3.8087	0.0087	2.3	1.9	−15.6[b]	
		3.7838	0.0090	2.4	2.2	−22.1[b]	
		3.8094	0.0105	2.7	2.2	−15.5[b]	
	Average					−18.7[b]	1.7

Standard IMt-1 is analyzed to determine IMF for each analytical session. This value is subtracted from the delta value.

S.D. is standard deviation of the ratio, S.E. is standard error of the average. Predicted error is the best possible error based on counting statistics. If the actual errors are > 2 times predicted, the results are anomalous.

[a] IMF.

[b] δ^{11}B.

2.9‰. The thin section was soaked in mannitol ∼ 72 h, sonified and rinsed to see if the solution could remove adsorbed-B from the surface of the section. SIMS analytical craters are < 5 μm deep; therefore, the mannitol must penetrate the surface to at least that depth in order to be effective. After soaking, the area of the thin section previously analyzed gave a significantly lower δ^{11}B value of − 18.9 ± 3.5‰ (13 analyses). In order to check this result, the surface of the section was polished again to remove the Au-coat and analytical craters and re-analyzed without a second soaking in mannitol, giving an average of − 18.7 ± 1.3‰ (3 analyses). This indicates that adsorbed-B was successfully removed from the thin section and that the analyses represent the composition of the fixed-B component.

4. Results

4.1. Water and oil

The results of total-B analyses by ICP and isotope ratio measurements by NTIMS are shown in Table 1. The B-content of the oil field waters range from 8 to 85 ppm. These data and the δ^{11}B results are plotted in Fig. 5. Fluids were introduced to the sandstones through the fault, therefore the distance of migration increases away from the fault, and from the deepest (W-12) to shallowest reservoir (Sparta B). The B-content of most of the reservoir waters is in the range of 10 to 20 ppm, however there is a slight increase in the B-content at the edges of the field.

The highest B-content was found in the shallowest reservoir in a well located closest to the regional fault (Fig. 5). The δ^{11}B of the reservoir waters is in the range of values reported for oil field brines (e.g., Vengosh et al., 1994), but notably the deepest reservoir has δ^{11}B values ∼ 10‰ lower than the upper reservoirs. The exception to this is the water from a gas well at the edge of the field where δ^{11}B values are similar to the upper reservoirs.

The analyses of the oil are given in Table 1 and indicated on Fig. 3. Results reflect the ∼ 10‰ difference in δ^{11}B between the deepest reservoir (5‰) and shallowest reservoir (17‰), but the B-contents of the oils are very low (ppb levels), suggesting that B prefers the aqueous phase.

4.2. Clay minerals

Analyses of the δ^{11}B of clay minerals in Fordoche Field were done by SIMS on thin sections of representative mudstones and sandstones. To test for changes in δ^{11}B with burial depth, samples were examined from the shallowest (3540 m) and deepest (4212 m) sandstone reservoirs, and from mudstones at 3536 m and near the oil source region at 4334 m. There is no significant change in the average isotopic composition of the clays over this depth interval (Table 2). The pore-filling clays from sandstone had an average δ^{11}B value of − 2.5 ± 0.2‰ in the shallowest reservoir and − 2.1 ± 1.7‰ in the deepest reservoir. The mudstones surrounding the sandstone reservoirs contains clays with a much lower fixed B-isotope composition averaging − 18.8 ± 3‰.

Table 3
TIMS analyses of kerogen extracted from source rock, compared to SIMS analyses of kerogen in thin section from the same depth (4334 m)

TIMS analyses of extracted kerogen

Mass 11/10	Std. dev.	$\pm$ SD ‰	Std. error	$\delta^{11}B$ (std = 4.0377)	Std. error
4.0100	0.0183	4.5	1.1	-6.9	
4.0280	0.0191	4.7	1.1	-2.4	
4.0356	0.0149	3.7	0.9	-0.5	
4.0233	0.0126	3.1	0.7	-3.6	
4.0236	0.0112	2.8	0.7	-3.5	
4.0279	0.0142	3.5	0.8	-2.4	
4.0408	0.0128	3.2	0.7	0.8	
4.0225	0.0126	3.1	0.7	-3.8	
4.0399	0.0125	3.1	0.7	0.5	
4.0273	0.0145	3.6	0.8	-2.6	
4.0387	0.0112	2.8	0.7	0.2	
4.0277	0.0123	3.0	0.7	-2.5	
Average				-2.2 ± 2.2	0.6

SIMS analyses in situ using 5 nA primary current, defocussed beam to reduce sputtering rate

Mass 11/10	Std. Dev.	Error ‰	Pred. error ‰	$\delta^{11}B$, IMF = -48‰	Std. error
3.8410	0.02020	2.9	2.3	-2.1	
3.8009	0.02050	2.1	2.4	-12.0	
3.8158	0.02791	4.0	2.1	-8.4	
3.8339	0.02812	4.0	2.3	-3.9	
3.8430	0.02785	4.0	2.1	-1.6	
3.8455	0.02638	3.8	2.1	-1.0	
3.8353	0.02565	3.7	2.1	-3.5	
Average				-4.7 ± 4.1	1.5

4.3. Kerogen

The kerogen extracted from mudstone beneath the Fordoche reservoirs (4334 m) contained as much B (140 ± 1.4 ppm) as is commonly found in clay minerals. The high-B concentration allowed analysis by NTIMS without need for ion exchange. The results (Table 3) indicated a $\delta^{11}B$ value of -2 ± 2.2‰. We considered the possibility that some clay minerals could be entrained in the kerogen fraction and could thus contribute to the $\delta^{11}B$ measured. In order to test this, kerogen was analyzed directly by SIMS in a thin section taken from the same core depth (14,220 ft.; 4334 m) as the extracted kerogen. The absence of K, Al, and Si ions detected by SIMS rules out the presence of clay minerals in the analyzed area. Adsorbed-B had been removed by soaking the whole sample in mannitol solution. Seven analyses, each < 50 μm in diameter, were made on a large kerogen fragment found in this section. The $\delta^{11}B$ values measured by SIMS gave a range of -4.7 ± 4.1‰,

confirming that the $\delta^{11}B$ of kerogen is negative. This result also suggests that the technique for extraction of B from kerogen by Parr Bomb does not significantly fractionate the boron.

5. Discussion

The geochemistry of the pore waters in the Gulf Coast basin should reflect chemical changes in the sediments because of the high rock:water ratio. Evaluation of B-trends thus requires an understanding of how B interacts with the clastic sediments. We know that boron is incorporated in clay minerals during diagenesis (Perry, 1972). At the surface, this interaction is complicated by the fact that B is both adsorbed onto clay surfaces and fixed into tetrahedral sites of authigenic clays. The amount of boron adsorption on detrital clay minerals depends on the specific clay type (Keren and Mezuman, 1981), but ^{10}B prefers to be in tetrahedral coordination at clay

surfaces (Palmer and Swihart, 1996) causing a fractionation between aqueous B(OH)$_3$ and adsorption sites of clay minerals in excess of 31‰ (Palmer et al., 1987) at 25°C. Spivack et al. (1987) showed that the adsorbed-B accounts for < 20% of the total-B in shallow marine sediment and has a mean δ^{11}B of + 14‰. The quantity of fixed-B in marine sediments studied by Spivack et al. (1987) is greater than the adsorbed-B and has δ^{11}B values between 0 and − 5‰. Ishikawa and Nakamura (1993) found fixed-B δ^{11}B of marine sediments as low as − 8 to − 13‰ reflecting variations in detrital source material. They suggested that ^{10}B is incorporated into illitic clay during recrystallization.

Adsorbed-B is not significant above 100°C where the distribution coefficient between fluid and sediments approaches zero (You et al., 1996), therefore it does not play a role in isotopic variations observed deep in sedimentary basins. At this temperature in the Gulf Coast, the most common clay mineral reaction is the illitization of smectite. The Wilcox Fm mudstones contain 25–30% clay minerals, while the sandstones contain < 10% clay minerals that are predominantly illite/smectite (Williams et al., 1995). The Fordoche Field reservoirs are located at a depth where authigenic illite formation is nearly complete (70–80% authigenic illite, T ~ 120°C). Authigenic illite forms in equilibrium with local pore fluids at this depth (Williams, 2000). This is supported by 100% isotopic resetting of O-isotopes during neoformation of illite (Whitney and Northrup, 1988). Any B in the pore fluids will go into the new illite crystals with a B-isotope ratio reflecting the T and δ^{11}B of the fluid.

At depths where illitization is complete (~ 150°C) illite ceases to incorporate B, thus any B released from other phases (such as kerogen) may accumulate in the pore fluid. By ~ 150°C, kerogen begins to break down to dry gas and graphite (Fig. 6). Release of B from kerogen could significantly affect the δ^{11}B of pore waters. These pore waters might migrate upwards, along with hydrocarbons, into shallower reservoirs undergoing active illitization.

In order to evaluate the potential influence of organic matter on the B-isotope systematics of basin fluids, the discussion will first focus on local B-trends
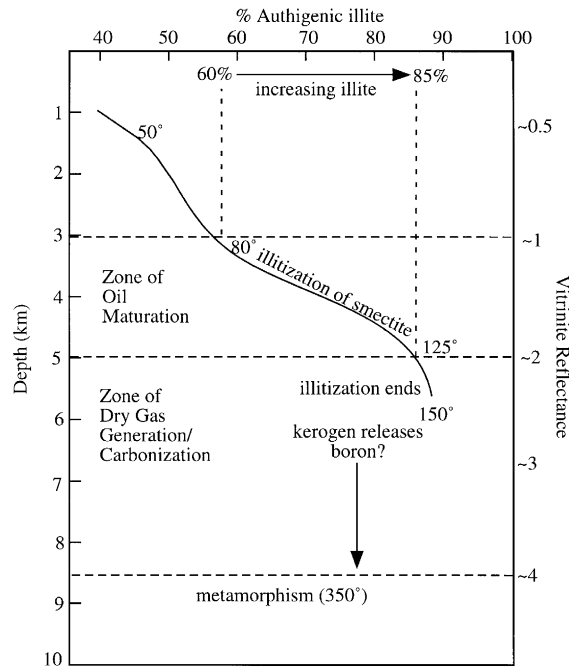

Fig. 6. Schematic diagram showing the progress of illitization during stages of organic matter maturation in a sedimentary basin. It is inferred that kerogen begins to release B at temperatures > 150° after illitization ends.

within Fordoche Field, and factors that could cause the observed isotopic changes. These factors include fractionation due to pH, temperature changes causing mineral/water or organic/water fractionation, a gas phase separation, isotope exchange due to mineralogical changes, and fluid migration. After evaluation of these variables on a local scale, the regional B-trends will be assessed in light of the new B-isotope data for kerogen.

6. Fordoche field boron

6.1. pH and temperature

Aqueous-B speciation is pH and temperature dependent (Keren and Mezuman, 1981). The predominant species are boric acid ($B(OH)_3$), which shows a preference for ^{11}B, and borate anion ($B(OH)_4^-$), which prefers ^{10}B. At low pH (< 7), boron occurs primarily as boric acid, $B(OH)_3$. Under diagenetic temperatures in the Gulf Coast (up to 200°C) siliciclastic reactions buffer the pore water pH to values between 5 and 6 where $B(OH)_3$ species dominate (Bassett, 1980). Therefore, we can dismiss the possibility of isotopic fractionation due to variable aqueous speciation. The effect of polynuclear B-species that might form at high concentrations of B (Bassett, 1976), has not been assessed.

The temperature difference between W-12 and Sparta B reservoirs is ~ 25°C. Although this temperature difference seems small, we must evaluate if it causes significant B-fractionation between the clay minerals and water, or organic matter and water.

6.2. Clay mineral / water fractionation

There is no significant change in the fixed-B content or $\delta^{11}B$ of pore-filling clay minerals in the sandstone reservoirs over the cored interval examined. There is however a significant difference in the water $\delta^{11}B$ from an average of 28‰ in the W-12 reservoir (excluding the gas well) to 36‰ in the shallower Sparta B reservoir. Although sandstone reservoirs are rock-dominated, the volume of fluid flow through the rock is much greater than in mudstones and thus trace elements may potentially be transferred from the fluid into pore-filling authigenic minerals. If this is the case, one might expect a

difference in the $\delta^{11}B$ of authigenic pore-filling clays in Fordoche reservoirs that reflects the differences in water chemistry. If the illite had released ^{10}B to lower the water $\delta^{11}B$ in the W-12 reservoir, the fixed-B in clay should be ^{11}B-enriched relative to the shallower Sparta B reservoir. Since no changes in the $\delta^{11}B$ of the clay minerals was observed, it is unlikely that they are a source for ^{10}B-enrichment of the formation waters.

The $\delta^{11}B$ of fixed-B in the mudstone at 11,600 ft (3535 m) and in the source rock (14,220 ft; 4334 m) is much lower (-19‰) than that measured in clays from the adjacent sandstones (-2‰; Table 2). The clay minerals in the mudstone at this depth are dominated by authigenic I/S (Perry, 1972), and they contain 200–300 ppm fixed-B. This is twice as much B as depositionally equivalent sediments at the surface (Spivack et al., 1987). Our measurements (Table 2) show that the clay minerals in the sandstone have similarly high B-contents, and their textures indicate that they also formed in-situ. The high-B content and negative $\delta^{11}B$ of the authigenic clay minerals at this depth (4 km) supports further that authigenic clay minerals retain ^{10}B rather than releasing it to the pore fluid.

Based on recent experimental work to determine the B-isotope fractionation between illite and water (Williams et al., 1999; Williams, 2000) it is expected that pore waters in equilibrium with -19‰ I/S in the mudstones will be isotopically light at these reservoir temperatures ($\sim +6$‰). If there were large-scale exchange of fluids between mudstones and sandstones, one would expect the authigenic pore-filling clays in the sandstone to have lighter $\delta^{11}B$ values, similar to the mudstones. Since this is not the case, it suggests that the reservoir waters were either diagenetically altered or migrated into the sandstone from another source region. It is also possible that the sandstone clay minerals formed at an earlier time (lower burial temperature) in equilibrium with fluids that previously passed through the unit. Regardless of the timing, it is clear that authigenic clay minerals in the sandstone reflect equilibrium with a different fluid than the fluid that originally filled the pore space. The mudstones on the other hand are in equilibrium with pore fluids that have not migrated far, and probably represent original pore fluids that have been diagenetically altered.

6.3. Oil / water fractionation

The variation in $\delta^{11}B$ of oil samples reflects the trend of lighter values with depth shown by the waters, but the B-content of the oils is so low that their affect on $\delta^{11}B$ of coexisting water is unlikely to be significant. It would be more reasonable to attribute these trends to incorporation of some of the aqueous-B into the oil.

It is unclear why these oils contain so little B (ppb levels). It is possible that they are low in the napthenic fraction that Gulyayeva et al. (1966) identified with higher B-content. It is likely that the type of oil will determine whether or not it contains significant B. Further work is needed to identify the organic-B compounds in oil.

6.4. Gas phase separation

The water $\delta^{11}B$ changes observed across the field (Fig. 5) may be complicated by the fact that the gas reservoirs within the field are found where the highest $\delta^{11}B$ values are found. It is possible that ^{11}B is fractionated preferentially into a gas phase (Palmer and Sturchio, 1990). Leeman et al. (1992) found a fractionation of only ~ 3‰ between water and vapor at 150°C; however, that work focused primarily on $B(OH)_3$ species alone. No information is available on possible fractionation of B between water and gaseous organic compounds. If ^{11}B is preferentially associated with a gas phase, and the gas accumulates in the uppermost regions of the hydrocarbon reservoirs, then there may be some ^{11}B enrichment of phases in contact with those gases. The variations in $\delta^{11}B$ and B-content of the waters may be correlated with the gas/oil ratios in each reservoir.

6.5. Isotope exchange

The mechanism of B-isotope exchange between clay minerals and water is important to our interpretation of the field data. A solid state transformation of smectite to illite would gradually redistribute B from adsorbed-sites to sites in the tetrahedral layers, and might result in an "inherited" B-isotope composition from the original detrital mineral. However, in the Gulf Coast, the B-content of the authigenic portion of mixed-layered illite/smectite increases by more than 100 ppm with depth (Perry, 1972). These sediments originated largely as volcanic ash (Bloch et al., 1998) which alters to smectite and gradually to I/S (Perry and Hower, 1972). Eberl (1993) presented evidence suggesting that at the depths (temperature) of the Fordoche reservoirs, authigenic illite forms by dissolution/precipitation. If detrital smectite dissolves and precipitates as more stable illite during burial, the authigenic mineral will not retain the $\delta^{11}B$ inherited from the original detritus, but will precipitate in equilibrium with the coexisting fluids, reflecting their B isotope composition at the temperature of crystallization. These pore fluids have been modified by siliciclastic reactions occurring at that depth, which is observed in the O-isotope variations with depth (Yeh and Savin, 1977) and could be substantially influenced by organic reactions taking place concurrently, especially in hydrocarbon-rich environments.

6.6. Fluid migration

The range of values for B-content and $\delta^{11}B$ of formation waters in the Fordoche reservoirs is consistent with the range of values reported for Cenozoic reservoirs throughout the Gulf Coast (Fig. 1). There is a minor increase in B-content and $\delta^{11}B$ in the uppermost reservoir over the lower Wilcox reservoirs, which may reflect variability in the original porewaters, or may reflect differences related to diagenesis. The Wilcox reservoirs are overpressured and less saline than the uppermost reservoir (Sparta), suggesting the addition of water from dehydration of smectite (Bruce, 1984). This dilution effect could result in the lower B-content of these waters. The temperatures of the reservoirs are 90–126°C (Williams et al., 1995), therefore, B-adsorption is negligible (You et al., 1996). Nonetheless, as recrystallization of I/S occurs ^{10}B is preferentially substituted in the silica tetrahedron, therefore, waters migrating through the rock should become gradually ^{10}B depleted with migration distance.

7. Regional boron

The regional trends for boron in waters from the Gulf Coast sedimentary basin (Macpherson and Land,

1989; Land and Macpherson, 1992; Moldovanyi et al., 1994) show an increase in B-content and decrease in δ^{11}B with depth basinwide (Fig. 1). At depths equivalent to Fordoche Field B-contents are as high as 300 ppm, and δ^{11}B values as low as 12‰, but a majority of the water analyses have δ^{11}B values between 18‰ and 30‰. The B-content of Fordoche Field is slightly low in comparison to regional waters, but this could be explained by dilution of Fordoche brines due to overpressuring in the region (Boles and Franks, 1979; Williams et al., 1995). Our investigation of the Fordoche Field does not reveal a mechanism for generating the regional B-trends (Fig. 1). Therefore, an additional source of ^{10}B must be responsible for the low δ^{11}B values in the deep Gulf Coast basin. Below we consider dissolution of other boron minerals, or degradation of organic matter at higher thermal grades.

7.1. Other boron minerals

Depending on the scale of fluid flow within the Gulf Coast sedimentary basin, the potential exists for B-rich minerals such as tourmaline or evaporite borate phases to contribute significant B to waters and modify the δ^{11}B, particularly in reservoir sandstones. Detrital tourmaline grains have been found, for example, in the Wilcox Fm. However, tourmaline is extremely chemically and mechanically stable in clastic sedimentary environments (Henry and Dutrow, 1996) and therefore is not expected to release B. Boracite has been recovered from Jurassic bittern salts beneath Eocene sediments (Macpherson and Land, 1989), but this evaporite deposit (and other marine evaporites; Palmer and Swihart, 1996) has high δ^{11}B values ($\sim$ 30‰), so that dissolution of that phase the would not generate the observed regional decrease in δ^{11}B of formation waters.

7.2. Organic matter boron

The general enrichment of ^{10}B in waters from deep clastic reservoirs of the Gulf Coast must be examined in light of the new isotopic data on B in kerogen. We acknowledge that there is insufficient kerogen in the basin to provide all of the B in the clay minerals, and assume that adsorbed and dis-

solved-B from breakdown of detrital clays provided most of the B incorporated into authigenic illite (Perry, 1972). However, illitization stops at $\sim$ 5 km in the Gulf Coast (Perry and Hower, 1972), approaching depths equated with the later stages of organic maturation (Fig. 6). At this depth, clay minerals will no longer be a sink for boron. Their fixed-B is unlikely to be released until metamorphic recrystallization occurs ($>$ 350°C). Therefore, clays should not play a significant role in the B mass balance as temperatures approach 150°C. The reactivity of organic matter becomes important at that stage however, as organic molecules release heteroatoms (i.e., boron) during carbonization of kerogen (Durand, 1985). Examination of B in coal that is thermally altered shows 99% B-depletion at temperatures above 200°C (Williams, 2000).

Our source rock sample contained 5 g kerogen out of a 50 g sample of mudstone at $\sim$ 4.3 km indicating a very high kerogen content (10%). This very high organic content is not representative of the entire basin, however, the fact that the δ^{11}B of the kerogen is -2 ± 2‰ (Table 3) indicates that B released from kerogen could still be a source of ^{10}B. The burial temperature of the extracted kerogen was $\sim$ 125°C (vitrinite reflectance $\sim$ 1.5 (Sassen, 1990)) indicating organic maturity in the wet gas zone (Fig. 6). At this temperature, there is still a significant amount of B held in the kerogen (140 ppm). However, studies of B in graphite from metasedimentary rocks (slate) have indicated B-contents averaging $<$ 20 ppm (Douthitt, 1985). Therefore, at some temperature near 125°C and low grade metamorphism, B will be released from kerogen. We infer that B is released from organic matter during the generation of dry gas (vitrinite reflectance $>$ 2.0).

Based on the δ^{11}B for B in kerogen, we can estimate the amount of B potentially released during late thermal maturation, and its influence on the isotopic composition of the water that would migrate with the hydrocarbons. In the Wilcox Fm, the amount of shale is $\sim$ 70% and sandstone comprises $\sim$ 30%. A conservative estimate of the amount of kerogen in the source region of the Wilcox Fm is 2% (Tissot and Welte, 1984). Porosity is estimated at 20% in the sandstones and 10% for mudstones (including fracture porosity). Assuming the pores are 70% filled with water (the rest being oil and gas), then an

isotopic mass balance for B can be calculated. Fig. 7 shows the isotope changes expected if the water $\delta^{11}B$ was initially 28‰ (observed in Fordoche reservoir W-12), and all of the B from kerogen was released (with no isotopic fractionation). We have calculated the results for a range of kerogen $\delta^{11}B$ values from $+10$ to -10‰ to show that even large variations in the kerogen $\delta^{11}B$ could achieve the range of $\delta^{11}B$ observed in the deep basin waters. Obviously there could be isotopic fractionation during the release of B, especially if there is a gas phase involved. But the validity of this calculation is justified by the fact that negligible amounts of B are found in the oil and essentially all of the B is lost from kerogen during carbonization. This leaves the water as the primary host for released-B.

The typical Gulf Coast oilfield water could have a $\delta^{11}B$ reduced to ~ 17‰ by release of B from a -2‰ kerogen. This value approximates the low $\delta^{11}B$ waters in the Gulf Coast basin found at temperatures between 160°C and 175°C (Land and Macpherson, 1992). The amount of B in kerogen could account for the increase in B-content and decrease in $\delta^{11}B$ of waters deep in the Gulf Coast basin. The mobility of B released from kerogen will depend on its interactions with minerals along the migration path. Boron is not expected to adsorb onto clays at these temperatures (>100°C), but it can

exchange with authigenic illite as long as illite neoformation occurs.

The importance of organic-B cannot be ignored in our efforts to understand the B-geochemistry of sedimentary basins. Our results indicate that B is released during late stages of organic maturation with a distinctly negative $\delta^{11}B$ that could provide a means for tracing hydrocarbon migration paths.

8. Conclusion

The boron content and isotopic composition of oil field brines increases with increasing distance of fluid migration both upwards and laterally across Fordoche Field. The isotopic composition of the oil varies similarly, however, the amount of B in the oil is insignificant. One possibility for the high $\delta^{11}B$ of oil field waters is the preferential incorporation of ^{10}B into the tetrahedral layers of authigenic illite, leaving the water ^{11}B-enriched. The very low $\delta^{11}B$ of fixed-B in mudstone (-18‰) relative to sandstones (-2‰) at the same depth indicate that ^{10}B is retained in the mudstone clay minerals and is not released into the reservoir waters. The reservoir waters most likely contain fluids that migrated with the hydrocarbons. Illitization ceases at ~ 5 km of burial and therefore B ceases to exchange between clay minerals and pore waters.

This study has demonstrated that kerogen in the Gulf Coast basin contains a significant amount of organically bound B (140 ppm), with a negative $\delta^{11}B$. After illitization has ceased ($\sim 150°$), B released from kerogen becomes a potential source of ^{10}B that could cause the low $\delta^{11}B$ in deep sedimentary brines. We deduce that >100 ppm B can be released from organic matter during dry gas generation (vitrinite reflectance ~ 2.0). Although kerogen makes up only a small percentage of the sedimentary basin, its significance as a source of boron in deep sedimentary basins cannot be ignored when considering its reactivity compared to clay minerals.
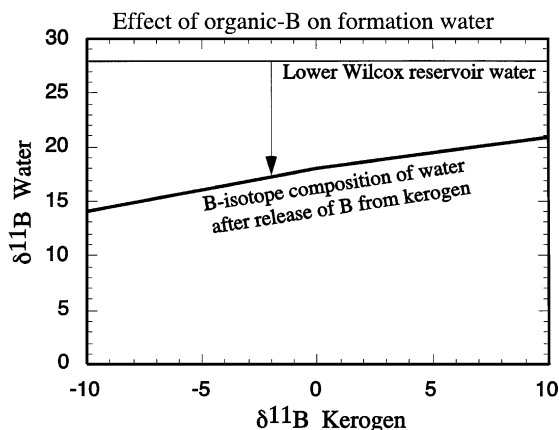

Fig. 7. Plot showing results of isotope mass balance calculations between kerogen and water in the deep Gulf Coast sedimentary basin. If kerogen with a -2‰ $\delta^{11}B$ releases all of its B (>100 ppm), a 28‰ water from the lower Wilcox Fm would decrease in $\delta^{11}B$ to ~ 17‰, assuming no fractionation.

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