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IODINE-129, $^{87}Sr/^{86}Sr$, AND TRACE ELEMENTAL GEOCHEMISTRY OF NORTHERN APPALACHIAN BASIN BRINES: EVIDENCE FOR BASINAL-SCALE FLUID MIGRATION AND CLAY MINERAL DIAGENESIS

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ABSTRACT. Evidence for basin scale brine migration and clay mineral diagenesis in the northern Appalachian Basin was investigated using elemental and isotope ($^{129}I/I$, $^{87}Sr/^{86}Sr$) geochemistry of formation waters collected from the Middle to Upper Devonian section of the northern basin margin in western New York, northwest Pennsylvania, and eastern Kentucky. One sample from each of the Mississippian Berea sandstone and the Silurian Medina sandstone were analyzed for comparison. Measured iodine ratios range between 28 to 1,890 × 10^{-15} and are anomalously high compared to cosmogenic iodine sourced from Devonian age organic matter. Iodine-129 in the waters was largely derived from fissiogenic sources, the spontaneous fission of ^{238}U to produce ^{129}I, with estimated $^{129}I/I$ values up to 270 × 10^{-15}, which occur locally in the organic-rich shales. There are three water samples that have values of 490 × 10^{-15}, 860 × 10^{-15}, and 1,890 × 10^{-15}, which are above the range for local fissiogenic ^{129}I and may be accounted for by topographically driven, basin scale fluid flow through a regionally high fissiogenic source. Relatively large uranium occurrences lie along the structural front of the Appalachian Basin in the Blue Ridge Province and are situated within hypothesized flow paths parallel to the main compressional direction of the Alleghanian orogeny. Estimated $^{129}I/I$ values for these uranium occurrences are in excess of 55,000 × 10^{-15}. The strontium isotope composition and Sr concentration of brines display a mixing trend between a highly radiogenic end-member (0.7210) with low Sr (51 mg/L) and a non-radiogenic (0.7100), high Sr (4789 mg/L) end-member. Potassium and boron concentrations are notably depleted relative to evaporated Paleozoic seawater, the hypothesized source of Appalachian Basin brines. The K/Rb values of formation waters are depleted relative to seawater values, but in some cases are well above values indicative of water-rock reactions. The Sr isotopic composition, K and B depletion, and intermediate K/Rb ratios are consistent with smectite diagenesis and paleo-temperatures that are likely greater than approximately 150 °C. These temperatures may be high given the burial history of the study area and support the flow of formation waters from deeper within the basin. The combined isotopic and elemental results of formation waters provide compelling evidence for basin scale fluid migration in the northern Appalachian Basin and are consistent with previously published evidence documented from the rock record, including clay mineral diagenesis and ore deposition.

Key words: Illitization, topographic flow, tectonic flow, fissiogenic iodine, strontium

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INTRODUCTION

Tectonics and topographic gradients are important drivers of fluid, solute, and heat transport in sedimentary basins. Numerous studies in the Appalachian foreland basin have invoked the migration of heat and solutes with tectonically- and topographically-driven fluids during orogenesis to explain the diagenetic transformation of clay mineral assemblages, the migration of petroleum hydrocarbons, and the emplacement of ore deposits at the distal basin margins (Oliver, 1986; Elliott and Aronson, 1987; Deming and Nunn, 1991; Lu and others, 1991; Oliver, 1992; Schedl and others, 1992; Garven and others, 1993; Carlson, 1994; Elliott and Haynes, 2002). Some of these studies have speculated on the chemical character of the migrating/diagenetic fluids, yet there has been very little accompanying formation water geochemistry as supportive evidence.

In this study, we present evidence for basin-scale fluid migration and water-rock reactions based on iodine ($^{129}I/I$) and strontium ($^{87}Sr/^{86}Sr$) isotopic compositions, and the elemental (major, minor, and trace) chemistry of formation waters predominately from the Devonian section of the northern Appalachian Basin margin. Iodine-129 is a useful tracer in reconstructing deep regional paleohydrologic flow systems because of its relatively long half-life ($t_{1/2}$ = 15.7 Ma) and mobility in aqueous environments. It has previously been used to investigate fluid migration and organic matter diagenesis in sedimentary basins and subduction zones (Fabryka-Martin and others, 1989; Moran and others, 1995a; Rao and Fehn, 1999; Snyder and others, 2003; Muramatsu and others, 2004; Birkle, 2006; Fehn and others, 2007). Here, we use fissiogenic iodine-129 to investigate basin scale fluid flow. The strontium isotopic composition and elemental analyses of formation waters has been used extensively to investigate fluid migration, water-rock reactions, the source of solutes, and mixing relationships between different water types in crystalline fractured bedrock and sedimentary basins (for example, McNutt and others, 1987; Stueber and Walter, 1991; Stueber and others, 1993; Jacobson and Blum, 2000).

Elemental analyses have long been used to investigate the origin of salinity and the chemical evolution of basinal brines. Published chloride and bromide relationships in formation waters, mostly from the Silurian section of the northern Appalachian Basin have established that salinity was largely sourced from evaporated Paleozoic seawater (Breen and others, 1985; Dresel, ms, 1985; Lowry and others, 1988; Siegel and others, 1990; Sanders, 1991; Osborn and McIntosh, 2010) and some have hypothesized the existence of basin scale fluid migration (Breen and others, 1985; Dresel, ms, 1985; Lowry and others, 1988; Siegel and others, 1990; Sanders, 1991) based on these same relationships.

Iodine and the ^{129}I Isotopic System

Iodine generally occurs as a minor constituent in minerals due to its high ionic radius (133 pm). It preferentially accumulates in marine organic matter by more than 100 times relative to its concentration in seawater (0.05 mg/L) (Moran and others, 1995b; Muramatsu and others, 2004). The presence of buried organic matter has a strong control on the total iodine concentration of formation waters and may be used as a first order approximation for tracing interactions between fluids and organic-rich geologic formations. The iodine isotopic composition ($^{129}I/I$) of formation waters may provide a stronger constraint on fluid flow, however. There are three main sources of ^{129}I in the subsurface: (1) anthropogenic, due to nuclear weapons testing and fuel processing since the 1950's and 1960's (may be significant in surface and shallow subsurface environments), (2) fissiogenic, due to the spontaneous fission of ^{238}U in rocks, and (3) cosmogenic, due to cosmic ray bombardment of Xenon in the atmosphere, uptake by organic matter, and burial (Fabryka-Martin and others, 1985).

The use of cosmogenic ^{129}I as a tracer of reaction with buried organic matter is limited to organic matter with depositional ages younger than ~90 Ma, because of the radioactive decay of cosmogenic ^{129}I in the subsurface; beyond ~90 Ma the ^{129}I/I values are typically below the sensitivity limits of accelerator mass spectrometry (AMS). The only production of ^{129}I in the deep subsurface comes from fissiogenic sources. Many studies of ^{129}I in basinal brines assume anthropogenic sources of iodine are negligible due to the long residence times of deep formation waters (significantly greater than 50 years; for example, Moran and others, 1995a; Moran, 1996; Fehn and Snyder, 2005; Birkle, 2006). Thus, the measured ^{129}I/I in deep formation waters may be considered a composite of fissiogenic and cosmogenic ^{129}I.

Cosmogenic ^{129}I ages are calculated using an initial, pre-anthropogenic ^{129}I/I ratio from labile marine organic matter value of $1{,}500 \pm 150 \times 10^{-15}$ (Moran and others, 1995b), which has been widely used in brine ^{129}I/I studies (Moran and others, 1995a; Bottomley and others, 2002; Snyder and others, 2003; Birkle, 2006). The ^{129}I age may be determined using the radioactive decay law for ^{129}I

$$^{129}\mathrm{I/I}_{\mathrm{measured}} = {}^{129}\mathrm{I/I}_{\mathrm{initial}} e^{-\lambda_{129} t} \tag{1}$$

and solving for time (t), where λ_{129} is the decay constant of ^{129}I (4.41×10^{-8}). Fissiogenic ^{129}I is produced over geologic time by the host aquifer matrix and is dependent on the concentration of ^{238}U and rock properties (density and porosity) affecting the emanation efficiency (probability of escape) of ^{129}I through the crystalline lattice and rock fabric.

Published brine research using iodine isotopes have not generally employed fissiogenic ^{129}I as a tracer of fluid migration, but have used it instead to explain anomalous ^{129}I/I values (Moran, 1996; Birkle, 2006). Fissiogenic ^{129}I production may be estimated by equation 2 if the ^{238}U concentration is known (Fabryka-Martin and others, 1989), where the calculated ^{129}I

$$^{129}\mathrm{I\ (calculated)} = [{}^{238}\mathrm{U}Y_{sf}\lambda_{sf}E/P(1 - e^{-\lambda_{129} t})]/\lambda_{129} \tag{2}$$

is the ^{129}I produced within the rock, ^{238}U is the concentration within the host rock (ppm), E/P is the ratio of the escape efficiency to the effective porosity of the rock, and Y_{sf} (0.0003) and λ_{sf} (8.5×10^{-17}) are the fission yield at mass 129 and the decay constant at mass 129, respectively. The $1 - e^{-\lambda_{129} t}$ term approaches a value of one at secular equilibrium as the time component approaches ~79 Ma (Moran and others, 1995a). This equation then becomes the calculated fissiogenic ^{129}I/I in rock for $t > 79$ Ma by dividing by the iodine concentration ^{127}I within the rock

$$^{129}\mathrm{I/I\ (calculated)} = ({}^{238}\mathrm{U}Y_{sf}\lambda_{sf}E/P)/(\lambda_{129}\mathrm{I}^{-}) \tag{3}$$

Although there may be some uncertainties with the fission yield value and the ^{238}U concentration cannot be known at all locations, the greatest uncertainty may be associated with the E/P value (Sabu, 1971; Moran, 1996). The E/P term can be ignored (all fissiogenic ^{129}I/I goes into solution) as a conservative approach for estimating fissiogenic ^{129}I/I (Moran, 1996). This assumption constrains the maximum fissiogenic ^{129}I/I value as a first order approximation, which may be especially important in systems where cosmogenic ^{129}I is negligible (old organic-matter), such as the Appalachian Basin. The combination of iodine and strontium isotopic composition with elemental analyses may further elucidate the flow of diagenetic fluids and water-rock reactions, effecting smectite diagenesis.

Smectite to Illite Diagenesis

Clay mineral assemblages, such as illite-smectite have been used extensively as geothermometers for maximum diagenetic temperatures less than 300 °C (Hoffman and Hower, 1979; Velde and others, 1986). During smectite to illite diagenesis, there is a decrease in expandable layers and cation exchange capacity coupled with increases of Al, Si, and K content in the clay size fraction (Hower and Mowatt, 1966; Hower and others, 1976; Boles and Franks, 1979; Moore and Reynolds, 1997). Hower and others (1976) proposed a progressive burial model for smectite to illite diagenesis (illitization) where the dissolution of K-feldspars and micas locally, release potassium and aluminum to pore waters

$$\text{K-feldspar} + \text{mica} + \text{smectite} \rightarrow \text{illite} + \text{quartz} + \text{chlorite} \tag{4}$$

$$K^{+} + Al^{+3}/B^{+3} + \text{smectite} \rightarrow \text{illite} + Si^{+4} \tag{5}$$

The increased activity of K and Al in pore waters react with smectite to form illite and other clay minerals. Mixed layer phases (I/S) with an increasing proportion of illite are formed as a result of elevated temperature and the increased activity of potassium in pore waters. Shales and smectite/illite are abundant in the Upper to Middle Devonian section of the Appalachian Basin and smectite diagenesis may provide an important record of water-rock reactions.

GEOLOGIC BACKGROUND

The Appalachian Basin provides an ideal geologic setting in which to investigate basin scale fluid flow and diagenetic reactions. The Appalachian province includes an elongate foreland basin with relatively undeformed sedimentary rocks of marine origin deposited through the Paleozoic and a mountain belt consisting of metamorphosed rocks of the Blue Ridge and Piedmont physiographic provinces of Pre-Cambrian through Paleozoic age (fig. 1; Colton, 1970). The basin extends from Canadian Shield in Quebec and Ontario, Canada southwest to the northern portions of Alabama and Georgia in the United States and had four major tectonic events through the Paleozoic. The Alleghanian was the most recent orogeny, which had a main compressional phase that lasted into the Permian (315-275 Ma). The Alleghanian orogeny is most strongly pronounced in the north and central parts of the Appalachian region, overprinting tectonic features from previous orogenies (Grenville, Taconic, and Acadian). The asymmetric Appalachian Basin deepens and thickens east and south of structural highs that separate the Appalachian Basin from the Michigan and Illinois basins (Findlay, Algonquin, and Cincinnati arches). These structural highs were thought to be reactivated as a result of flexural loading and sedimentation of the foreland basin during orogeny (Colton, 1970; Quinlan and Beaumont, 1984).

This study primarily focused on formation waters from the Devonian section of the Appalachian Basin. The Devonian clastic sequence, as defined by Colton (1970), was deposited from the Lower Mississippian through the Middle Devonian and comprises approximately 17.6 percent of the basin fill. A stratigraphic column for the Appalachian Basin is provided as figure 2. This Devonian clastic sequence largely consists of organic-rich black and gray shales, siltstones, and sandstones that lap onto the Findlay and Cincinnati arches. The Middle Devonian Marcellus organic-rich shale has recently garnered a lot of attention as a hydrocarbon source rock (Engelder, 2008; Krauss, 2008) and is the oldest organic-rich shale member in the Middle to Upper Devonian sequence. The Marcellus overlies the Onondoga limestone, which separates the Middle and Lower Devonian and lower sections (fig. 2). The Upper and Middle Devonian organic-rich shales grade to sandstones, which act as hydrocarbon reservoirs, east and south of the northern basin margin at Lake Erie. The lower Devonian through Silurian section largely consists of carbonate and sandstone (the Medina, Clinton, and Salina formations) with bedded evaporite units and minor organic-rich shales (fig. 2; Colton, 1970). Illite and smectite clay minerals are ubiquitous in shale formations and

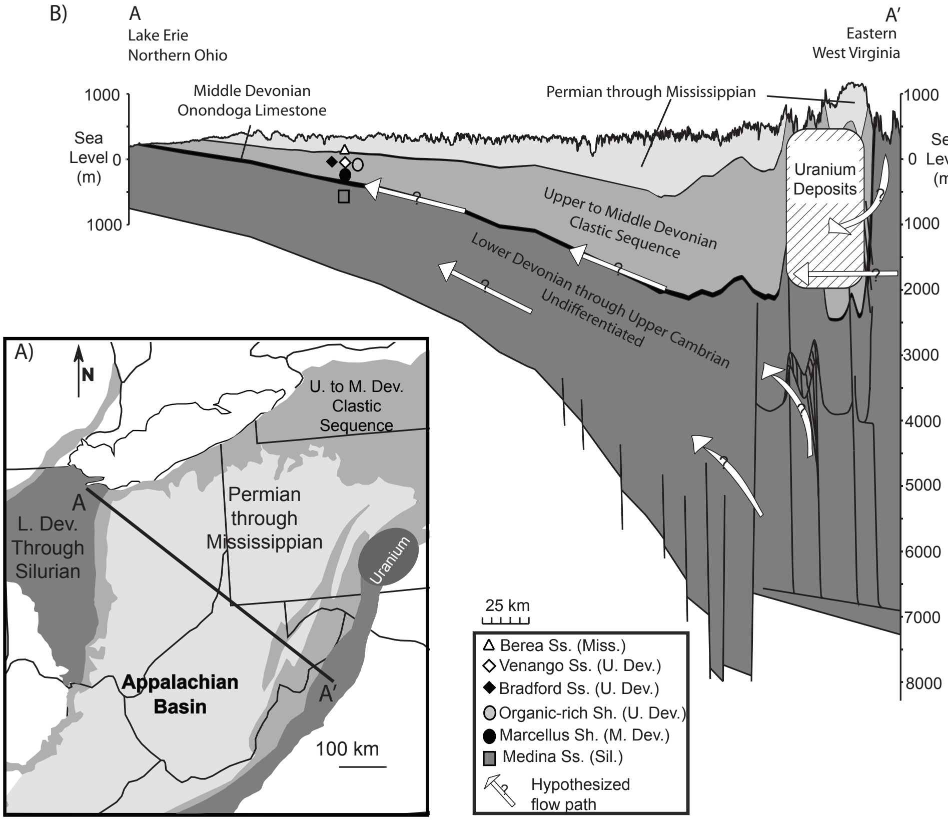

Fig. 1. (A) Generalized geologic map of the northern Appalachian Basin depicting dominant geology (modified from McIntosh and Martini, 2008). A northwest to southeast line of section (A-A′) is provided and is perpendicular to the structural front of the Appalachian Basin. (B) Generalized cross-section of the Appalachian Basin (modified from Ryder and others, 2009) and conceptual model for basin-scale fluid flow. Cross-hatched area represents large uranium occurrences located near the structural front of the Appalachian Basin and in the Mississippian through Devonian sections (Klemic, 1962; USGS, 1968). Arrows indicate hypothesized flow paths at the structural front and within the Middle Devonian Onondoga formation and lower sections.

may be useful for recording diagenetic events associated with orogeny and thrust sheet emplacement (Hoffman and Hower, 1979; Elliott and others, 2006).

Mechanisms for Basin-Scale Fluid Migration

Tectonically and topographically driven fluids provide an important mechanism for transport of heat and dissolved mass in hydrologic systems. Oliver (1986 and 1992) compiled previous research and surmised that sub-continental scale fluid migration resulted from thrust sheet emplacement and orogeny. He hypothesized that relatively hot fluids were “squeegeed” from underneath deforming structures such as thrust sheets and into a foreland basin due to elevated pore fluid pressures. He hypothesized that these waters migrated up to several hundred kilometers toward the distal margins and even into the continental interior of North America. Topographically driven groundwater flow, also due to uplift from orogeny, becomes an increasingly important component of large-scale fluid flow because the hydrostatic pressure from elevated recharge areas and water column may drive deep regional scale fluid migration.

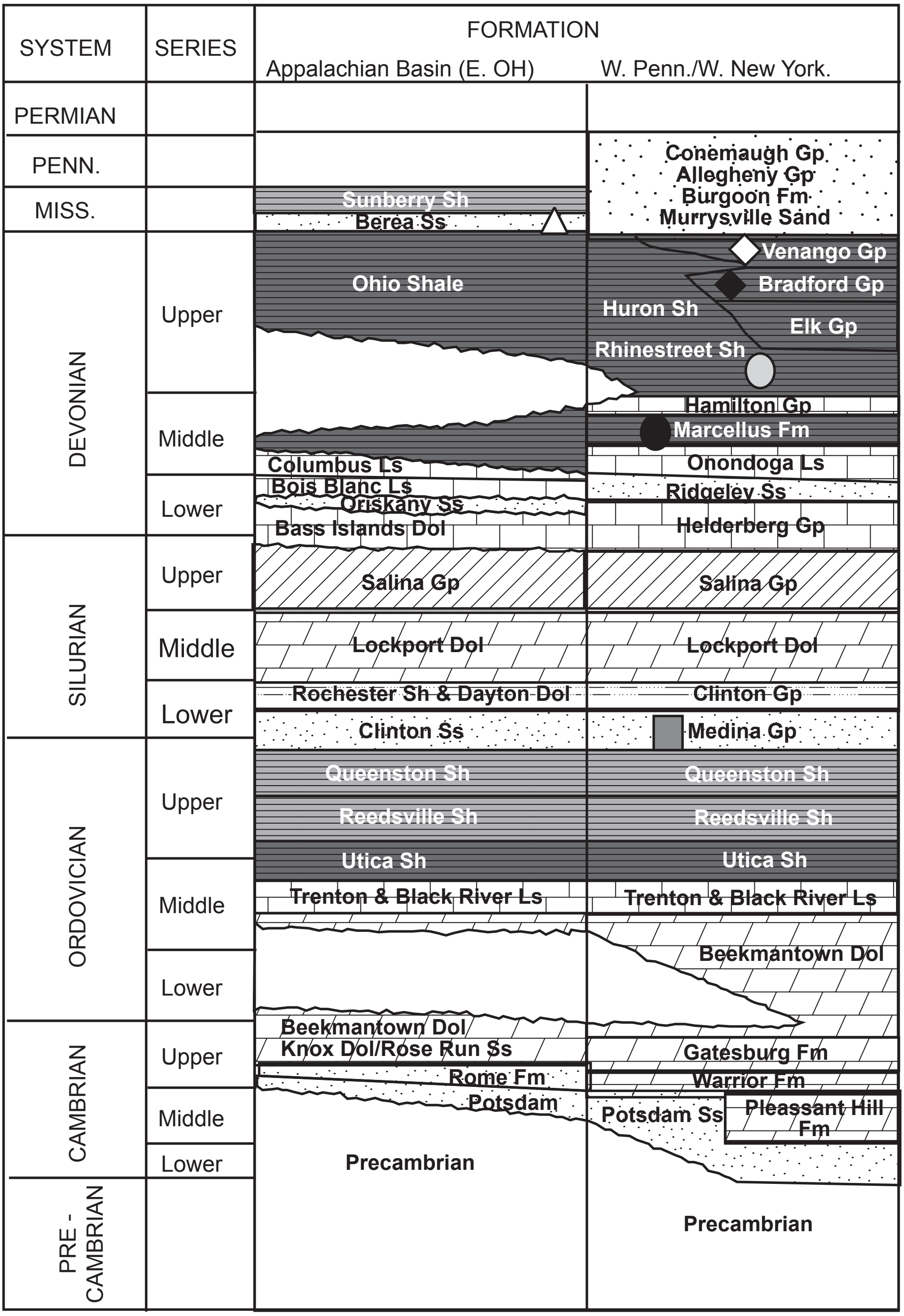

Fig. 2. Stratigraphy of the Appalachian Basin in eastern Ohio and western New York/Pennsylvania (modified from Laughrey and Baldassare, 1998). Symbols are placed on geologic formations that were sampled for this study. The symbols correspond to the sample location map (fig. 3) and subsequent figures.

Large-scale fluid movement of hot solute-laden brines during orogenesis has been invoked to explain the deposition of ore deposits that rim the Appalachian Basin (Garven and others, 1993; Carlson, 1994).

Mechanical and hydrologic models of tectonic compression, pore pressures, and fluid migration demonstrate that tectonically driven fluids can be expelled from underneath a thrust sheet 1 to 10 km thick at flow rates on the order of 10^{-4} to 10^{-3} m/yr (Ge and Garven, 1992; Cutillo and others, 2006; Screaton and Ge, 2007). These studies further conclude that the original excess pore pressures from tectonic loading would dissipate within 10^3 to 10^4 years once thrusting ceased and that continued propagation of the thrust sheet into the foreland wedge can cause basinal scale fluid and heat transfer over relatively long distances and time scales. Conversely, topographically driven regional scale fluid flow may operate for longer timescales than the main compressional phase of orogeny provided denudation rates are relatively slow and elevated recharge areas persist. The Appalachian mountain chain has been characterized as having similar paleo-topography and elevation as the modern Andes in South America, with an extended altiplano and mean elevations in the range of 4 km (Faill, 1998). The Appalachian Mountains have largely been denuded through the Cretaceous to their present approximate configuration (Rodgers, 1967; Miller and Duddy, 1989).

ILLITE-SMECTITE (I/S) DIAGENESIS IN THE APPALACHIAN BASIN

Elliott and Aronson (1987) and Elliott and Haynes (2002) examined I/S in Ordovician age bentonites hosted within the carbonate section at the structural front of the central and southern Appalachian Basin, south of West Virginia. They measured diagenetic illite in I/S between 65 and 90 percent. The majority of potassium-argon ages were consistently between 256 and 317 Ma, and thus matched well with the age of the Alleghanian Orogeny. High K/Rb ratios (by weight) were also measured in bentonites with values that ranged between 196 and 505 (Elliott and Haynes, 2002). The high K/Rb of authigenic illites (>270) relative to silicate rocks is thought to be an indicator of reaction with saline brines of marine origin that have K/Rb values of up to 3200 (Reynolds, 1963). The high illitic character of I/S (>85%), high K/Rb ratios and consistent K-Ar ages were interpreted as resulting from hot K-rich brines that migrated through the carbonate sequence coeval with the Alleghanian orogeny.

Bentonite samples collected from the Middle Devonian Onondoga outcrop in western New York contain illite in I/S up to 90 percent with minor amounts of chlorite (Lu and others, 1991). The authors concluded that Al (part of the I/S reaction) is likely sourced locally from detrital minerals, but that K is sourced at least in part from elsewhere in the basin, based on high K/Al ratios in the I/S assemblage. The authors suggested that the exotic K was introduced with fluids expelled from deeper parts of the basin during orogenesis, which is in contrast to the progressive burial model of Hower and others (1976), where K is sourced by the dissolution of K-feldspars locally. Altaner (ms, 1985) collected samples from the Tioga Bentonite near the structural front of the Blue Ridge Province from central Pennsylvania to Virginia and at the basin margins in western New York, within the sampling area for this study. The Tioga is associated with the Middle Devonian Marcellus Shale and the Onondoga Limestone, which underlies the Marcellus. Altaner (ms, 1985) found that the Tioga contained a high diagenetic illite character (>85% illite in I/S) with minor chlorite, which the author claims is due to the interaction of hot K-rich fluids expelled basinward during the Alleghanian Orogeny. McCarty (ms, 1993) observed a high proportion of diagenetic illite in I/S measured from the Tioga bentonites in western New York that are consistent with the studies of Altaner (ms, 1985) and Lu and others (1991), and have high K/Rb values ranging between 312–334.

Evans and Battles (1999) argued that extensive fluid flow occurred through the Oriskany Sandstone based on vein-hosted fluid inclusions sampled closer to the Appalachian structural front and south of the research area of this study. The Oriskany sandstone underlies the Onondoga limestone regionally. Thus, there is evidence for the migration of diagenetic fluids within the Middle Devonian Onondoga Formation, and raises the question if diagenetic fluids moved through the Middle to Upper Devonian clastic sequence.

Evans and Hobbs (2003) concluded, on the basis of the study of vein-hosted fluid inclusions collected in the Blue Ridge province and basinward, that there is no evidence for the flushing of "warm" fluids through the Middle and Upper Devonian clastic sequence towards the basin center. Lash (2006) and Lash and Blood (2007) observed that the high illitic character of shales (overlying the Onondoga) from the Upper Devonian section in western New York reflect a detrital origin, not uncommon for illites in shales, rather than a diagenetic origin. Thus, a model based on published research of clay mineral diagenesis and fluid inclusions for the focused flow of diagenetic fluids may be restricted to the Middle Devonian Onondoga limestone and Middle Devonian Oriskany sandstone from the structural front toward the basin margins in western New York (research area for this study). Figure 1 (cross-section and map view) presents a graphical representation of this model for basin scale fluid flow perpendicular to the structural front of the Appalachian Basin and within the Middle Devonian Onondoga and Oriskany formations.

METHODS

In order to investigate basin scale fluid migration and water-rock reactions, 22 formation water samples were collected from the Appalachian Basin margin, of which 19 were collected from the Upper and Middle Devonian sections (fig. 3; table 1). Due to the paucity of oil/gas wells producing formation waters at the northern basin margin (see Osborn and McIntosh, 2010); only two formation water samples from the Mississippian age Berea sandstone were collected toward the basin margin in eastern Kentucky. One sample was collected from the Silurian age Medina sandstone. The samples collected from the Berea and Medina were collected for comparison with the Devonian section samples. All water samples were measured for major, minor, and trace elemental composition (table 2), 12 samples for iodine (^{129}I/I) and 8 samples for strontium (^{87}Sr/^{86}Sr) isotopic analyses (table 3). The eight samples collected for the strontium isotopic analyses were collected from the same wells as samples for the iodine isotopic analyses. The depth of oil/gas wells sampled ranged between 314 and 2233 m (table 1).

Field Sampling and Analyses

Formation water samples were collected from actively producing oil and gas wells at the well head or from dedicated storage tanks. Due to the paucity of oil/gas wells that produced water within the study area (see Osborn and McIntosh, 2010) and the coordination of timing of sampling with well owners, dedicated and covered storage tanks to oil/gas wells were sampled instead when available and where waters had been purged within 24-hours of sampling. Samples collected for the iodine and strontium isotopic analyses were collected directly from well heads (no storage tanks were sampled for these analyses). All water samples for elemental and strontium isotopic analyses were filtered with a 0.45 μm nylon filter into pre-cleaned containers. Water samples for the iodine isotopic analyses were placed directly (unfiltered) into pre-cleaned 1-liter high-density polyethylene (HDPE) bottles with no headspace and placed in an ice chest with no ice for storage and transport to the University of Arizona AMS facility. Samples for strontium isotopic, cation, and trace elemental analyses were collected into separate 30 ml HDPE bottles with no headspace and preserved with

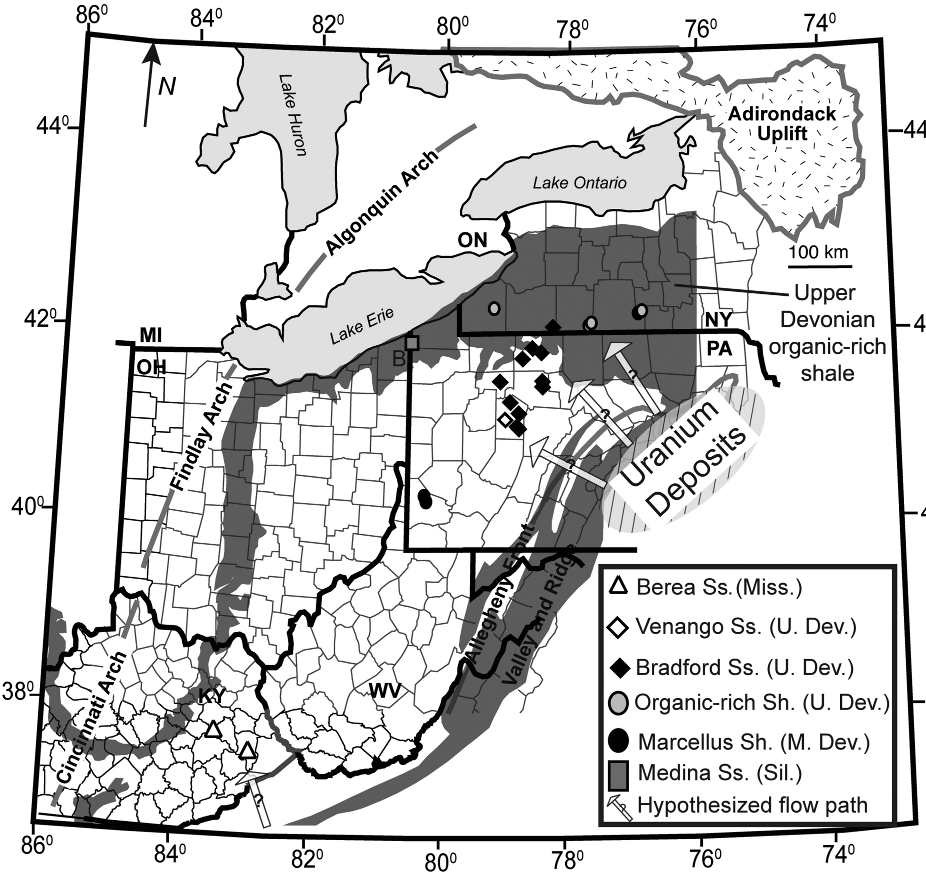

Fig. 3. Sample location map. The grayed area depicts the extent of the Middle and Upper Devonian organic-rich shale subcrop (modified from Osborn and McIntosh, 2010). The cross-hatched area in the southeast corner of Pennsylvania represents the location of large uranium occurrences at the structural front of the Appalachian Basin. Arrows represent the hypothesized direction of basin scale flow, perpendicular to the structural front (Klemic, 1962; Butler and Stansfield, 1968).

concentrated Optima grade nitric acid (HNO_3) to a pH of less than 2. Formation water samples for anion analyses were collected into 30 ml HDPE bottles with no headspace. All samples for strontium isotopic, cation, anion, and trace analyses were placed on ice for transport and refrigerated in the lab at 4 °C until analyses were completed. The pH was immediately measured in the field with an Oakton 110 series pH meter and an Orion Ross Combination electrode with a precision of ± 0.01 pH units.

Iodine ($^{129}I/I$) and Strontium ($^{87}Sr/^{86}Sr$) Analyses

The iodine ratios ($^{129}I/I$) were measured at the University of Arizona's Accelerator Mass Spectrometry facility on a NEC 3 MV pelletron accelerator mass spectrometer. Nominal $^{127}I^-$ currents produced from the groundwater samples were in the 500 to 1000 nA range. Measurements were made with the post-acceleration charge state of +5 at a terminal voltage of 2.75 MV, with a transmission of roughly 5 percent. After further magnetic and electrostatic filtering, the $^{129}I^{+5}$ ions were counted with a solid state, dE/dX surface barrier detector. Samples were current normalized and calibrated

TABLE 1

Sample location, depth, and producing formation, northern Appalachian Basin

Sample ID [(a)]	Date Sampled	State	County	Formation [(b)]	Age [(c)]	Latitude	Longitude	Depth (m)
M1	7/3/07	KY	Floyd	Berea Ss.	L. Miss.	37.569	-82.649	915
M4	7/3/07	KY	Magoffin	Berea Ss.	L. Miss.	37.676	-83.132	915
D6	6/20/07	NY	Alleghany	Organic-rich Sh.	U. Dev.	42.125	-77.819	624
D7	6/20/07	NY	Alleghany	Organic-rich Sh.	U. Dev.	42.130	-77.819	640
D10	6/21/07	NY	Cattaraugus	Bradford Grp. Ss.	U. Dev.	42.056	-78.408	314
D14	6/1/07	NY	Chautauqua	Organic-rich Sh.	U. Dev.	42.258	-79.315	457
D17	5/31/07	NY	Stueben	Organic-rich Sh.	U. Dev.	42.293	-77.069	832
D27	5/25/07	PA	Forrest	Bradford Grp. Ss.	U. Dev.	41.464	-78.601	668
D29	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.007	-78.974	848
D30	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.006	-78.979	972
D31	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.107	-79.101	902
D32	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.106	-79.105	874
D33	5/24/07	PA	Jefferson	Venango Grp. Ss.	U. Dev.	41.337	-79.083	663
D34	5/24/07	PA	Jefferson	Bradford Grp. Ss.	U. Dev.	41.156	-78.956	802
D37	5/30/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.820	-78.656	609
D38	5/30/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.860	-78.742	615
D39	5/25/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.727	-78.912	496
D40	5/25/07	PA	McKeen	Bradford Grp. Ss.	U. Dev.	41.738	-78.909	532
D60	5/31/07	NY	Stueben	Marcellus Sh.	M. Dev.	42.281	-77.079	866
D61	5/23/07	PA	Washington	Marcellus Sh.	M. Dev.	40.283	-80.284	2233
D62	5/23/07	PA	Washington	Marcellus Sh.	M. Dev.	40.280	-80.292	2014
S73	6/22/07	PA	Erie	Medina Ss.	Sil.	41.899	-80.474	980

[(a)] M = Mississippian; D = Devonian; S = Silurian.
[(b)] Ss. = sandstones; Sh. = shales.
[(c)] L. Miss. = Lower Mississippian; U. Dev. = Upper Devonian; M. Dev. = Middle Devonian; Sil. = Silurian.

with two iodine standards of $^{129}I/^{127}I$ values of 8.38×10^{-12} and 63.6×10^{-12}. Each sample was measured six times with ^{129}I counting times of 200 seconds, and the final result was calculated by taking the weighted average of the six measurements. Chemistry blank corrections (roughly 1 count per 50 seconds) were applied to all groundwater samples. Stable iodine measurements were made with an Orion iodide selective electrode, model 9453 and an Orion 710A pH/iodide selective electrode meter (error of ±2%). The analytical error for the iodine ratio and stable iodine measurements are reported in table 3. The strontium isotopic analyses were performed on a Fisons Sector 54 Multi-Collector Thermal Ionization Mass Spectrometer (TIMS) in dynamic mode (2σ standard error $\pm 1.3 \times 10^{-5}$).

Elemental Analyses

Major and minor cation analyses were conducted on a Perkin Elmer Inductively Coupled Plasma Optical Emission spectrometer (ICP-OES), Model 5300 DV (precision of ±2%), and anion chemistry was measured on a Dionex Ion Chromatograph model ICS-3000, AS23 column (±1%) in the University of Arizona Department of Hydrology and Water Resources. Rubidium concentrations were measured on an Elan DRC-II ICP-MS (precision of ±2%) in the Arizona Laboratory for Emerging Contaminants at the University of Arizona. Boron concentrations were measured on an Agilent 7500ce ICPMS operated in reaction gas mode to eliminate mass interference (precision of ±2%), at Amherst College in the Geology Department.

Table 2

Elemental results for formation waters, northern Appalachian Basin

Sample ID	pH	Cl (mM)	Br (mM)	Na (mM)	Ca (mM)	Mg (mM)	K (mM)	B (μM)	Rb (μM)	K/Rb (molar)
M1	6.59	919	2.85	497	113	40	2.36	15.86	2.12	1111
M4	6.13	2479	11.19	1330	383	135	13.98	90.20	9.79	1427
D33	5.72	2815	11.49	1507	468	96	3.28	4.99		
D10	6.99	1732	8.17	1013	216	75	2.84		2.44	1164
D27	7.21	1752	7.90	1066	279	60	2.00	8.95	2.23	899
D29	5.25	3715	11.82	1947	619	100	4.04		6.55	617
D30	5.84	4197	12.98	2513	769	122	5.00			
D31	5.51	2285	8.66	1300	317	75	3.17	17.40		
D32	6.04	2344	9.19	1428	319	80	2.73	9.67		
D34	5.55	2573	10.06	1315	395	88	3.73	8.18		
D37	7.53	1280	5.79	843	211	49	3.55	6.96	2.19	1624
D38	7.15	2720	12.31	1517	402	100	2.91	2.29		
D39	6.66	2033	9.05	1269	272	73	4.67	2.20	3.16	1481
D40	6.47	2047	9.14	1194	274	69	3.11	9.53	2.54	1222
D6	6.70	1718	7.54	1106	239	66	2.01	6.54	2.15	935
D7	6.26	2272	9.80	1332	309	85	2.50			
D14	7.13	1711	8.45	1017	250	79	2.50	15.33	2.21	1131
D17	6.51	3680	14.88	1743	598	141	21.25		9.69	2194
D60	6.46	3726	15.18	1805	571	125	17.88		8.54	2094
D61	6.84	2986	13.53	1650	529	90	6.22	26.92	6.80	915
D62	6.59	3170	14.29	1629	568	116	7.83	31.17	6.86	1142
S73	5.38	3995	16.41	2383	626	138	24.10	101.4	8.90	2708

RESULTS AND DISCUSSION

Water samples collected for this study are broadly divided into three categories based on the depositional age of the target formation: (1) Mississippian (M) Berea Sandstone, (2) Middle and Upper Devonian (D) organic-rich shales and reservoir sandstones (Bradford Sandstone, Venango Sandstone, Organic-rich shale and Marcellus organic-rich shale), and (3) Silurian (S) Medina Sandstone. The major, minor, and trace elemental results of formation waters are presented in table 2. The isotopic analyses of formation waters are presented in table 3.

Basin Scale Fluid Migration

Measured $^{129}I/I$ values (28×10^{-15} to 1890×10^{-15}) in brine samples are 5 to 9 orders of magnitude higher than estimated cosmogenic values (10^{-19} to 10^{-21}) sourced from Paleozoic age organic matter (~320 to 450 Ma; fig. 4; table 3). The estimated cosmogenic values were calculated using equation 1 above and assuming an initial pre-anthropogenic value of 1500×10^{-15} for organic matter of Devonian depositional age (Moran and others, 1995b). Therefore, cosmogenic $^{129}I/I$ sourced from Devonian age organic matter may be considered negligible in these samples. Anthropogenic ^{129}I contamination of samples is likely not significant due to the depth of samples (314-980 m). The high measured ratios may be due to: (1) a regionally pervasive "young" (~50 to 90 Ma) organic matter source with high cosmogenic $^{129}I/I$; (2) anthropogenic $^{129}I/I$ contamination from surface waters; and/or (3) the addition of fissiogenic ^{129}I.

A regionally pervasive "young" subsurface organic matter source in the study area is not documented in the literature and may be discounted as an explanation for the observed high ^{129}I ratios. The production of ^{129}I in rocks from the spontaneous fission of ^{238}U is likely the major source of observed high ^{129}I concentrations in Appalachian Basin brines.

Of the bedrock types in the study area, organic-rich shales are on average likely to contain the highest concentrations of uranium (Turekian and Wedepohl, 1961;

Table 3

Isotopic results for formation waters

Sample ID	^{129}I/I (10^{-15})	^{129}I ($\times 10^{7}$) atoms/L	I (mM)	^{87}Sr/^{86}Sr	Sr (mM)	1/Sr (mM)$^{-1}$
M1	1890 ± 150	1.46 ± 0.12	0.0128 ± 0.0004	0.7108	2.5228	0.39638
D10	160 ± 20	2.4 ± 0.3	0.248 ± 0.011	0.7190	0.9746	1.026067
D30	29 ± 6	0.54 ± 0.11	0.31 ± 0.016			
D34	70 ± 6	0.94 ± 0.09	0.22 ± 0.011			
D37	28 ± 24	0.32 ± 0.27	0.187 ± 0.007			
D39	150 ± 20	3.4 ± 0.5	0.374 ± 0.013	0.7205	0.7062	1.41601
D40	490 ± 60	8.7 ± 1.1	0.296 ± 0.011	0.7210	0.5929	1.68649
D6	860 ± 40	13.9 ± 0.8	0.269 ± 0.01	0.7183	1.4045	0.71201
D14	170 ± 80	1.8 ± 0.8	0.173 ± 0.006	0.7158	1.1877	0.84194
D17	59 ± 14	2.2 ± 0.5	0.61 ± 0.022			
D60	70 ± 24	3.7 ± 1.3	0.869 ± 0.033	0.7100	54.658	0.0183
S73	240 ± 30	4.5 ± 0.6	0.314 ± 0.016	0.7119	8.0547	0.12415

Wedepohl, 1995). Organic-rich shales within the study area and Appalachian Basin contain uranium at concentrations between 12 and 38 ppm (Leventhal and Hosterman, 1982), which were used to estimate an ^{129}I/I ratio of between approximately 80×10^{-15} and 270×10^{-15} for this study. While the Leventhal and Hosterman study (1982) present geochemistry from organic-rich shales from other parts of the basin (TN, VA, and KY) and are limited in the number of samples, we assume the range of uranium that they report as representative of the basin for this study. Furthermore, there are reports of Devonian brine from western New York that have relatively high radium (up to 16,000 picocuries per liter), suggesting the possibility of localized high uranium concentrations (NYDOH, 2009). An estimate of fissiogenic ^{129}I/I in formation waters was then made with the following assumptions: (1) the emanation efficiency is 100 percent (all iodine contained in rock goes into solution), (2) published uranium concentrations are representative throughout the study area and that fissiogenic ^{129}I is the dominant control on the numerator of estimated ^{129}I/I ratios in brines, (3) One-L of the sampled waters have been in contact with 1 kg of the source rock for greater than 79 Ma (secular equilibrium), (4) the iodine content of crystalline rock was assumed at 1.4 ppm for calculating fissiogenic ^{129}I/I in rocks (Wedepohl, 1995), and (5) that the iodine content of brines, which is measured for this study (table 3), is likely to have the strongest control on the denominator of the estimated ^{129}I/I ratio.

These assumptions provide a conservative estimate of the maximum ^{129}I/I ratios produced by fissiogenic sources and in solution, dependant on the concentration of uranium in rocks (source of ^{129}I) and iodine content of basinal brines. These estimated ratios are likely to be lower as most waters approach a lower average ^{129}I/I value that reflect the fact that uranium concentrations are variable within the source areas (Klemic, 1962; Butler and Stansfield, 1968). However, the maximum estimated iodine isotopic composition from uranium concentrations in rocks can provide a frame of reference to evaluate fissiogenic ^{129}I as a tracer of fluid flow (fig. 5). Increasing the uranium content of rock by 20 percent from the maximum published values increases the high estimated ^{129}I/I from 270×10^{-15} to 328×10^{-15}, still below the anomalously high measured values (490×10^{-15} to 1890×10^{-15}). The uranium concentration of shales locally would have to be on the order of 260 ppm to account for the highest measured ^{129}I/I values for this study and represent a 684 percent increase from published values.

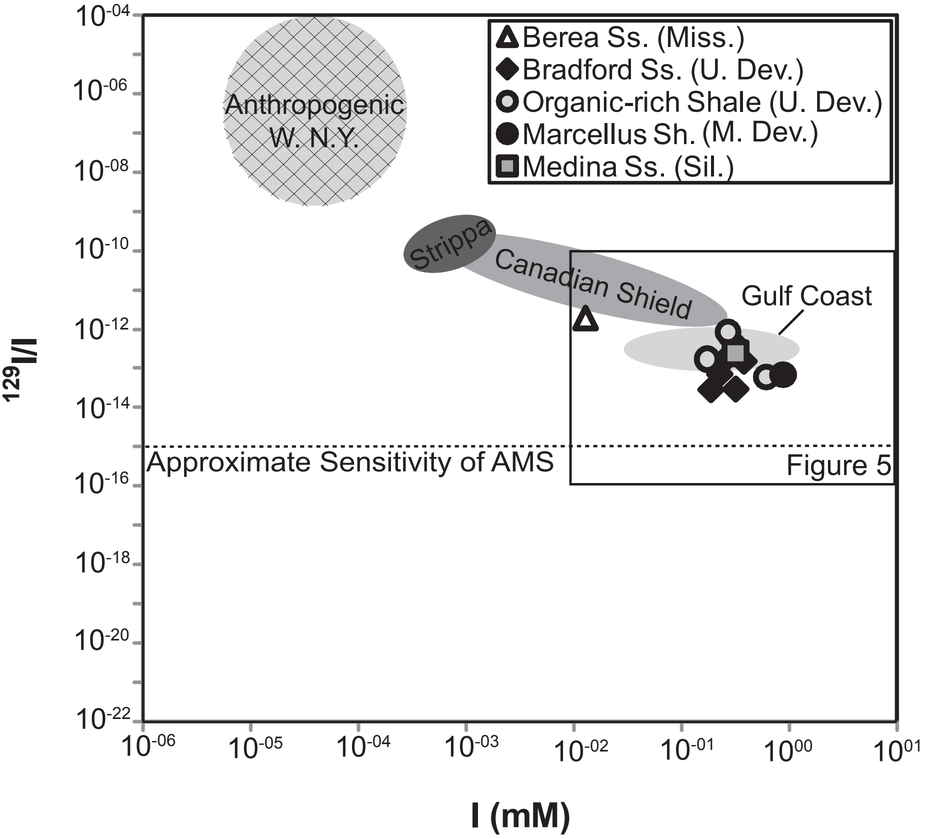

Fig. 4. Plot of ^{129}I/I versus iodine concentration. The range of values collected from anthropogenic sources in western New York are from Rao and Fehn (1999). Fields from other brine studies [Gulf Coast (Moran and others, 1995a); Canadian Shield (Bottomley and others, 2002); and Stripa Granite Mine (Fabryka-Martin and others, 1989)] are provided for reference. The range of cosmogenic ^{129}I/I sourced from Devonian age organic matter in the shales was estimated from equation 1 in the text.

The Atomic Energy Commission during the cold war era (Klemic, 1962; Butler and Stansfield, 1968) concluded that the Appalachian Basin contained large uranium occurrences that are economically mineable (concentrations up to 7,600 ppm total uranium). These occurrences, with maximum concentrations considerably higher than measured in shales by Leventhal and Hosterman (1982), correspond to estimated ^{129}I/I values of up to $55{,}000 \times 10^{-15}$ (fig. 5). Furthermore, they occur within the Pennsylvanian and Devonian section along the structural front of the Appalachian Basin from central/eastern New York south through North Carolina (fig. 1; Klemic, 1962; Butler and Stansfield, 1968). The highest concentrations are noted to occur in southeast Pennsylvania and northern New Jersey (Klemic, 1962; Butler and Stansfield, 1968) and represent plausible high ^{129}I/I sources that lie along a hypothesized flow path parallel to the main compressional direction of the Alleghanian orogeny (fig. 1). For this study, there are two likely sources of fissiogenic ^{129}I: (1) shales, which are pervasive in the study area and henceforth referred to as local fissiogenic ^{129}I; and (2) large uranium occurrences at the structural front of the Appalachian Basin and henceforth referred to as regional fissiogenic ^{129}I.

Most brine samples collected as part of this study (9 out of 12) plot within or below the field for local fissiogenic ^{129}I (fig. 5). There are three samples (D6, D40, and M1)

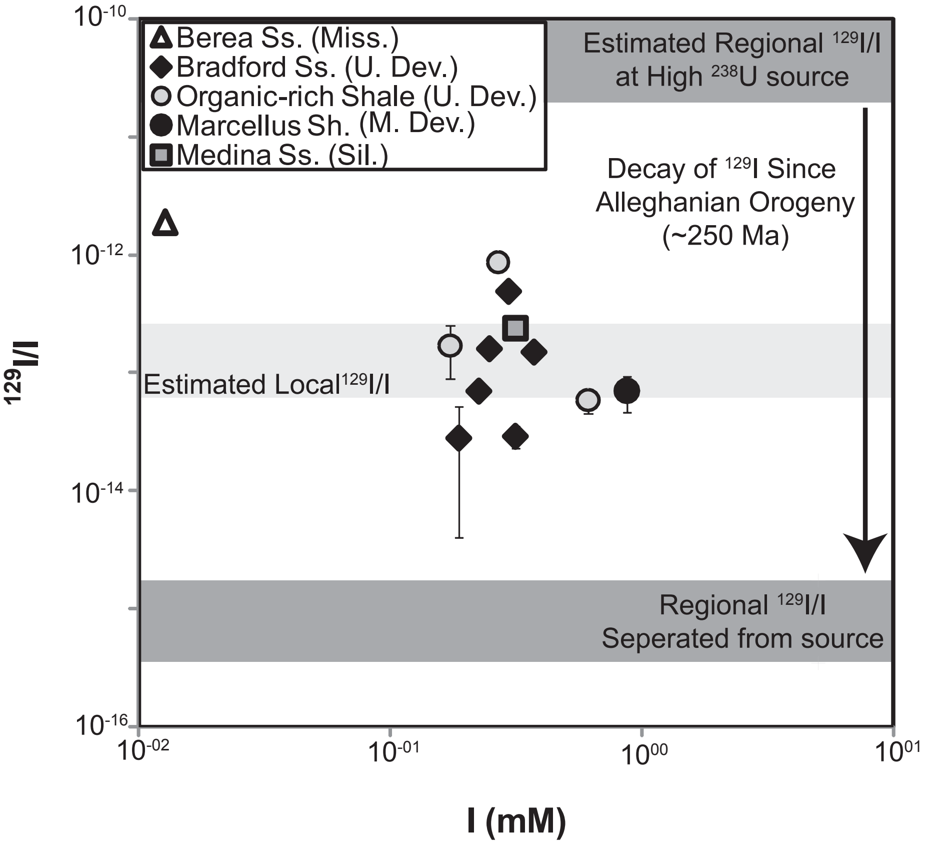

Fig. 5. Plot of ^{129}I/I versus iodine concentration of samples at a finer scale. Vertical error bars, associated with the ^{129}I/I measurement are presented. Error bars that are not visible are within the symbol size. Ranges for locally and regionally produced fissiogenic ^{129}I are estimated from equations 1 through 3 in the text and are provided for reference. The estimate of local and fissiogenic ^{129}I is discussed in the text in more detail.

that have measured values (490×10^{-15} to 1890×10^{-15}) above the maximum local fissiogenic ^{129}I source (80×10^{-15} to 270×10^{-15}) on the log-log scale in figure 5 and may be explained by the high regional source, assuming that published uranium concentrations are representative. Brines at the basin margin, if tectonically driven, would have been separated from this regional source since the last orogeny (~275 Ma ago) and at present regional fissiogenic ^{129}I/I values would have decayed to values in the range of 10^{-15}, still well below the measured values. This suggests that tectonically driven basin scale fluids from the Alleghanian orogeny cannot explain the anomalously high measured ^{129}I/I values.

The fact that the location of samples with anomalously high measured ^{129}I/I values lie along a hypothesized flow path parallel to the main compressional direction of the Alleghanian orogeny, make a regionally high fissiogenic ^{129}I/I source still very compelling for future research, and we hypothesize that topographically driven basin scale fluid flow occurred after the Alleghanian orogeny. An ^{129}I age calculated using the maximum regional fissiogenic value as the initial ratio and the anomalously high measured values as the final ratio for equation 1 are between 80 and 110 Ma, in the middle Cretaceous. It has been suggested by Miller and Duddy

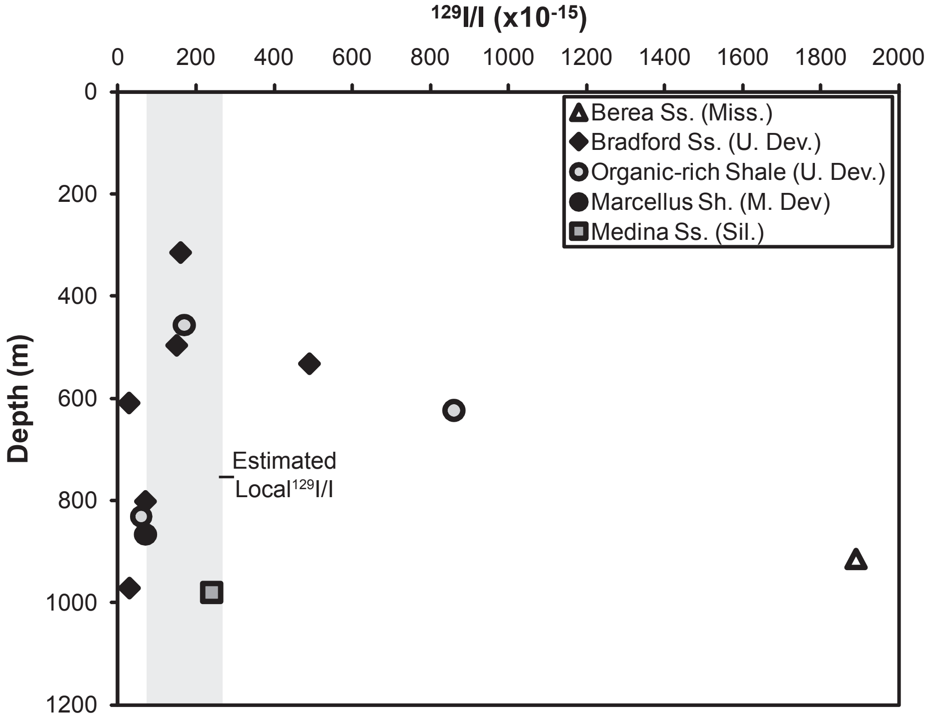

Fig. 6. Plot of ^{129}I/I with depth (meters below land surface). The range of local fissiogenic ^{129}I is provided for reference.

(1989) that there was basin scale uplift related to rifting and subsequent denudation in the early to middle Cretaceous. Flow rates can be estimated, as a first approximation, as being in the range of 10^{-3} m/y, given the ^{129}I age above and a horizontal distance from the structural front to sample locations at the margin (150 to 200 Km). This flow rate likely represents a minimum value, as the geometry of topographic flow within the basin is likely greater than the horizontal distance. This is generally consistent with basin scale fluid flow rates (10^{-4} to 10^{-3} m/yr) modeled from Ge and Garven (1992), Cutillo and others (2006), and Screaton and Ge (2007).

In a plot of measured ^{129}I/I with depth (fig. 6), 9 of the 12 samples are relatively invariant with depth and are consistent with a local fissiogenic source within the shales. Three of the 12 samples plot with increasing ^{129}I/I ratios with depth. If anthropogenic contamination was the source of high ^{129}I ratios, the highest ^{129}I/I values would be expected to be at the shallowest depths. This supports the assumption that anthropogenic ^{129}I is likely to be negligible in deep basinal brines and that *in-situ* production is the main source of ^{129}I. Furthermore, it suggests the possibility of a high ^{129}I/I source mixing from depth, which is consistent with brine studies of Lowry and others (1988), Siegel and others (1990), and Saunders (1991) that show mixing of brine sourced from deeper in the basin with shallow brines at the basin margin. Other tracers, strontium and elemental analyses of formation water, were used in combination with ^{129}I analyses in this study to test basin scale fluid flow and water rock reactions.

Evidence for Illitization in Brine Geochemistry

Strontium isotope ratios and Sr concentrations of Appalachian Basin formation waters display a mixing trend ($R^2 = 0.87$) between a highly radiogenic end-member

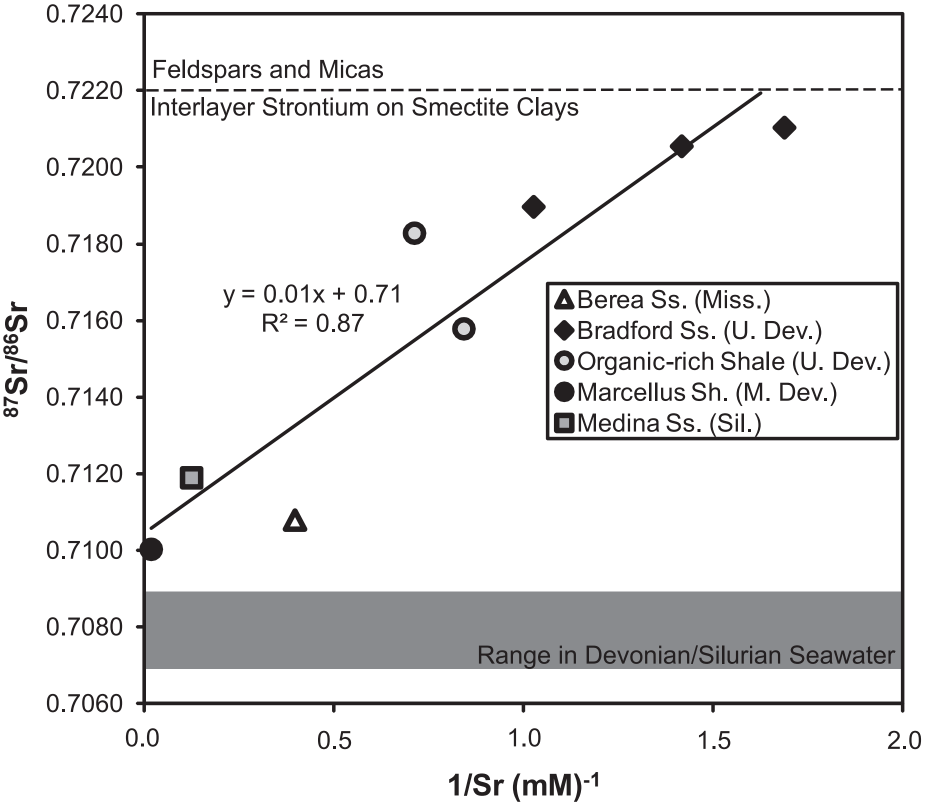

Fig. 7. Plot of strontium isotopic ratios versus the inverse of strontium concentration of formation waters. The range of $^{87}Sr/^{86}Sr$ in Silurian-Devonian seawater is from Burke and others (1982). The limit of $^{87}Sr/^{86}Sr$ values from interlayer strontium on smectite clays is provided for reference (Chauduri and Clauer, 1993).

with low Sr concentrations (0.7210 $^{87}Sr/^{86}Sr$, 0.592 mmole/L Sr) and a relatively non-radiogenic end-member with high Sr concentrations (0.7100 $^{87}Sr/^{86}Sr$, 54.66 mmole/L) (fig. 7; table 3). The composition of the non-radiogenic end member is generally consistent with Silurian/Devonian seawater values measured from marine carbonates, which range between 0.7078 to 0.7090 (Burke and others, 1982). The radiogenic strontium values measured in this study are generally higher than values measured in the Silurian section at the most distal part of the Appalachian Basin in Southern Ontario, Canada as well as the Silurian and Devonian sections of the Michigan and Illinois basins (McNutt and others, 1987; Stueber and Walters, 1991). The radiogenic strontium may be due to reaction with micas and feldspars or from the interlayer position of smectite clays. Leaching studies on smectite clay minerals have demonstrated that interlayer Sr can have $^{87}Sr/^{86}Sr$ values up to 0.7220 (Chauduri and Clauer, 1993). It is possible that there are actually more radiogenic values in brines that were not captured within the sample set of this study that most likely would have been from reaction with K-feldspars or micas. Within the limits of the current data set, however, the radiogenic $^{87}Sr/^{86}Sr$ values can be interpreted as being interlayer strontium expelled into solution during smectite diagenesis. Diagenetic illite is observed in relatively high proportion with smectite (I/S) in shales within the Middle Devonian Onondoga limestone formation. The strontium results, as a first approximation are consistent

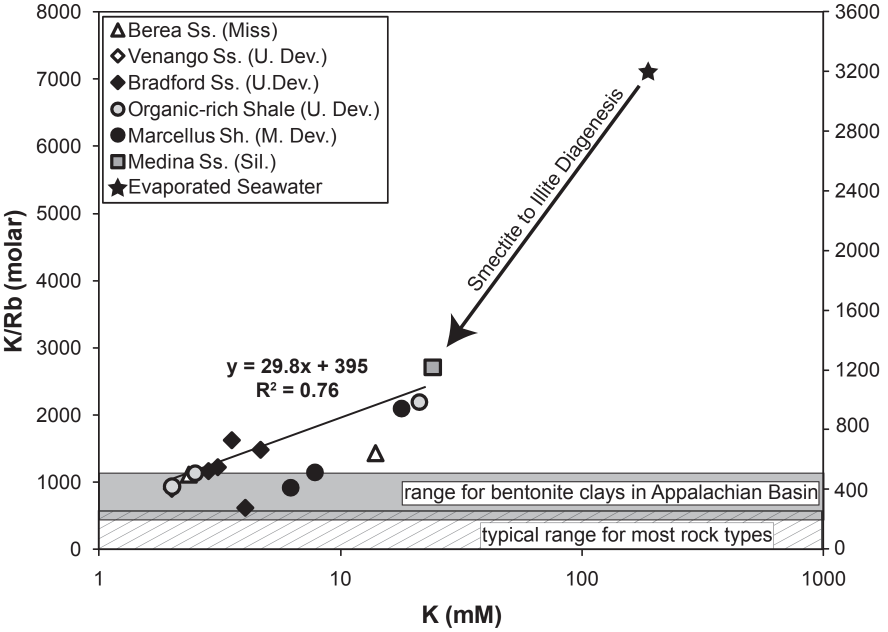

Fig. 8. Plot of potassium/rubidium ratios versus potassium concentration. The K/Rb ratios for evaporated seawater are taken from Bottomley and others (2002). The K concentration for evaporated seawater is estimated from the K and Br trend from McCaffrey and others (1987) and bromide concentrations reported in Osborn and McIntosh (2010) (see fig. 10B). The range of K/Rb values in silicate rocks and bentonite clays in the Appalachian Basin are from Reynolds (1963) and Elliott and Haynes (2002).

with diagenetic fluids that have interacted with a marine carbonate and shale. The elemental analyses of brines may constrain evidence for clay mineral diagenesis even further.

Previous studies have demonstrated that K/Rb values of most rock types of the upper crust and bentonite clays are on average less than ~270 (Turekian and Wedepohl, 1961; Reynolds, 1963; Wedepohl, 1995). Values greater than 270 have been observed in diagenetic illite in I/S and interpreted as resulting from the interaction with saline fluids of a marine origin (K/Rb values of seawater are ~3200; Reynolds, 1963; Chaudhuri and Clauer, 1993; McCarty, ms, 1993; Elliott and Haynes, 2002). There is an apparent mixing trend ($R^2 = 0.76$) between a high K/Rb (2708 molar ratio) and K (24.10 mmole/L) end-member that is consistent with brines of an evaporated marine source and a low K/Rb (>1000 molar ratio) and K (2.00 mmole/L) end-member consistent with diagenetic illite in I/S in the Appalachian Basin (fig. 8; table 2).

Measured K/Rb values that are intermediate between values from water-rock reactions ($\lesssim 500$) and that of seawater (~3200) have been interpreted by Chauduri and Clauer (1993) as resulting from smectite to illite diagenesis. The combined strontium isotopic analyses and K/Rb values of formation water may be the strongest evidence for smectite diagenesis in the Appalachian Basin based on formation water analyses. The illitization reaction may occur at relatively low temperatures over long periods of time as with progressive burial or a sudden increase in temperatures locally associated with migration of diagenetic fluids. Thus, the question of where the smectite diagenesis reaction occurred, at the basin margin or deeper in the basin, remains.

Since boron can exchange for silica in the tetrahedral layer of illite clays at relatively high temperatures ($\gtrsim 150$ °C), the depletion of boron in formation waters may be an indicator of high paleo-temperatures from formation water analyses (Williams and others, 2001a). Figure 9 demonstrated the origin of salinity as evaporated seawater (A) and the depletion of both potassium (B) and boron (C) relative to the seawater evaporation trend. The depletion of K may be due to the precipitation of feldspars locally. Brines of the Devonian section of the northern Appalachian Basin are notably depleted of B relative to the estimated evaporated seawater trend and modern seawater values (~0.42 mmole/L; Bottomley and Clark, 2004) with concentrations that range between 0.0022 and 0.1000 mmole/L (table 2). Other brines studies report B concentrations that are generally greater than what is measured for this study in the Gulf Coast and Mississippi Salt Dome (2.4 to 64 mmole/L; Kharaka and others, 1987; Moldovanyi and Walter, 1992), Alberta Basin (0.28 to 13.1 mmole/L; Connolly and others, 1990), and the Canadian Shield (0.27 to 159 mmole/L; Bottomley and Clark, 2004). The depletion of B relative to evaporated seawater in brines may be due to: 1) precipitation of boron containing minerals, 2) boron that is adsorbed to mineral surfaces, and 3) boron that is structurally bound in the tetrahedral layer of illite clays during smectite diagenesis (Williams and others, 2001a). Minerals containing boron as a major component are not observed in the study area and at the scale of this study are likely to be rare. Thus, adsorption or fixation may account for the boron depletion in brines.

Previous studies of clay diagenesis have demonstrated that B is several orders of magnitude more abundant with I/S clays than other diagenetically altered minerals and that increased adsorption/fixation of B (depletion of B in formation waters) is dependent on temperature, pH, and the ionic strength of the solution (Harder, 1970; Williams and others, 2001a; Williams and others, 2001b). At low temperatures (<120 °C), the pH of formation waters will tend to control the adsorption of boron (You and others, 1996). The adsorption of boron to mineral surfaces approaches a value of zero (all boron is in solution) as the pH of the solution becomes more acidic (to a pH of 5). In general, the boron concentration is relatively invariant as the pH changes from values that are circum-neutral to slightly acidic values, which is not expected at low temperatures and suggests that there is a different control on boron concentrations in solution (fig. 10A). High ionic strength solutions will have greater adsorption to mineral surfaces, however, at the boron concentrations measured for this study (>0.1 mmole/L), there will be little sensitivity to changing ionic strength conditions (Keren and O'Connor, 1982). Therefore, the depletion of B in brines may be interpreted as functionally controlled by temperature. There is some correlation ($R^2 = 0.76$) of boron concentration in solution increasing with depth (proxy for temperature), which may be expected (fig. 10B). However, the depletion of boron is most likely due to fixation within the tetrahedral layer of diagenetic illite, indicating that paleo-temperatures of these formation waters were at one time greater than 150 °C. This can be explained by the migration of formation waters from depth in the basin where temperatures are greater than 150 °C and is consistent with models of the thermal history of the Appalachian Basin (Rowan and others, 2004; Rowan, 2006).

Since most of the formation water samples were collected at the basin margin, within the Middle to Upper Devonian clastic sequence where there is little evidence for diagenetic illite in I/S, it may be interpreted that these waters instead migrated through the Onondoga formation, where I/S is most strongly pronounced. Furthermore, these waters probably would have migrated from deeper in the basin where temperatures were higher. Miller and Duddy (1989) estimated that there was between 2 to 3 km of overburden in the study area in western New York since the Alleghanian orogeny. Assuming a geothermal gradient of approximately 25 °C/km, and an average depth of 853 m of samples collected for this study, the maximum paleo-temperature based on burial depth would have been approximately 96 °C, lower than the 150 °C

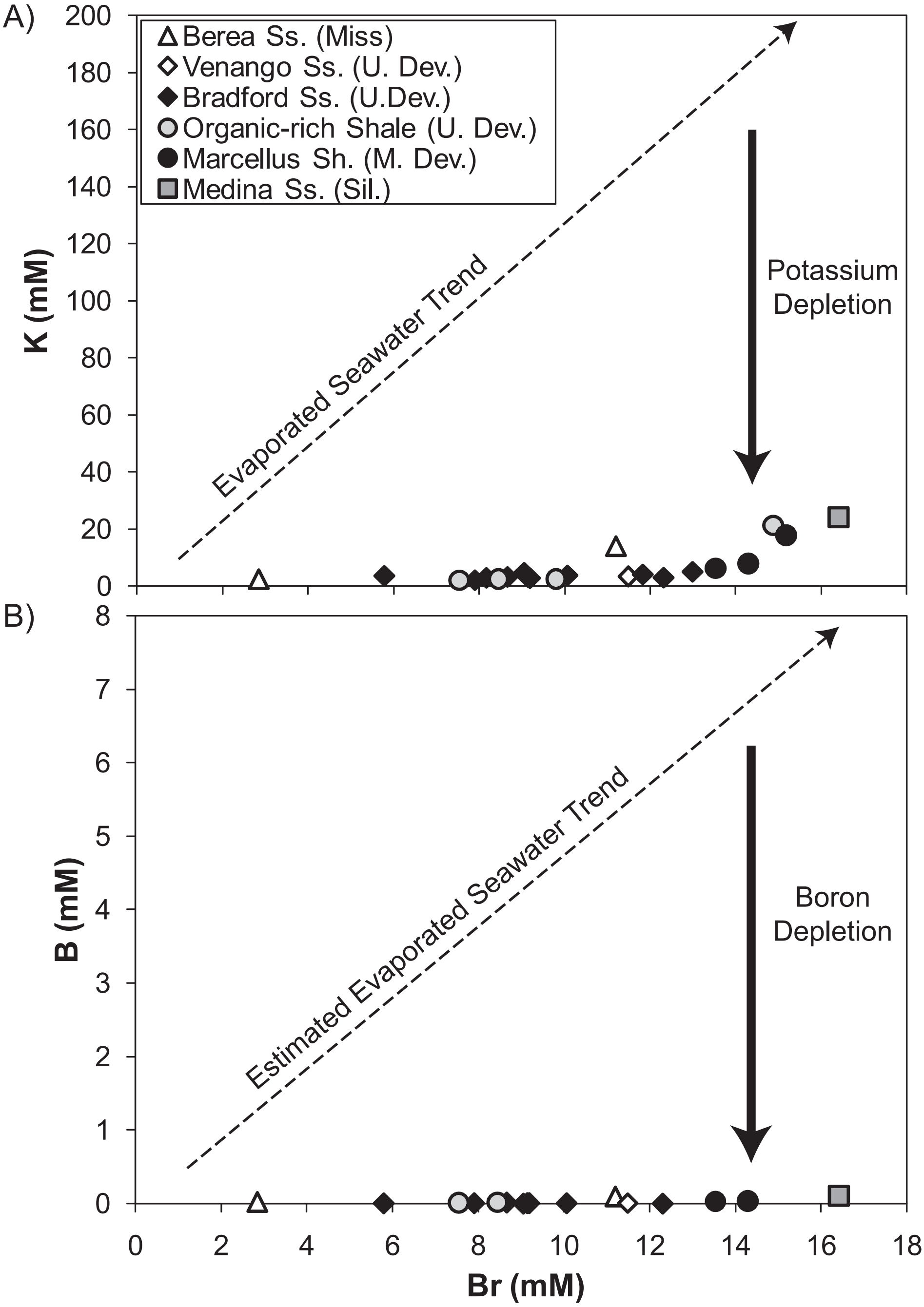

Fig. 9. Plots of boron (A) and potassium (B) versus bromide concentration in formation waters. Data for K, and Br are taken from Osborn and McIntosh (2010). Seawater evaporation trends are taken from McCaffrey and others (1987) and assumes that the evaporation trends for K and Br are similar to Paleozoic evaporation trends.

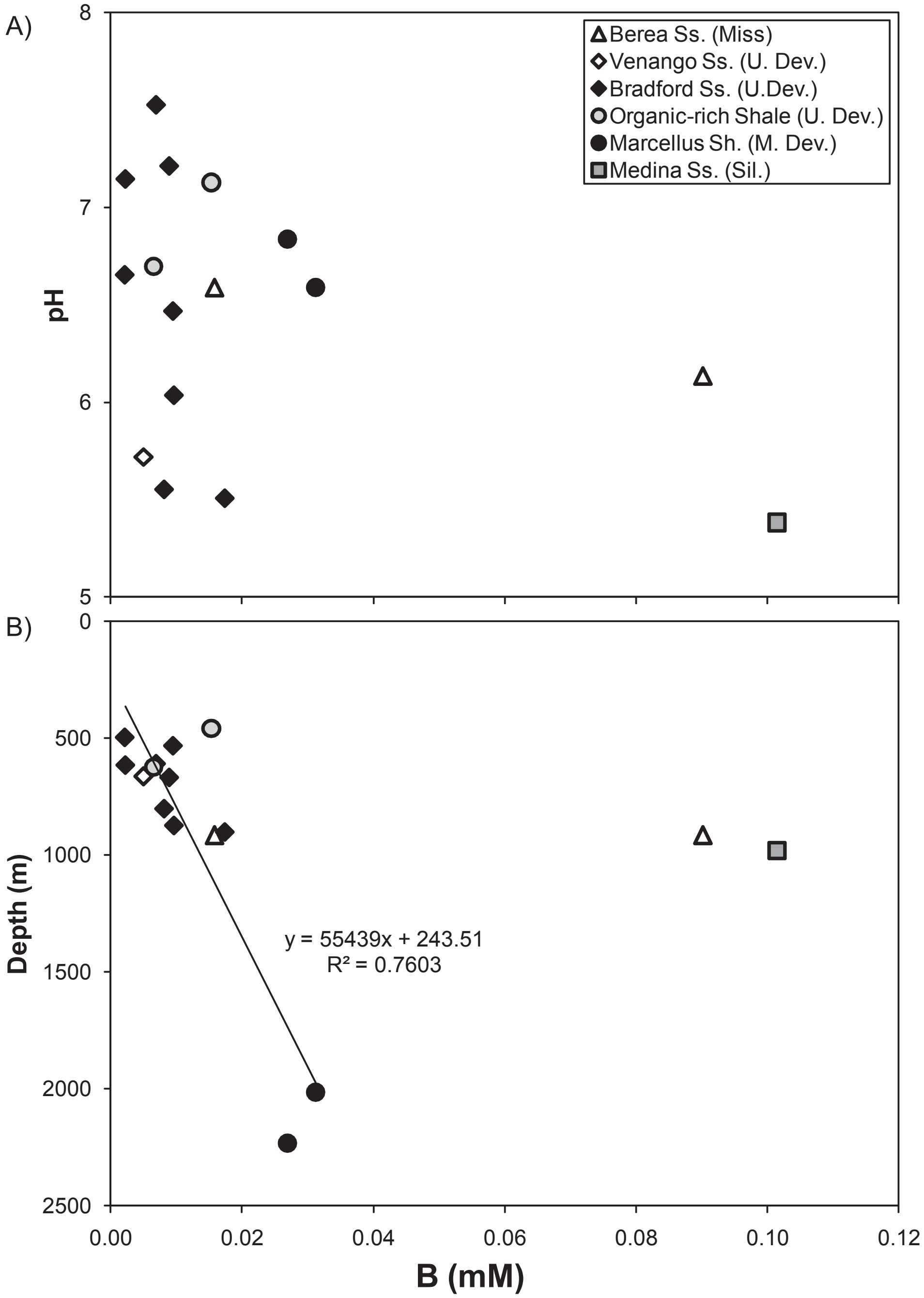

Fig. 10. Plots of pH (A) and depth (B) versus boron concentration of formation waters.

estimated from the fixation of B, suggesting that these waters would have come from deeper in the basin and along flow paths in the Middle Devonian Onondoga limestone and Oriskany sandstone.

CONCLUSIONS

Evidence for basin-scale fluid flow and clay mineral diagenesis within the Appalachian Basin from formation water geochemistry is presented in this study. These results are generally consistent with the published literature on smectite to illite clay mineral diagenesis and ore deposition within the study area that invoke the migration of diagenetic fluids expelled basinward during orogeny.

Conclusions from this study are:

1) Iodine-129 in Appalachian basin brines is largely from fissiogenic sources. The use of fissiogenic ^{129}I in formation waters of the Appalachian basin as a tracer of basin scale fluid flow is compelling, given some spatial control on uranium concentrations. The fissiogenic source for ^{129}I in basinal brines is based on the Devonian depositional age of organic matter contained in shales (negligible osmogenic source), the depth (>300 m) of samples (likely negligible anthropogenic source), and the relatively invariant values of measured ^{129}I/I in a subset of samples with depth that are consistent with ^{129}I/I estimated from average uranium concentrations in shales.
2) A second subset of three samples have measured ^{129}I/I that are anomalously high compared to local fissiogenic ^{129}I and increase with depth. This is important because this supports the assumption that anthropogenic ^{129}I is likely negligible (highest ratios would be at the shallowest depths) and suggests the possibility of brine that may have interacted with a high ^{129}I/I source mobilized from depth.
3) The migration of brines from depth is also supported by the strontium isotopic composition and elemental analyses of formation waters. Radiogenic Sr values (up to 0.7210) are generally consistent with interlayer strontium, expelled from the interlayer of smectite clays during diagenesis. This is supported by K/Rb values in formation waters that are intermediate between seawater ($\sim$3200) and rock values ($\lesssim$500).
4) The depletion of K and B, relative to evaporated seawater, provides further evidence for clay diagenesis in the northern part of the basin. The depletion of B in formation waters is based on the relatively invariant concentration with pH and very low B concentration. The depletion of B may be due to substitution of silica in the tetrahedral layer of illite during I/S diagenesis at temperatures that were at one point greater than approximately 150 °C. Importantly, this temperature is a minimum paleo-temperature estimate and may be interpreted as high given the burial history of the study area and a constant geothermal gradient. Combined with the fact that there is little evidence for diagenetic illite in shales from the Middle to Upper Devonian clastic sequence (sampled for this study), and the high proportion of diagenetic illite in bentonites from below the Devonian clastic sequence, there is support for the flow of diagenetic fluids within the Onondoga and from deeper in the basin.
5) There is some evidence based on the elevated ^{129}I/I of the formation waters that topographically driven basin scale fluid flow may have occurred following the Alleghanian Orogeny.

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