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**Environmental Earth Sciences**

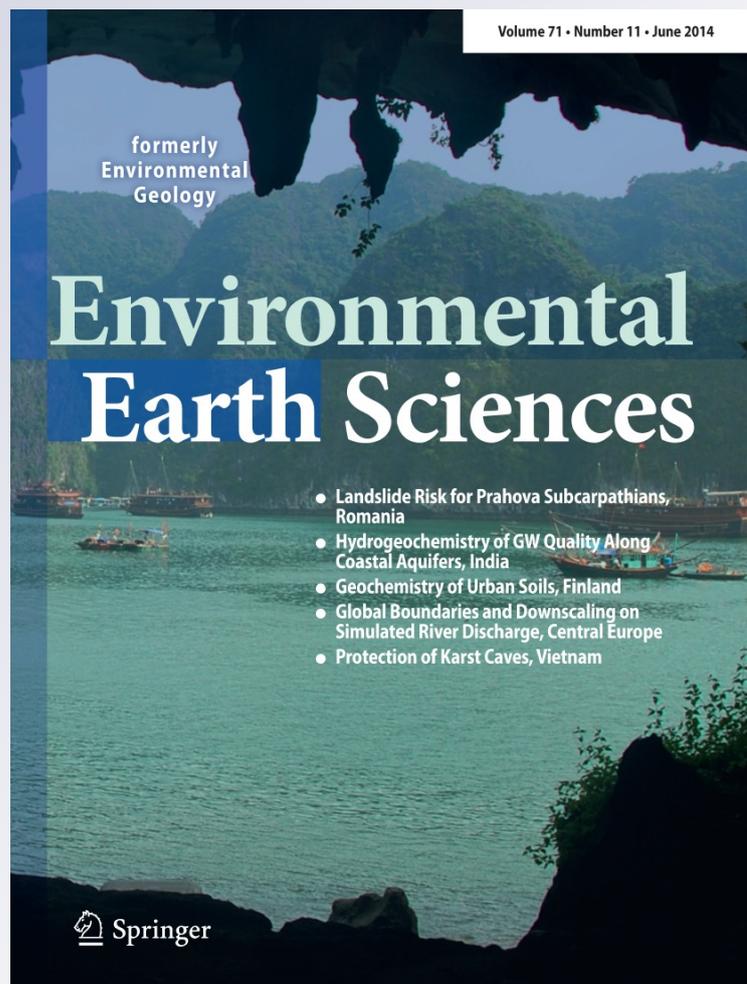
ISSN 1866-6280

Volume 71

Number 11

Environ Earth Sci (2014) 71:4715–4724

DOI 10.1007/s12665-013-2862-5



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# A multi-isotope approach for understanding sources of water, carbon and sulfur in natural springs of the Central Appalachian region

Andrea L. Sack · Shikha Sharma

Received: 16 April 2013 / Accepted: 6 October 2013 / Published online: 17 October 2013  
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**Abstract** Natural springs have been reliable sources of domestic water and have allowed for the development of recreational facilities and resorts in the Central Appalachians. The structural history of this area is complex and it is unknown whether these natural springs receive significant recharge from modern precipitation or whether they discharge old water recharged over geological times scales. The main objective of this study was to use stable isotopes of water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$ ), dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and dissolved sulfate ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ) to delineate sources of water, carbon and sulfur in several natural springs of the region. Our preliminary isotope data indicate that all springs are being recharged by modern precipitation. The oxygen isotope composition indicates that waters in thermal springs did not encounter the high temperatures required for O isotope exchange between the water and silicate/carbonate minerals, and/or the residence time of water in the aquifers was short due to high flow rates. The carbon isotopic composition of dissolved inorganic carbon and sulfur/oxygen isotopic composition of dissolved sulfate provide evidence of low-temperature water–rock interactions and various biogeochemical transformations these waters have undergone along their flow path.

**Keywords** Natural springs · Recharge · Stable isotopes · Water–rock interaction

## Introduction

The Appalachian Basin was an area of sediment accumulation and two significant orogenies during the Paleozoic era (~570–225 mya). The Appalachian orogeny occurred from ~320 to 220 mya, mainly during the Pennsylvanian through mid-Triassic time periods. Coal-bearing and carboniferous rocks formed from sediments eroding these mountains. As deformation continued, the Appalachian Basin was faulted and folded. Erosion later created what is known today as the Valley and Ridge Province (Hobba et al. 1979). The complex composition and structure of the Appalachian region give rise to different types of waters that contribute to surface and groundwater in this area.

A spring is defined as any location where groundwater naturally emerges from the subsurface in a distinct flow (Manga 2012). Many different types of springs exist in nature and are often classified based on their hydrogeology. Springs and groundwater seeps often form along structural deformation pathways and act as conduits for the transfer and surfacing of water and its dissolved components to flow and resurface at another location. The natural springs in the Central Appalachians have been reliable sources of domestic water and development of recreational facilities and resorts since the late 18th century (Rader and Gathright 1984). Some studies have also highlighted the importance of thermal springs to produce geothermal power (Costain et al. 1980; Lund 1997). For sustained use of these springs as drinking water sources or geothermal energy, it is important to understand whether the springs are receiving significant contributions from modern precipitation or

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whether they are discharging old water recharged over geological time scales.

The main objective of this study was to use stable isotopes of water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$ ), dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and dissolved sulfate ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ) to delineate sources of water and understand processes affecting carbon and sulfur dynamics in waters discharging from natural springs in the Central Appalachian region.

### Study sites

A total of 20 water samples were collected from natural springs located in Pennsylvania, West Virginia and Virginia. Spring sites located in Pennsylvania include Port Royal, Cedar Creek, Smithton and Mayview. The one spring site located in Monroe County West Virginia is Old Sweet spring. Springs in Virginia include Octagon, Magnesia, Boiler and Hot Sulfur springs, which are all located in the Homestead Resort in Bath County, Virginia.

Jefferson and Big springs are also in Bath County, but are not part of the resort. Sweet Chalybeate spring, Spellman spring and Cesspool cave are located in Alleghany County, Virginia. A few of the springs had multiple sampling points including Cedar Creek, Smithton, Sweet Chalybeate and Magnesia (Table 1). The springs in Virginia and West Virginia are located within the Valley and Ridge Province. The structural complexity of this area is a result of the Alleghanian Orogeny 320 mya, which corresponded to a large mountain-building event associated with large folds and thrust faults in the Central Appalachian Mountain region (Hobba et al. 1979). An effect of this deformation was that the sedimentary rock in the basin was compressed perpendicular to the direction of forces. Deformation associated with the orogeny was the greatest in the southern Appalachians (North Carolina, Tennessee, Virginia and West Virginia) where a series of thrust faults and folds developed in addition to the large folds, with the amount of deformation lessening to the north (Evans and Battles 1999). A combination of the topography, lithology and structure provides conduits for the water and dissolved

**Table 1** Site-specific information including site name/code, sampling date, location, and relevant geology for each sampled location in this study

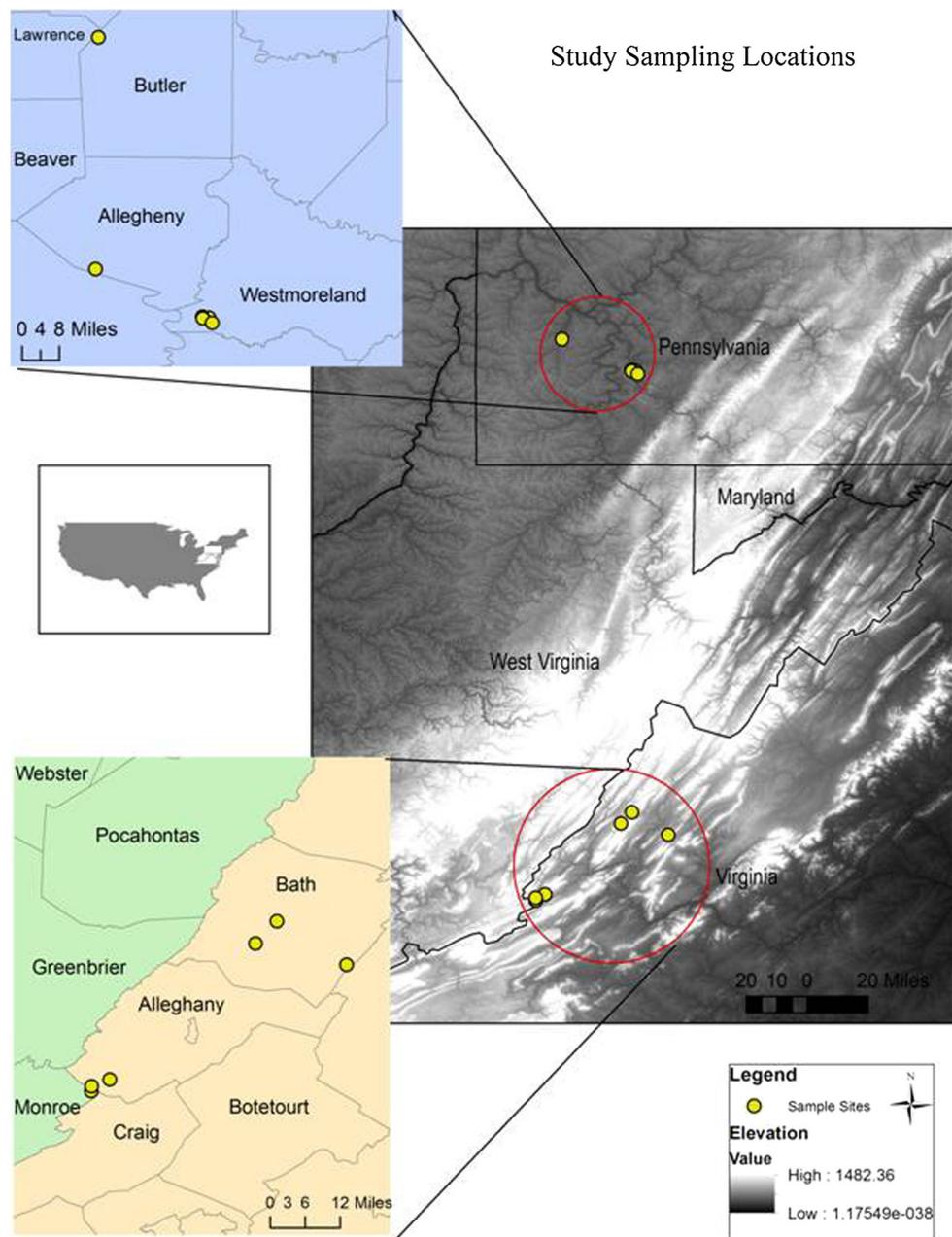
Site name	Site code(s)	Sampling date	Site location	Pertinent geology	Classification
Port royal	PR	6/15/2011	Westmoreland county, PA	Bentwood Ls., Monongahela group	Tufa
Cedar creek	CC02.CC03.CCSS	6/15/2011	Westmoreland county, PA	Bentwood Ls., Monongahela group	Tufa
Smithton	SM01, SM02	6/15/2011	Westmoreland county, PA	Bentwood Ls., Monongahela group	Tufa
Mayview	MV	6/15/2011	Allegheny county, PA	Bentwood Ls., Monongahela group	Tufa
Old sweet spring	OLDSWT	6/28/2011	Monroe county, WY	Middle ordovician undivided	Thermal
Octagon spring	OCTAG	6/29/2011	Bath county, VA	Juniata, Oswego, Martinsburg and Eggleston Formations, Ordovician	Thermal
Magnesia spring	MAGNESA, MAGCOLD	6/29/2011	Bath county, VA	Juniata, Oswego, Martinsburg and Eggleston Formations, Ordovician	Magnesia Cold (Non-thermal) Magnesia (Thermal)
Boiler spring	BOJLER	6/29/2011	Bath county, VA		Thermal
Hot sulfur spring	HOTSULF	6/29/2011	Bath county, VA		Thermal
Jefferson spring	JEFFD	6/29/2011	Bath county, VA		Thermal
Big spring	VABIG	6/29/2011	Bath county, VA	Juniata, Oswego, Martinsburg and Eggleston Formations, Ordovician	Non-thermal
Sweet chalybeate spring	CHAL, CHAL2C, CHAL2 M	6/28/2011	Alleghany county, VA	Beekmantown group/lower ordovician	Thermal
Spellman spring	SPELM	6/28/2011	Alleghany county, VA	Middle ordovician undivided	Non-thermal
Cesspool cave	CESS	6/28/2011	Alleghany county, VA	Middle ordovician undivided	Non-thermal

constituents (i.e., DIC and  $\text{SO}_4^{2-}$ ) to return to the surface resulting in the possibility of deep circulation of meteoric waters (Hobba et al. 1979). These springs are stratigraphically located in Ordovician aged carbonate rocks along the axes of anticlines or on the flanks of anticlines in Silurian–Devonian limestones (Rader and Gathright 1984). The Ordovician age rocks are primarily in the Beekmantown group, which is composed of thick-bedded limestones and dolomite. The Silurian–Devonian system includes the Helderburg group and the Tonoloway and Wills Creek formations, which comprised mainly limestones with chert, sandstone and also shale. The springs in this area are both thermal and non-thermal, ranging in temperatures from 12

to 40 °C. The National Oceanic and Atmospheric Administration (NOAA) defines the cut-off between a non-thermal and thermal spring at 20 °C. In this region, according to the NOAA definition of thermal and non-thermal springs, there are four non-thermal springs including Magnesia Cold, Cesspool cave, Spellman and Big spring and 8 thermal springs which include Octagon, Magnesia, Boiler and Hot Sulfur, Sweet Chalybeate and Old Sweet springs (Table 1).

The springs in Pennsylvania are located in Westmoreland and Allegheny counties (Fig. 1). These springs actively precipitate calcium carbonate deposits, also known as tufa. The formation of these deposits plays an important

**Fig. 1** Map showing location of springs sampled in this study. Note the two zoomed in boxes of the different sampling regions



role in understanding inorganic chemistry, the reactions involved in carbon transformations as well as sources of water. The carbonate rocks in this area are Pennsylvanian in age (~318–299 mya) and are included in the Monongahela and Allegheny groups. The primary limestone unit in this region is the Bentwood formation of the Monongahela group (Table 1). Although the springs in Pennsylvania are all non-thermal springs, they are classified as tufa-depositing springs for ease of clarification in this study.

## Sampling, methods and calculations

### Sampling and methods

Water samples were taken at or near the discharge points for all springs. If the exact discharge point was unidentifiable, samples were taken as close to the source as possible. Samples were collected after field parameter measurements (i.e., temperature and pH) were obtained with a YSI-556MP meter. Samples were collected for  $\delta^2\text{H}_{\text{H}_2\text{O}}$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  analysis at each sampling site. Random duplicate samples of water were also taken for quality control checks. Samples for  $\delta^2\text{H}_{\text{H}_2\text{O}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  were collected by filling an 8-mL glass-threaded vial with no headspace. Parafilm was used to seal caps and samples were refrigerated at ~4 °C until analysis. Samples collected for  $\delta^{13}\text{C}_{\text{DIC}}$  were filtered using a 60-mL Luer-Lok syringe fitted with a Cameo 0.45  $\mu\text{m}$  nylon pre-filter into a 10-mL glass Wheaton serum vial with no headspace. About two drops of benzalkonium chloride (17 % w/w) was added to the water in the vial to halt bacterial activity. Vials were sealed with a Teflon/Butyl septum and aluminum caps using a crimper. Samples for  $\delta^2\text{H}_{\text{H}_2\text{O}}$ ,  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  were analyzed on a GasBench II device coupled to a Finnigan Delta V Advantage mass spectrometer at the West Virginia University Stable Isotope Laboratory. Dissolved sulfate samples were collected in a 1-L polyethylene bottle with no headspace. Each sample was then filtered through a 0.45- $\mu\text{m}$  PCM filter with the aid of a vacuum pump. The 1-L aqueous sulfate samples were subsequently precipitated as  $\text{BaSO}_4$  powder following USGS RSIL lab Code 1951 (Révész and Qi 2006). The  $\text{BaSO}_4$  solid precipitate was sent to University of Arizona's Environmental Stable Isotope Facility for analysis of  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  on an Elemental Analyzer coupled to a Finnigan Delta Plus mass spectrometer. The reproducibility and accuracy were monitored by duplicate analysis of samples and internal lab standards, previously calibrated to international standards, and were better than 0.2 ‰ for  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$ , 0.4 ‰ for

$\delta^{18}\text{O}$  and 1.0 ‰ for  $\delta^2\text{H}$ . All isotope values are reported in per mil (‰) relative to international standards, i.e.,  $\delta^{13}\text{C}_{\text{DIC}}$  relative to VPDB (Vienna Pee Dee Belemnite),  $\delta^{34}\text{S}$  relative to VCDT (Vienna Cañon Diablo meteorite) and  $\delta^{18}\text{O}/\delta^2\text{H}$  relative to VSMOW (Vienna Standard Mean Ocean Water).

Water samples for major cations and anions were collected as a collaborative effort with (Moore 2012). Water was filtered in the field through a 0.45- $\mu\text{m}$  filter using a 60-mL Luer-Lok syringe. Cation samples were collected in a 125-mL HDPE bottle and preserved with 1 mL  $\text{HNO}_3$ . Anion samples were collected in a 60-mL HDPE bottle. All samples were kept on ice or refrigerated to minimize bacterial growth. Samples were analyzed at the US Department of Energy (DOE) National Energy and Technology Laboratory (NETL) located in Pittsburgh, PA. Inductively coupled plasma-optical emissions spectroscopy (ICP-OES) was used for analysis of major cations on a Perkin Elmer Optima 3000 Radial View spectrometer using US EPA method 200.7. Ion Chromatography (IC) on a Dionex ion chromatography system was used for analysis of major anions. Field titrations were done at the spring sites using the Gran Titration technique, titrating to pH 4.2 and 3.9 using 1.6 N  $\text{H}_2\text{SO}_4$ . Bicarbonate ( $\text{HCO}_3^-$ ) concentrations were subsequently calculated (Moore 2012).

### Calculations

The carbon cycle begins with the formation of carbonic acid in the atmosphere which then enters the soil zone. The cycle continues with dissolution of soil  $\text{CO}_2$  in water until equilibrium is reached. Further evolution of C can be traced in the aqueous carbonate system where carbonic acid ( $\text{H}_2\text{CO}_3$ ) dissociates to bicarbonate ( $\text{HCO}_3^-$ ) which can then further dissociate into carbonate ( $\text{CO}_3^{2-}$ ). These reactions and the relative proportions of all carbonate species are pH dependent and can be calculated for specific systems (Karim and Veizer 2000). The total concentration of DIC for each sample was calculated from the addition of the concentrations of carbonate, bicarbonate and carbonic acid species. Bicarbonate concentration was derived from the alkalinity titration of each sample and  $\text{H}^+$  concentrations were derived from pH measurements. The concentration of the carbonate and carbonic acid was calculated using the following equations:

$$[\text{H}_2\text{CO}_3] = [\text{H}^+][\text{HCO}_3^-]/K_1 \quad (1)$$

$$[\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-]/[\text{H}^+] \quad (2)$$

The constants  $K_1$  and  $K_2$  are temperature-dependent constants that were derived using the Van't Hoff equation and measured temperatures from the field [Drever 1997]:

$$\ln K_{T_2} = \ln K_{T_1} + \left( \frac{\Delta H_R^\circ}{2.303 R} \right) \left[ \left( \frac{1}{T_1} \right) + \left( \frac{1}{T_2} \right) \right] \quad (3)$$

where  $K_{T_1}$  is the constant at 25 °C (i.e., the reference temperature),  $K_{T_2}$  the constant of interest at the specified temperature,  $\Delta H_R^\circ$  the standard enthalpy of the reaction in kJ/mol (i.e., tabulated value from Drever 1997) and  $T_1$  and  $T_2$  are temperatures in kelvin at 25 °C and the measured temperature, respectively. All data can be found in Table 2.

## Results and discussion

### Hydrogen and oxygen isotopic composition of water

Samples for hydrogen and oxygen isotope analyses were collected from each sample location to understand the sources of water discharging from the springs. The values for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  in tufa springs from Pennsylvania range from  $-8.4$  to  $-8.7$  ‰ and from  $-55.1$  to  $-57.4$  ‰ VSMOW, respectively (Table 2). The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  values of waters collected from thermal and non-thermal springs in southern West Virginia and Virginia range from  $-7.8$  to  $-8.7$  ‰ and from  $-50.0$  to  $-54.4$  ‰ VSMOW, respectively (Table 2). Precisions for the measured values were  $\pm 0.06$  ‰ for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\pm 1$  ‰ for  $\delta^2\text{H}_{\text{H}_2\text{O}}$ . All

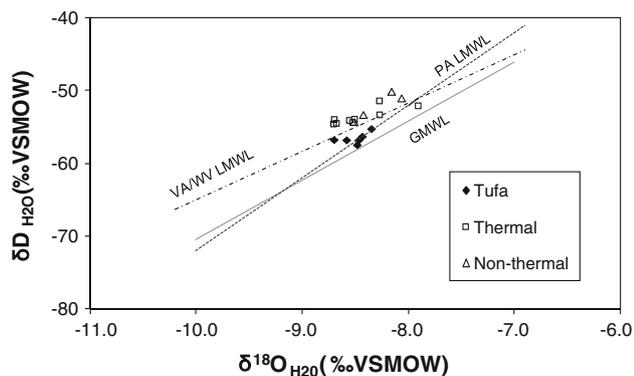
values measured for  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  for this study were plotted relative to the global meteoric water line (GMWL) and local meteoric water lines (LMWL) for the specific region (Fig. 2). A regression line representing the LMWL was constructed using the latitude, longitude and altitude of the sampling sites to calculate the expected  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  values of precipitation in the study region (Bowen 2012). The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  of waters from the tufa springs in Pennsylvania is slightly more depleted compared to the thermal and non-thermal springs in southern West Virginia/Virginia. The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$  values lie within the range of isotopic variation in precipitation to be expected based on the difference in latitude between the southern West Virginia/Virginia sites and the northern Pennsylvania sites.

The O and H isotopic composition of waters in different geological formations will primarily be dependent on the sources of recharge and the water–rock interactions. In low-temperature systems, isotopic exchange with dissolved gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ) and hydration with silicates; and in high-temperature systems isotopic exchange with carbonate and silicate minerals can shift the O and H isotopic signatures of waters away from the LMWL (e.g., Kharaka and Berry 1973; Witttrup et al. 1987; Rostron and Holmden 2000; Kharaka and Mariner 2005; Blasch and Bryson 2007; Mutlu 2007; Qin et al. 2005; Kumar et al. 2011). The isotopic values of

**Table 2** Stable isotope values and a few pertinent geochemical parameters for each sampled location in this study

Site code	Temp. (C)	$\delta\text{D}$	$\delta^{18}\text{O}$ (water)	$\delta^{13}\text{C}$ (DIC)	$\delta^{34}\text{S}$ ( $\text{SO}_4^{2-}$ )	$\delta^{18}\text{O}$ ( $\text{SO}_4^{2-}$ )	Alk (mg/L $\text{HCO}_3$ )	DIC mmol/L	Ca (mg/L)	$\text{SO}_4$ (mg/L)
CC02	15.2	-56.7	-8.6	-8.5	3.1	3.7	268.5	4.5	62.7	58.4
CCT03	13.5	-56.7	-8.5	-16.2	*	*	555.4	9.5	87.2	85.0
CCSS	13.9	-55.1	-8.4	-8.0	*	*	353.2	6.0	63.4	103.0
SM01	15.2	-57.4	-8.5	-10.1	0.3	3.5	378.7	6.3	32.0	59.0
SM02	16.4	*	*	-10.7	*	*	330.6	5.5	35.7	35.0
PRT	12.1	-56.2	-8.4	-12.4	0.2	1.1	401.3	7.7	93.6	95.0
MV	11.3	-56.7	-8.7	-11.5	3.4	2.7	430.3	7.3	60.1	117.0
BOILER	40.1	-54.4	-8.7	-3.2	37.6	14.8	436.2	13.5	119.0	126.8
CESSPE	13	-50.9	-8.1	-13.0	25.8	8.3	468.5	9.0	149.4	114.8
CHAL2C	18.95	-53.8	-8.5	-3.8	40.2	14.5	627.1	25.3	250.5	417.9
CHAL2M	21.06	-53.9	-8.6	-3.2	40.4	14.7	637.5	23.4	271.1	434.9
CHAL	23.19	-54.2	-8.5	-2.4	40.4	15.1	731.4	23.2	284.0	426.6
HOTSULF	35.9	-53.8	-8.7	-3.3	37.8	14.2	399.6	8.1	118.5	131.1
JEFFD	35.4	-51.3	-8.3	-5.8	39.3	15.0	200.7	4.3	97.4	225.5
MAGCOLD	12.25	-50.0	-8.2	-13.8	19.9	8.9	153.7	3.6	48.0	13.5
MAGNESIA	30.98	-51.9	-7.9	-3.1	36.3	14.3	433.7	9.3	119.6	129.2
OCTAG	36.72	-54.3	-8.7	-3.0	37.9	14.1	172.0	3.4	124.5	127.6
OLDSWT	22.65	-53.2	-8.3	-2.4	40.2	15.3	784.5	14.5	295.1	395.1
SPELM	12.51	-54.2	-8.5	-10.2	30.2	11.8	270.2	5.2	58.2	20.3
VABIG	13.2	-53.2	-8.4	-11.7	*	*	111.0	2.0	29.1	5.9

All geochemical data were collected as part of collaborative research effort (Moore 2012)



**Fig. 2** The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of samples plotted with the global meteoric water line (GMWL) and the calculated local meteoric water lines (LMWL). Samples for all the springs cluster around the local precipitation lines

the natural springs cluster around the LMWL, providing evidence that meteoric water is the primary source of recharge in the study sites. The deuterium values are not significantly altered by water–rock exchange reactions because most rocks have very little hydrogen in their structures. The  $\delta^{18}\text{O}$  signature of water from the thermal springs does not show the characteristic enrichment of  $^{18}\text{O}$  with respect to the isotopic composition of the local meteoric water. This oxygen isotope shift is considered a characteristic of waters in which the oxygen in water exchanges with oxygen in silicate and/or carbonate minerals in the rock matrix at higher temperatures (Kharaka and Mariner 2005). As meteoric water infiltrates through the ground into the geothermal reservoir, the water is in isotopic disequilibrium with the surrounding rock matrix and the isotopic exchange is controlled by the temperature (Geyh 2001). This indicates that the waters collected from warm springs have not undergone high-temperature isotope exchange with the minerals in the formations through which they circulated. This could be due to the fact that (1) the temperatures in the geological formations through which these waters circulated were not high enough, i.e.,  $>100\text{ }^\circ\text{C}$ , to cause significant  $^{18}\text{O}$  exchange, or (2) the residence time of water in host aquifer was very short, or (3) the water to rock ratios were very high.

This also confirms that waters discharging at these locations have the same meteoric source; hence transformations in carbon isotopic signatures (discussed below) can be attributed to variations in water–rock interactions and/or biogeochemical transformations, not due to variations in sources of water.

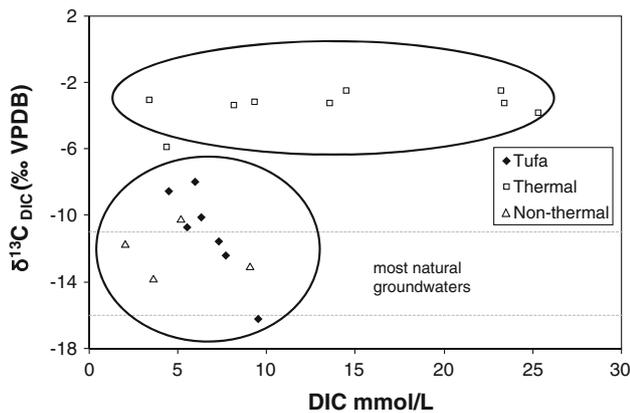
### Carbon isotopic composition of DIC

The  $\delta^{13}\text{C}$  signatures of DIC for all natural spring samples in this study range from  $-2.4$  to  $-16.2\text{ }‰$  VPDB.

Precision for the measured values was  $\pm 0.05\text{ }‰$  for  $\delta^{13}\text{C}_{\text{DIC}}$ . Values for the thermal springs ranged from  $-2.43$  to  $-5.82\text{ }‰$ , while values for the non-thermal springs and tufa springs range from  $-7.95$  to  $-16.21\text{ }‰$  (Table 2).

The  $^{13}\text{C}/^{12}\text{C}$  isotope ratios can be used to trace the evolution of DIC and sources of carbon in water. In most natural waters, the primary sources of DIC are  $\text{CO}_2$  derived from decaying organic matter ( $\delta^{13}\text{C} \approx -26\text{ }‰$ ) and carbonate rock dissolution ( $\delta^{13}\text{C} \approx +1\text{ }‰$ ) (Mook and Tan 1991). Most natural groundwaters which receive equal contribution from both end-members will have  $\delta^{13}\text{C}_{\text{DIC}}$  signatures ranging between  $-11$  and  $-16\text{ }‰$ . Spring samples in this study have values ranging from  $-2.4$  to  $-16.2\text{ }‰$  VPDB, with only 5 % of these samples falling within the range for natural waters (Fig. 3). Deviation from the natural range indicates a greater contribution from either end-member. A majority of the samples are more enriched in  $^{13}\text{C}$  relative to the normal groundwater range, indicating a greater contribution from carbonate carbon. The  $\delta^{13}\text{C}$  of the measured carbonate units in the study areas ranged from  $-5.0$  to  $-5.6\text{ }‰$  for the springs in West Virginia and Virginia and from  $-1.7$  to  $-2.7\text{ }‰$  for the spring sites in Pennsylvania. Most Pennsylvania springs fall close to the range of normal groundwaters, with few samples slightly enriched in  $^{13}\text{C}$ . Of 12 of the springs in WV and VA, only 3 are in or near the range of most natural groundwaters. These springs include Spellman Spring, Big Spring and Cold Magnesia, which are all non-thermal springs with temperatures  $<13.2\text{ }^\circ\text{C}$  (Fig. 3; Table 2). A majority of the springs in this region are enriched in  $^{13}\text{C}$  relative to natural groundwaters and their carbonate end-member, assuming that these waters are in contact and reacting with these formations somewhere along their flow paths. However, other contributing carbon sources (i.e., different carbonate units) and/or kinetically controlled fractionation processes may be occurring in these spring sites.

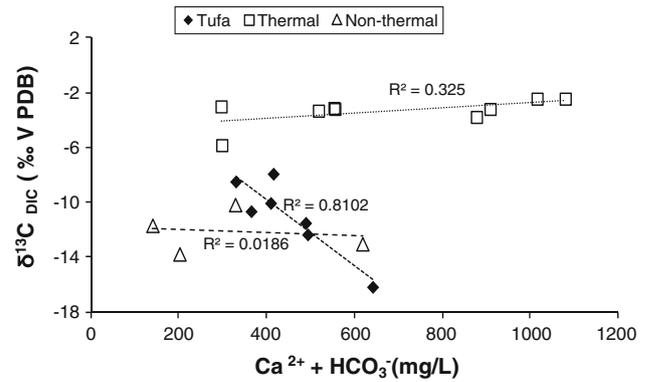
One possible explanation of this  $^{13}\text{C}$  enrichment in the spring waters is the isotope fractionation due to  $\text{CO}_2$  outgassing. The  $\text{CO}_2$  will diffuse out of the waters when concentrations in water are higher than atmospheric concentrations. The isotopically lightest species of the total DIC is  $\text{CO}_2$ , thus outgassing of  $\text{CO}_2$  to the atmosphere results in a shift in the remaining DIC to more enriched values (Doctor et al. 2008; Atekwana and Fonyuy 2009; Sharma et al. 2013). Many of the springs in WV and VA have  $P_{\text{CO}_2}$  values higher than that of atmospheric, thus outgassing will occur (Moore 2012). In many of the PA springs, the exact discharge location could not be found; hence it is very likely that the waters have been exposed to the atmosphere before sample collection. In addition, the springs in PA are all associated with tufa formations which



**Fig. 3**  $\delta^{13}\text{C}_{\text{DIC}}$  of spring samples versus DIC concentrations calculated in mmol/L. The dashed lines indicate the range of most natural groundwaters. Approximately 70 % of the samples are more enriched in  $^{13}\text{C}$  relative to expected range for natural groundwaters. This indicates that higher contribution from carbonate carbon and/or outgassing of isotopically depleted  $\text{CO}_2$  is dominant in these waters

are formed by the outgassing of  $\text{CO}_2$ -rich groundwater (Hendy 1971; Pentecost 2005). Therefore, the enrichment in  $^{13}\text{C}$  in all the springs is likely a combination of a greater input from carbonate carbon and  $\text{CO}_2$  outgassing. Similar results have been shown by several researchers (Sharma et al. 2013; Doctor et al. 2008; Andrews 2006).

Typically, increased  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations support the processes of carbonate dissolution which adds heavier carbon ( $^{13}\text{C}$ ) to the total DIC. The  $\text{Ca}^{2+}$  concentrations in all the springs range from 29.1 to 295.1 mg/L and the bicarbonate concentrations range from 111 to 784 mg/L (Table 2). If dissolution of carbonates is the main source of carbon to the system, it should be accompanied by an increase in  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations and a shift to more positive values of  $\delta^{13}\text{C}_{\text{DIC}}$ . These trends are shown in Fig. 4 where the thermal springs show a positive correlation, supporting that carbonate dissolution might be contributing to the more positive values of  $\delta^{13}\text{C}_{\text{DIC}}$ . On the other hand, non-thermal and tufa-depositing springs show no or a negative correlation (i.e., enriched  $\delta^{13}\text{C}_{\text{DIC}}$  values are accompanied by lower  $\text{Ca}^{2+} + \text{HCO}_3^-$  concentration), respectively. This indicates that other kinetic fractionation effects like outgassing of isotopically light  $\text{CO}_2$  species may have more of an effect on  $\delta^{13}\text{C}_{\text{DIC}}$  in these systems rather than purely carbonate dissolution. Variations in  $\delta^{13}\text{C}_{\text{DIC}}$  among different springs could be a result of any of the processes discussed above, or a combination of processes. However, it is important to note that we have not considered how other sources of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  to the system and/or processes like ion exchange could affect their concentrations.



**Fig. 4** Relationship of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations to  $\delta^{13}\text{C}_{\text{DIC}}$  in springs. Note the positive correlation in thermal springs as evidence of carbonate dissolution

### Sulfur and oxygen isotopic composition of dissolved sulfate

The  $\delta^{34}\text{S}_{\text{SO}_4}$  of the springs show a wide range from 0.2 to 40.4 ‰ VCDT and the  $\delta^{18}\text{O}_{\text{SO}_4}$  values range from 1.1 to 15.3 ‰ VSMOW (Table 2). Tufa springs ranged specifically from 0.2 to 3.4 ‰ VCDT for  $\delta^{34}\text{S}_{\text{SO}_4}$  and from 1.1 to 3.7 ‰ VCDT for  $\delta^{18}\text{O}_{\text{SO}_4}$  values. The thermal springs and non-thermal springs in WV/VA area were significantly different, with the thermal springs ranging from 37.6 to 40.4 ‰ VCDT for  $\delta^{34}\text{S}_{\text{SO}_4}$  and from 14.1 to 15.3 ‰ VCDT for  $\delta^{18}\text{O}_{\text{SO}_4}$  and the non-thermal springs ranging from 19.9 to 30.2 ‰ VCDT and 8.3 to 11.8 ‰ VCDT for  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ , respectively. Sulfate concentrations for the springs cover a large range from 5.9 to 434.9 mg/L (Table 2).

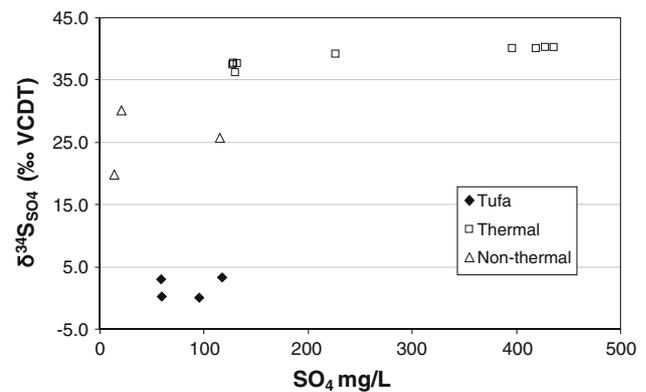
Sulfate isotopes are useful indicators of sources of sulfate to discharging waters and various biogeochemical processes that affect the carbon isotopes of DIC. The S isotope composition usually characterizes the sources, thus enabling the use of S isotopes as fingerprints. Potential sources include (1) dissolution of sulfate minerals (i.e., gypsum/anhydrite) which have  $\delta^{34}\text{S}$  values representative of the time of deposition, usually enriched values ranging from 10 to 30 ‰ (Claypool et al. 1980); (2) sedimentary sulfides (i.e., pyrite) which typically have more negative values but can range from 10 to  $-50$  ‰ (Karim and Veizer 2000); (3) atmospheric deposition of sea spray which has S isotope values similar to modern sea water (+21 ‰) (Geyh 2001); and (4) atmospheric deposition of anthropogenic sources of sulfate which can range from 4 to 6 ‰, depending on local sources (Karim and Veizer 2000).

The isotopic composition of oxygen in sulfate is more complicated, as oxygen both in the atmosphere and water can contribute to  $\delta^{18}\text{O}_{\text{SO}_4}$ . Once formed, the rate of oxygen

isotope exchange between  $\text{SO}_4^{2-}$  and environmental waters is extremely slow (Karim and Veizer 2000; Geyh 2001; Clark and Fritz 1997; Seal 2003). In addition, differences in  $\delta^{18}\text{O}_{\text{SO}_4}$  of sources allows for implications in tracer studies. For example, the  $\delta^{18}\text{O}$  of atmospheric oxygen is  $\sim 23.5\text{‰}$  (Krouse and Mayer 2000), surface/groundwater  $\delta^{18}\text{O}$  depends on the geographic location, but is mostly negative, and seawater which varies but is presently around  $9.5\text{‰}$  (Karim and Veizer 2000; Claypool et al. 1980). Oxygen isotopes in sulfate therefore offer insight into the mechanism of sulfate formation and its origin. Biological processes can also have an effect on the O isotope composition since these processes can fractionate both the sulfur and oxygen isotopes; thus, both have been used in combination in several studies to identify the occurrence of biological processes (Sharma et al. 2013; Clark and Fritz 1997; Gammons et al. 2010; Krouse and Mayer 2000; Van Donkelaar et al. 1995).

The sulfate concentrations and S isotopic composition of  $\text{SO}_4^{2-}$  for all sampling sites are shown in Fig. 5. With the exception of one spring in Virginia (cold Magnesia Spring), the samples for the thermal and non-thermal springs in WV/VA cluster around  $+30$  to  $+40\text{‰}$ , while the tufa-depositing springs in PA sites are more depleted in  $^{34}\text{S}$  and are concentrated around  $0$  to  $+9\text{‰}$ . The fact that the  $\delta^{34}\text{S}_{\text{SO}_4}$  values of the springs in WV/VA vary within a narrow range and the springs in PA vary within a narrow range, both independent of sulfate concentrations, indicates that the waters have different sources of dissolved sulfate. There is no sulfur isotopic fractionation during dissolution hence the  $\delta^{34}\text{S}$  values likely corresponds to the sulfur isotopic composition of the formation rocks with which these waters are interacting (Krouse and Mayer 2000).

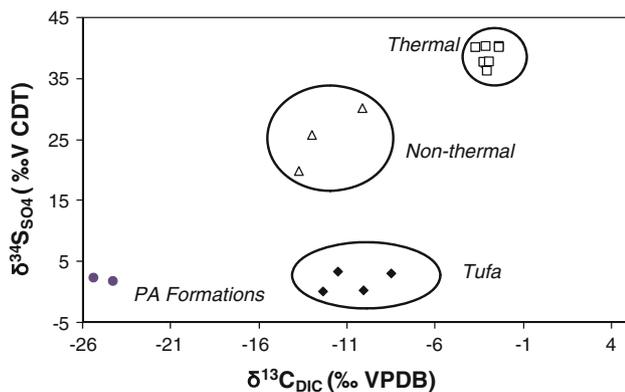
The tufa springs in PA likely derive their  $\text{SO}_4^{2-}$  from oxidation of reduced sedimentary sulfides (i.e., pyrite in shales and coals). In the Pennsylvania spring region, coals and shales containing pyrite are in abundance. The measured  $\delta^{34}\text{S}_{\text{SO}_4}$  values of pyrite in coal and shale in the region ranged from  $+0.6$  to  $+2.4\text{‰}$  VCDT (Fig. 6). The sampled springs in this region fall very close to or within this range ( $0.2$ – $3.4\text{‰}$ ) indicating that the dissolved sulfate originated from the oxidation of pyrite in this area. The  $\delta^{34}\text{S}$  values of samples collected from thermal and non-thermal springs in the WV/VA range from  $35$  to  $40\text{‰}$  and  $20$  to  $30\text{‰}$  VCDT, respectively. The source of sulfate in these waters is most likely from dissolution of evaporite minerals in the rock matrix (i.e., gypsum) (Moore 2012). The  $\delta^{34}\text{S}_{\text{SO}_4}$  values are slightly enriched in  $^{34}\text{S}$  compared to the evaporite sulfate source. High concentrations of dissolved sulfate are evident in all but three springs in this region (Table 2). The springs which have low concentrations of sulfate include Big Spring, Magnesia Cold and



**Fig. 5**  $\delta^{34}\text{S}_{\text{SO}_4}$  values of springs plotted versus sulfate concentrations. The  $\delta^{34}\text{S}_{\text{SO}_4}$  values of waters collected from thermal springs are much enriched compared to the waters from non-thermal and tufa-depositing springs

Spellman, which are all non-thermal springs with temperatures  $<20\text{°C}$ . Evaporite sulfates are the most soluble and thus most readily available form of sedimentary sulfur compounds (Krouse and Mayer 2000). Claypool et al. 1980 described the isotopic composition of sulfate in marine evaporates deposited throughout the Earth's history. Variations in  $\delta^{34}\text{S}_{\text{SO}_4}$  values ranged from  $+10\text{‰}$  to a maximum of  $+35\text{‰}$  in the Cambrian era. The  $\delta^{34}\text{S}_{\text{SO}_4}$  values for Silurian–Devonian and Ordovician aged evaporates (the age of the rocks in this study area) are in the range of  $+25$  to  $+30\text{‰}$  (Claypool et al. 1980; Krouse and Mayer 2000). The  $\delta^{34}\text{S}_{\text{SO}_4}$  values for the thermal springs are slightly more enriched in  $^{34}\text{S}$  than the expected values, therefore suggesting that additional processes may occur to cause this enrichment. Bacterial sulfate reduction is one process which may take place to a certain extent in some of these springs to enrich S values beyond the isotopic composition of the source.

The  $\delta^{18}\text{O}_{\text{SO}_4}$  signatures were also used as an additional proxy to understand the sources of sulfate. The springs in PA have  $\delta^{18}\text{O}_{\text{SO}_4}$  values ranging from  $1.1$  to  $5.1\text{‰}$  which fall within the boundary of sulfate originating from oxidation of inorganic sulfur compounds (i.e., pyrite) (Krouse and Mayer 2000). In contrast, the springs in WV and VA have  $\delta^{18}\text{O}_{\text{SO}_4}$  values more enriched in  $^{18}\text{O}$  in the range of  $8.9$  to  $15.3\text{‰}$  (Table 2). In accordance with the reconstructed oxygen age curve by Claypool et al. (1980),  $\delta^{18}\text{O}_{\text{SO}_4}$  values during the Ordovician and Silurian–Devonian eras (age of rocks in this region) ranged from  $\sim 12$  to  $17\text{‰}$ . Various other factors such as oxidation of intermediate sulfoxy anions and biological sulfate reduction can also affect the  $\delta^{18}\text{O}_{\text{SO}_4}$ , but is beyond the scope of this study.



**Fig. 6**  $\delta^{34}\text{S}_{\text{SO}_4}$  versus  $\delta^{13}\text{C}_{\text{DIC}}$  for all samples. Pennsylvania rock formations (Little Pittsburgh Coal and Pittsburgh Shale) were plotted to show sources of sulfate

## Summary

A multi-isotope approach was used in this study to trace sources of water, carbon and sulfur in different natural spring settings of the Central Appalachian region. In conjunction with stable isotopes of water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and  $\delta^2\text{H}_{\text{H}_2\text{O}}$ ), DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and  $\text{SO}_4^{2-}$  ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ), major ion chemistry and field parameters were also measured by our collaborators to understand various processes occurring in each system. The preliminary isotope data indicate that isotope compositions differ in natural springs due to variations in recharge sources, water–rock interactions and biogeochemical reactions. These variations impart a unique isotope signature to water, DIC and dissolved sulfate at these sampling sites.

The natural springs appear to be receiving recharge from modern precipitation as O and H isotopic compositions of waters discharging on the surface were similar to that of local precipitation. Carbon isotopes of DIC showed a wide range of values and were found to deviate from expected values of natural groundwaters at several sampling locations. Values enriched in  $^{13}\text{C}$  in natural springs indicate greater contributions from old carbon released by dissolution of carbonates and carbon lost via  $\text{CO}_2$  outgassing. The direct correlation of higher calcium and bicarbonate concentrations with enriched  $\delta^{13}\text{C}_{\text{DIC}}$  values supports enhanced carbonate dissolution in the thermal springs. On the other hand, inverse correlation of enriched  $\delta^{13}\text{C}_{\text{DIC}}$  with calcium and bicarbonate concentrations in tufa-depositing springs indicates that isotope fractionation associated with outgassing of isotopically lighter aqueous  $\text{CO}_2$  species is playing a prominent role in  $^{13}\text{C}$  enrichment of waters in these systems. Sulfur and oxygen isotopes of dissolved sulfate in natural springs were used to examine sources of sulfate and biogeochemical processes. The  $\delta^{34}\text{S}_{\text{SO}_4}$  and

$\delta^{18}\text{O}_{\text{SO}_4}$  signatures support that dissolved sulfate most likely originated from the oxidation of pyrite in tufa springs and dissolution of Silurian–Devonian and Ordovician aged evaporates in thermal and non-thermal springs. The S and O isotope values of dissolved sulfate were enriched compared to the source rock in the thermal springs indicating that waters might have undergone bacterially mediated sulfate reduction. Since all the springs are recharged by modern precipitation, the dissolved carbon and sulfate isotope variations at these sites can be linked to water–rock interaction and biogeochemical processes occurring along their flow paths. The interpretations and conclusions for these natural springs were based on the limited data collected for this preliminary study. The structural history and hydrology of these spring sites are extremely diverse and complex and was beyond the scope of this study. Our study provides a foundation for delineating sources of water and investigating the possible carbon and sulfur transformations taking place in different natural spring sites in this area. Future research is needed to explore how hydrological connections control the spatial and temporal isotopic and geochemical trends at these sites.

**Acknowledgments** This research was performed as part of the collaborative initiative of National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), under the RES contract DE-FE0004000. J. Moore is acknowledged for help in sampling and sharing some of his thesis geochemical data. The isotopic data presented in the paper is part of bigger ongoing collaborative project with Drs. D. Vesper, H. Edenborn, A. Hartsock, R. Capo and B. Stewart. The study design and sampling were made possible by their prior knowledge of these sites. We thank two anonymous reviewers for their comments and suggestions.

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