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Arsenic and other oxyanion-forming trace elements in an alluvial basin aquifer: Evaluating sources and mobilization by isotopic tracers (Sr, B, S, O, H, Ra)

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ABSTRACT

The Willcox Basin is a hydrologically closed basin in semi-arid southeastern Arizona (USA) and, like many other alluvial basins in the southwestern USA, is characterized by oxic, near-neutral to slightly basic groundwater containing naturally elevated levels of oxyanion-forming trace elements such as As. This study evaluates the sources and mobilization of these oxyanionic trace elements of health significance by using several isotopic tracers of water-rock interaction and groundwater sources (87 Sr(86 Sr, 34 S_{SO4}, δ^{11} B, δ^{2} H, δ^{18} O, 3 H). Values of δ^{2} H (-85% to -64%) and δ^{18} O (-11.8% to -8.6%) are consistent with precipitation and groundwater in adjacent alluvial basins, and low to non-detectable ³H activities further imply that modern recharge is slow in this semi-arid environment. Large variations in ⁸⁷Sr/⁸⁶Sr ratios imply that groundwater has interacted with multiple sediment sources that constitute the basin-fill aquifer, including Tertiary felsic volcanic rocks, Paleozoic sedimentary rocks, and Proterozoic crystalline rocks. In general, low concentrations of oxyanion-forming trace elements and F⁻ are associated with a group of waters exhibiting highly radiogenic values of ⁸⁷Sr/⁸⁶Sr (0.72064-0.73336) consistent with waters in Proterozoic crystalline rocks in the mountain blocks (0.73247-0.75010). Generally higher As concentrations $(2-29 \ \mu g \ L^{-1})$, other oxyanion-forming trace element concentrations (B, V, Cr, Se, Mo, Sb), and F⁻ concentrations are associated with a group of waters exhibiting lower ⁸⁷Sr/⁸⁶Sr ratios (0.71012-0.71503), suggesting that sediments derived from Tertiary felsic volcanic rocks are a significant source of these trace elements in groundwater. $\delta^{34}S_{SO4}(2.0-13.4\%)$ and $\delta^{11}B(-6.7\%$ to 18.2%) variations suggest that rain-derived B and SO_4^{2-} plus marine gypsum derived from Paleozoic sedimentary rocks and B derived from felsic volcanic rocks explain the observed values. In addition to the sources of these elemental and isotopic signatures, down-gradient hydrogeochemical modification associated with silicate weathering and perhaps cation exchange are recorded by the decreasing Ca/Na ratio. Very low levels of ²²⁶Ra in groundwater relative to U throughout the basin-fill aquifer are consistent with the oxic, neutral to high-pH conditions in which mobility of U is strongly favored relative to Ra. Used in combination, multiple isotopic and geochemical tracers can provide valuable information for understanding the relative importance of sediment source and hydrogeochemical processes for observed levels of As and other naturally-occurring trace elements. These tracers, in particular ⁸⁷Sr/⁸⁶Sr with its sensitivity to aquifer sediment source, can be applied to other alluvial basin-fill aquifers in the southwestern USA where multiple sediment types contribute varying amounts of As and other oxyanion-forming trace elements to groundwater.

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1. Introduction

Occurrence of oxyanion-forming trace elements, primarily As, imposes limitations on the use of groundwater from alluvial basin aquifers in the semi-arid western USA (Robertson, 1989; Welch et al., 2000; Smedley and Kinniburgh, 2002). Population growth, degradation of existing water resources, and the 2001 reduction of the US Environmental Protection Agency (EPA) maximum contaminant level (MCL) for As to 10 μ g L⁻¹ have emphasized the need to provide sustainable sources of high-quality drinking water for the region. Other related elements may co-occur with As and form oxyanions that are mobile under similar conditions, including B, Cr, V, Mo, Se and Sb. Numerous published studies have implicated both lithologic and geochemical controls on these elements. Volcanic rocks, especially felsic rocks, and clastic sediments derived from volcanic rocks, contain leachable As-bearing phases that yield significantly higher As to groundwater than other sediment sources (Welch et al., 2000; Smedley and Kinniburgh, 2002). In addition, the desorption of oxyanion-forming trace elements from mineral surfaces such as Fe oxides is enhanced by the oxic and



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near-neutral to slightly basic (pH ~ 6.5–9.5) conditions in alluvial basin-fill aquifers (Robertson, 1989; Smedley and Kinniburgh, 2002). Under these conditions, oxyanion-forming trace elements mainly occur as soluble species including HASO₄²⁻, H₂AsO₄⁻, MOO₄²⁻, CrO₄²⁻, SeO₄²⁻, VO₃OH²⁻, VO₂(OH)²⁻ and Sb(OH)₆⁻ (Baes and Mesmer, 1976; Fujii and Swain, 1995; Amrhein et al., 1998).

This study focuses on groundwater in Willcox Basin, a hydrologically closed alluvial basin in semi-arid southeastern Arizona (Fig. 1). The groundwater in this basin is characterized by concentrations of As commonly exceeding 10 μ g L⁻¹ (Towne and Freark, 2001), which is typical for basins of the region (Robertson, 1989; Coes et al., 2002). Because the observed As concentration in groundwater is a function of lithologic source, weathering and adsorption/desorption, the purpose of this study is to apply several isotopic tracers, including Sr, B, S and Ra isotopes, in order to evaluate (1) the variations in sediment source that affect oxyanionforming natural trace element abundances in groundwater in Willcox Basin and (2) the mechanisms that control their mobilization from the aquifer lithology.

Because only one naturally-occurring isotope of As exists, and because O isotopes of arsenate and arsenite ions are subject to rapid exchange reactions with water limiting their use as process tracers (Larese-Casanova and Blake, 2010), tracing of As sources and mobilization need to be obtained indirectly using other isotopic proxies. The ratio of radiogenic to non-radiogenic Sr (⁸⁷Sr/⁸⁶Sr) is a sensitive indicator of sediment sources and weathering in groundwater systems (Franklyn et al., 1991; Bullen et al., 1996;

Harrington and Herczeg, 2003). It is hypothesized that Sr would not directly relate to geochemical processes controlling oxyanions, but rather would indicate the origin of sediments (Sr sources) within alluvial basins. Due to the presence of Proterozoic granitic rocks containing K-feldpar adjacent to the Willcox Basin, it is inferred that highly radiogenic Sr would be present in sediments derived from these older materials, whereas the Tertiary felsic volcanic rocks would be characterized by non-radiogenic Sr isotope composition. The potential application of S isotopes is because some of the SO_4^{2-} in the system is hypothesized to be derived from oxidation of volcanic sulfide, which is also a possible As source (e.g. Smedley et al., 2002). In addition, S isotopes can diagnose the presence of SO₄ reduction, which could influence oxyanion-forming trace element mobility by converting them to reduced forms. The B isotope ratio is another tracer that could indicate the origin of oxvanion-forming elements and/or chemical controls on these elements. For example, B could possibly be used as an analog for As because high-As groundwater may also exhibit elevated B concentrations (e.g. Fujii and Swain, 1995; Scanlon et al., 2009) and the two stable isotopes of B are sensitive to B sources and mobilization (Vengosh and Spivack, 1999). A major difference between B and As(V) is that the dominant B species at neutral pH is the uncharged $B(OH)_3$, whereas the dominant As(V) species are the charged $H_2AsO_4^-$ (below pH ~ 6.5) and $HAsO_4^{2-}$ (above pH ~ 6.5; Smedley and Kinniburgh, 2002). Radium and U isotope occurrence may supply additional understanding of oxyanionic trace elements because U is a mobile anion in oxic conditions, primarily as carbonate



Fig. 1. Map of Willcox Basin showing the basin's extent, bedrock types in the mountain blocks, sample numbers, and ⁸⁷Sr/⁸⁶Sr ratios. Bedrock types derived from Richard et al. (2002); location of Apache Pass Fault Zone derived from Drewes (1985, 1986) and Erickson (1988). Approximate extent of cones of depression and groundwater flow directions derived from water level contours in Oram (1993). Inset shows location of Willcox Basin in the Basin and Range region (USGS, Principal aquifers of the 48 conterminous United States, Hawaii, Puerto Rico, and the US Virgin Islands, obtained from http://www.nationalatlas.gov).

complexes, whereas the major adsorption sites of Ra (e.g. Mn and Fe oxides) are most stable in oxic conditions. The surface charge of these metal oxides can influence both radionuclide activities and oxyanion concentrations. Because metal oxides can adsorb As(V) and Ra at near-neutral pH, the disequilibrium between ²²⁶Ra and ²³⁸U in the ²³⁸U decay series permits inferences on the reactivity of the U-decay chain nuclides and indirectly also on removal of other oxyanion-forming trace elements. Additionally, isotopes of the water molecule (³H, δ^2 H, and δ^{18} O) are reported to provide information on groundwater residence time and the relationship to modern precipitation.

2. Geologic setting

The complex geologic history of the Willcox Basin affects both groundwater evolution and the availability of oxyanion-forming trace elements. As a hydrologically closed inland basin, isotopic end members in the Willcox Basin are locally defined and represent a mixture of the mobile sources exposed in the basin.

2.1. Composition of the mountain blocks

The mountain blocks bounding the Willcox Basin and other tectonic basins of southern Arizona contain a complex assortment of rock types from ~1.7 Ga metamorphic rocks to Tertiary-Quaternary volcanic rocks (Richard et al., 2002). Briefly, the main rock types surrounding the Willcox Basin include: (1) 1.7 Ga metasedimentary and felsic metavolcanic rocks (Condie et al., 1985); (2) 1.4 Ga granitic rocks (Erickson, 1981); (3) Cambrian through Triassic sedimentary rocks (conglomerate, sandstone and carbonate; Hayes, 1978; Drewes, 1985); (4) Late Cretaceous to early Tertiary volcanic (felsic to intermediate tuff and breccia) and intrusive rocks (granodiorite; Drewes, 1985, 1986); and (5) mid-Tertiary felsic volcanic and intrusive rocks (Richard et al., 2002; Fig. 1). Of these, the Tertiary volcanic rocks and Proterozoic rocks are the most extensive around the perimeter of the Willcox Basin (Fig. 1). It may be inferred that the basin-fill sediments are dominated by nearby bedrock lithologies, but there is inadequate subsurface data to characterize the spatial variation in the composition of basin-fill sediments. The presence of outliers of Tertiary rocks in the southern Willcox Basin (Fig. 1) implies that these rocks also subcrop abundantly beneath the basin-fill sediments. Although the As content of specific rock units in the mountain blocks is not known, the mid-Tertiary felsic volcanic rocks are assumed to be a major As source due to their large spatial extent in the basin and the tendency of felsic volcanic rocks to contain reactive phases that readily yield high As to groundwater (Smedley and Kinniburgh, 2002).

2.2. Basin geometry

Depth to bedrock increases steeply from the edges of the Willcox Basin and from bedrock outliers (Drewes, 1986; Richard et al., 2007). At its center, the Willcox Basin exceeds 1500 m depth (Richard et al., 2007). Overall, the depth of basin-fill deposits greatly exceeds the depth of most of the wells in this study. The Apache Pass Fault Zone (Fig. 1), a major Precambrian structural feature, is preserved in the Dos Cabezas Mountains and beneath the eastern portion of the Willcox Basin. This fault has been hypothesized to supply high-As water to wells along its trace (Towne and Freark, 2001), and, in general, basement-penetrating faults in the southwestern USA have been observed locally to contribute waters with high levels of salinity, CO₂, and/or natural trace elements affecting water quality to basin-fill aquifers (e.g. Coes et al., 2002; Newell et al., 2005; Earman et al., 2008; Crossey et al., 2009).

2.3. Pleistocene-Holocene Lake Cochise

The surficial deposits at the center of the Willcox Basin are associated with a large Pleistocene–Holocene closed-basin lake. A distinctive shoreline deposit at 1274 m elevation (14 m above the present dry lake bed) formed approximately 13.5 ka and lower high stands occurred during the early Holocene (Waters, 1989). At least 40 m of sulfide-bearing clay is beneath the present-day dry lake bed (Schreiber et al., 1972; Vine et al., 1979). At greater depth (up to 300 m), the sediments become dominated by alternating calcite and gypsum layers (Vine et al., 1979), consistent with evaporation at the center of the basin being a major drain for the groundwater system during the basin's history.

2.4. Groundwater flow and residence time

Based on relationships between precipitation and water levels, Gardner and Heilweil (2009) suggested that mountain-front recharge and infiltration from ephemeral streams near the basin edges are the major source of recharge to the basin, and that natural groundwater flow directions follow the surface topography of the Willcox Basin. At the center of the basin, fine-grained lake bed deposits locally create a shallow (<30 m depth), perched groundwater system (Oram, 1993). Although historically, the main discharge point for the hydrologically-closed basin has been evapotranspiration at Willcox Playa, a significant mechanism today is water withdrawals for irrigation. The main irrigated areas, located north and SE of the Willcox Playa, are the sites of large cones of depression (Mann et al., 1978; Oram, 1993; Gardner and Heilweil, 2009) that significantly affect groundwater flow (Fig. 1). Quantitative data on groundwater residence time are sparse; however, one published ¹⁴C activity near the center of the basin (26% modern carbon; Robertson, 1991) is consistent with Holocene-aged groundwater, rather than the basin-fill groundwater being solely a remnant of elevated Pleistocene recharge.

3. Methods

3.1. Well sampling

Samples were collected from 15 domestic and high-capacity irrigation wells and one spring. Wells were sampled during a period of water use at a tap as close to the wellhead as possible. Depths are known in some cases (Table 1), but the lengths of well screens probably vary significantly among the irrigation and domestic drinking water wells sampled for this study. pH, temperature, and dissolved O₂ were measured in the field using meters that were calibrated daily. Trace metal, cation, anion, and Sr and B isotope samples were filtered in the field using 0.45 µm nylon filters. Major cation/trace metal samples were filtered directly into new polyethylene bottles that had been cleaned with trace metal grade HCl and HNO₃, then rinsed with deionized water having resistivity >18 M Ω cm⁻¹. Major cation/trace metal samples were immediately acidified with high-purity HNO₃ (Fisher Optima). Sample aliquots for anion and water stable isotope analyses were stored in DI-washed HDPE bottles and glass scintillation vials, respectively, with no headspace. Unfiltered samples were also collected for ³H and S isotope analysis; HNO₃ was added to the S isotope samples to prevent SO₄ reduction. All samples (except those for Ra) were kept on ice in the field and refrigerated in the laboratory prior to analysis. Forty liter unfiltered samples for Ra isotope analyses were collected in polyethylene containers and kept closed until processing upon return to the laboratory later the same day. An acidified blank was prepared by filling an acid-washed sample bottle with unfiltered deionized water (>18 M Ω cm⁻¹) in the

Table 1Major element results.

Well	Elevation (m)	Depth (m)	pН	Temp. (°C)	°C) Diss. O ₂ °C) (% saturation)		Ca (mM)	Mg	Na	К	Si	F ⁻	Cl-	NO_3^-	SO_4^{2-}	Alkalinity (meq L ⁻¹)
Mountain blocks																
1	2769	Spring	7.12	10.1	55	161	0.6	0.2	0.3	0.01	0.3	0.03	0.07	< 0.01	0.04	1.68
2	1545	92	7.00	21.4	3	704	2.0	0.9	4.0	0.08	0.4	0.08	2.83	0.19	0.81	4.80
3	1512		7.12	27.0	67	586	0.9	0.8	4.2	0.05	0.4	0.04	0.49	< 0.01	0.36	5.90
Willcox Basin – trend 1																
4	1446		7.13	27.3	95	352	1.0	0.5	1.1	0.04	0.7	0.07	0.35	0.07	0.15	3.23
5	1409		9.12	29.5	63	347	1.2	0.4	1.2	0.04	0.5	0.07	0.57	0.09	0.24	2.94
6	1342	153	6.67	20.7	122	156	0.4	0.2	0.5	0.02	0.6	0.02	0.15	0.18	0.05	1.12
7	1332	138	8.36	27.8	20	362	0.8	0.3	1.9	0.06	0.5	0.07	0.28	0.05	0.17	3.49
Willcox Basin – trend 2																
8	1288	86	9.27	23.0		639	0.03	0.002	7.8	0.05	1.2	0.42	1.39	0.19	1.41	2.96
9	1310	183	7.76	32.9	83	342	0.3	0.02	3.2	0.04	0.7	0.28	0.24	0.06	0.67	2.13
10	1303	245	7.54	28.4	71	452	0.4	0.1	5.2	0.04	0.4	0.04	2.88	0.09	0.37	2.35
11	1297	168	7.76	23.1	64	378	1.2	0.2	2.0	0.06	0.5	0.10	0.58	0.08	1.00	2.02
12	1294	245	7.94	31.7	53	950	1.0	0.1	12.6	0.06	0.4	0.06	11.77	0.06	1.05	1.19
13	1284	80	7.95	22.4	83	795	2.8	0.4	4.3	0.09	0.6	0.07	1.06	0.72	2.89	2.91
14	1274		7.08	21.3	51	600	0.8	0.3	5.0	0.07	0.7	0.26	1.03	0.30	0.61	4.61
15	1272	35	6.75	24.5	21	722	2.1	0.6	3.9	0.05	1.0	0.12	2.56	0.30	1.29	3.86
16	1266		7.11	19.8	50	1147	2.2	2.0	8.4	0.13	0.5	0.07	7.65	0.07	2.99	3.62

laboratory, with the same subsequent transportation, acid addition, and handling as for water samples.

3.2. Major and trace element analysis

Major cation concentrations (Na. K. Ca. Mg). Si, and Fe were determined using a Perkin Elmer Optima 5300 inductively-coupled plasma optical emission spectrometer, and major anion concentrations (F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-}) were determined using a Dionex ICS-3000 ion chromatograph with an AS23 analytical column. Alkalinity concentrations were determined by the Gran-Alk titration within 24 h of sampling (Gieskes and Rogers, 1973). Trace element (B, Sr, V, Cr, Mn, As, Se, Mo, Sb, Ba and U) concentrations were determined by inductively-coupled plasma mass spectrometry on a VG Plasmaquad 3 instrument. Calibration standards were prepared from serial dilution of certified trace metal solution NIST1643e. Samples and standards were diluted to similar proportions with an internal standard solution of 10 µg/L In, Tm and Bi in 2% HNO3 to monitor and correct for drift. Dilutions were carried out with solutions prepared from quartz-distilled deionized water and HNO₃. Instrument drift was also monitored and corrected for each element by analysis of one of the calibration standards at regular intervals. To allow for U analysis, NIST1643e was spiked with a plasma-grade single-element U solution prior to serial dilution. Trace element analysis included a field blank for which resulting concentrations were <1 μ g L⁻¹ except B (1.0 μ g L⁻¹), Sr (2.1 μ g L⁻¹), and Ba (2.9 μ g L⁻¹). Boron and As speciation were calculated using the PHREEQC geochemical code (Parkhurst and Appelo, 1999). The code was directed to use dissolved O₂ measurements to calculate pe. Arsenic speciation was not calculated for well 2 due to the anoxic nature of the well.

3.3. Stable and radiogenic isotopes

Hydrogen isotope analysis was conducted by Cr metal reduction at 750 °C (Gehre et al., 1996) and O analysis by CO_2 equilibration at 15 °C (Craig, 1957), both on a Finnigan Delta S gas-source isotope ratio mass spectrometer at the University of Arizona. Isotope ratios were standardized relative to VSMOW and VSLAP and are reported relative to VSMOW. Precision is within 0.9% for δ^{2} H and 0.08% for δ^{18} O based on replicate analyses. Sulfur isotope ratios of SO₄ were determined using a ThermoQuest Finnigan Delta PlusXL continuous flow isotope ratio mass spectrometer at the University of Arizona. ³⁴S/³²S ratios are normalized to the CDT standard and reported as δ^{34} S with precision of 0.15‰. Tritium activities were determined at the University of Miami Tritium Laboratory by gas proportional counting with precision (1 σ) of approximately 0.1 tritium unit (TU).

Due to the generally low B concentrations, samples were prepared for B isotope analysis by pre-concentrating filtered, nonacidified water samples to approximately 500 μ g B L⁻¹ at ~40 °C in ultra-clean Teflon vials in a laminar-flow hood using B-free filters and treating with 30% H₂O₂ (Fisher Optima) to oxidize labile organic matter. Approximately 2 ng B (less in the case of low-B samples) was loaded directly onto degassed Re filaments in a Bfree synthetic seawater solution prepared from plasma-grade standards (Dwyer and Vengosh, 2008) and analyzed by negative ion thermal ionization mass spectrometry (TIMS) on a ThermoFisher TRITON thermal ionization mass spectrometer at Duke University. Samples were analyzed by stabilizing the ¹¹BO₂ signal at a maximum of $\sim 1 \text{ V}$ (significantly less in the case of low-B samples), then $^{11}B/^{10}B$ ratios were measured for approximately 30 min (60 cycles). Boron isotope ratios were normalized to the long-term average $^{11}B/^{10}B$ of the NIST 951 standard (4.0067 ± 0.25%; 1 σ , *n* = 238) and reported as δ^{11} B. A two-step protocol was used to accept measured ¹¹B/¹⁰B ratios: (1) Potential interference at mass 42 (from CNO) was monitored by verifying CN at mass 26 (Hemming and Hanson, 1992) to be <5000 counts/s using the secondary electron multiplier. Although the relationship between CN and CNO in negative-ion TIMS is not completely understood, the CN signal on mass 26 is used as a proxy for possible interference at mass 42 and ratios are rejected in cases of CN > 5000 counts/s; and (2) stable ratios (maximum drift <~1%) during data acquisition, including samples for which temperature varied during acquisition. In addition to replicate analysis of the NIST 951 standard, five representative samples from this project were subjected to whole-process replication, yielding four replicates within a range of 1.8‰, and one sample rejected for less favorable replication. The overall precision is, therefore, estimated to be 1-2%.

Strontium isotope samples were prepared by dry-down, HNO₃ digestion, and subsequent column extraction of \sim 3 µg Sr using Eichrom Sr-specific resin conditioned with HNO₃ and eluted with quartz-distilled deionized water. The resulting Sr was loaded onto single degassed Re filaments in a Ta load solution (Birck, 1986) and analyzed by TIMS in positive ion mode at Duke University. The ⁸⁷Sr/⁸⁶Sr ratios are reported without normalization to the NIST

987 standard; long-term average 87 Sr/ 86 Sr of NIST 987 during the period preceding and including this study was 0.710245 ± 0.000010 (1 σ , n = 109). Whole-process replicates (n = 4) indicate precision within the expected analytical uncertainty reported for NIST 987.

3.4. Radium isotopes

Radium was preconcentrated onto two sequential plastic columns containing 10 g (dry weight) of Mn oxide-impregnated acrylic fibers (Moore and Reid, 1973) at a flow rate of \sim 500 mL min⁻¹ and analyzed at Duke University within 2 days of sampling. Radium-224 was determined by alpha counting of its daughter ²²⁰Rn using a delayed coincidence counter (Moore and Arnold, 1996) at a detector efficiency designed for hand-squeezed fibers. Low-activity samples were quantified by ²²⁰Rn coincidence counts and high-activity samples by total alpha counts. In both methods, count rates were corrected for counts attributable to ²²³Ra, ²²⁴Ra decay, and background count rate. High activity samples (>20 cpm) were re-analyzed ~1 week later for quantification of ²²³Ra interference (Moore and Arnold, 1996). For ²²⁶Ra analysis, fibers were sealed into an evacuated glass tube for 20 days, then analyzed for its daughter ²²²Rn using a Durridge RAD7 radon-inair monitor (Kim et al., 2001) calibrated using a NIST ²²⁶Ra solution transferred onto Mn oxide fibers and corrected for background count rate. For ²²⁸Ra analysis, fibers (first column only) were compressed into a wafer (5 mm tall and 65 mm in diameter) inside a metal can using a hydraulic jack and analyzed using the 911 keV peak of ²²⁸Ac on a Canberra broad-energy Ge gamma detector, corrected for background count rate and the fraction of Ra on the first column, and calibrated using an average of three ²³²Th (equilibrated with ²²⁸Ra) standards loaded to resemble the geometry of the compressed fibers. Stated 2σ errors represent counting statistics only based on methods for error calculation and propagation of error (Eaton et al., 2005; Garcia-Solsona et al., 2008), do not incorporate other potential uncertainties including moisture content (²²⁴Ra) or counting geometry within the compressed disk (²²⁸Ra), and, therefore, represent a minimum estimate of overall analytical uncertainty. The detection limit, defined as the activity with 95% probability of being detected at ±100% precision, is estimated by 1.96 σ (Eaton et al., 2005), so the 2 σ counting errors provide an estimate of the sample-specific detection limit for the counting time used.

4. Results

4.1. Groundwater salinity and major element chemistry

The 16 wells in the study yielded a large range of salinity with total dissolved solids of 156–1147 mg L^{-1} (Table 1). Groundwater with the highest dissolved solids is located near the center of Willcox Basin while groundwater with the lowest dissolved solids is in the mountain blocks and upper elevations of the basin-fill aquifer. However, salinity does not systematically increase down-gradient through the Willcox Basin groundwater system. In general, groundwater from the mountain blocks and upland areas is characterized by a Ca–Mg–HCO₃⁻ composition, and down-gradient waters in the basin are composed of a mix of dominant cations and anions. as well as a distinctive Na-HCO₂ water containing very low concentrations of Ca and Mg (e.g. well 8; Table 1). The widely varied anion concentrations include NO₃⁻ (>10 mg L⁻¹ as N, n = 1) and F⁻ $(>4 \text{ mg L}^{-1}, n=3)$ in excess of EPA standards. Temperature and pH exhibit a wide range of variability within the basin-fill aquifer (20-33 °C and 6.8-9.3, respectively; Table 1). Neither pH nor temperature is clearly associated with location within the basin. Almost all of the wells contain measurable dissolved O₂ (median 63% atmospheric saturation, range 3-95%).

4.2. Trace elements

Oxyanion-forming element concentrations (Table 2) have a wide range of concentrations: V 0.6–21.7 µg L⁻¹, Cr 0.8–26.2 µg L⁻¹, As 0.3–29.4 µg L⁻¹, Se 0.2–10.2 µg L⁻¹, Mo 1.0–11.1 µg L⁻¹ and Sb 0.3–1.9 µg L⁻¹. Among the oxyanion-forming trace elements, only As exceeded the US EPA MCL for public drinking water systems (10 µg L⁻¹, n = 4). Arsenic is also associated (Spearman's $\rho > 0.50$) with several major ions: SO₄^{2–} ($\rho = 0.76$), F⁻ ($\rho = 0.74$), Na ($\rho = 0.74$), Cl⁻ ($\rho = 0.67$), NO₃⁻ ($\rho = 0.58$), and Ca/Na

Table 2

Concentrations of	f oxyanion-:	forming and	other trace	elements. See	e Table 3	for B and	Sr concentrations.
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Concentrations in $\mu g L^{-1}$										Proportion of As
Well	v	Cr	Mn	Fe ^a	As	Se	Мо	Sb	Ва	as HAsO ₄ ²⁻
Mountain blocks										
1	1.0	1.0	0.2	10	0.3	0.2	1.3	0.3	18.3	0.62
2	2.0	3.8	15.7	18	1.5	2.2	11.1	2.0	81.4	
3	0.6	0.9	0.7	ND	0.4	0.6	3.8	0.3	49.8	0.67
Willcox Basin – trend 1										
4	1.6	0.8	0.6	ND	0.5	0.8	2.3	0.3	58.8	0.66
5	3.0	1.5	1.2	6	1.2	1.9	3.6	0.8	84.5	0.99
6	4.6	1.5	0.2	10	0.4	0.5	1.0	0.3	54.1	0.37
7	1.4	0.8	0.9	8	0.7	1.1	3.7	0.3	50.0	0.97
Willcox Basin – trend 2										
8	10.0	3.6	0.3	10	29.4	1.2	6.7	0.8	33.2	1.00
9	5.4	3.8	0.3	ND	5.5	0.6	4.7	0.5	33.3	0.89
10	20.3	8.8	0.3	ND	9.2	1.3	1.9	0.3	187.1	0.84
11	3.6	3.8	1.0	ND	2.1	1.1	4.7	0.8	44.4	0.89
12	12.2	26.2	0.2	ND	4.3	3.0	2.4	0.4	50.8	0.94
13	4.7	4.0	2.6	ND	3.1	4.1	3.9	1.8	47.1	0.94
14	21.7	4.9	0.5	ND	21.7	7.8	8.2	0.5	63.3	0.64
15	9.5	9.0	9.2	49	19.0	10.2	4.5	1.9	53.3	0.48
16	12.4	12.4	2.1	ND	13.1	1.3	6.4	1.7	47.1	0.70
USEPA primary maximum contaminant levels										
		100			10	50		6	2000	

^a ND indicates element not detected (detection limit $6 \ \mu g \ L^{-1}$).



Fig. 2. Hydrogen and O isotope ratios in Willcox Basin groundwater. Dashed line represents the global meteoric water line (GMWL; $\delta^2 H = 8 \times \delta^{18}O + 10\%$; Craig, 1961).

($\rho = -0.67$). Notably, As is not correlated with pH ($\rho = 0.11$). Among trace elements, As is correlated with V ($\rho = 0.87$), Cr ($\rho = 0.73$), Se ($\rho = 0.66$), Mo ($\rho = 0.62$), B ($\rho = 0.58$) and Sb ($\rho = 0.54$).

4.3. Environmental isotopes (δ^2 H, δ^{18} O, 3 H, 87 Sr/ 86 Sr, δ^{11} B, δ^{34} S)

Groundwater from the Willcox Basin and its mountain blocks exhibits some variation in H and O isotope ratios (δ^2 H –85‰ to –64‰, δ^{18} O –11.8‰ to –8.6‰; Fig. 2). In general, waters near the edges of the Willcox Basin exhibit similar isotopic values as the limited data for the mountain blocks (generally <–10‰). A slight apparent effect was observed in which higher values of δ^{18} O (>–10‰) occur in the southern and western samples, located near the center of the basin at relatively low elevation (Fig. 3). All waters analyzed for ³H are consistently near the detection limit (≤ 0.6 tritium units (TU); Table 3).

Wide geographic variability was observed among Sr isotope ratios, generally decreasing from highly radiogenic values up to 0.75010 in groundwater from the crystalline mountain blocks, to a minimum value of 0.71012 at the center of the basin (Fig. 1). Waters with 87 Sr/ 86 Sr > 0.720 in the northern and southeastern parts of the basin (Fig. 1) are associated with low concentrations of oxyanion-forming trace elements (B, As, V, Cr, Se, Sb, Mo) and high Ca/Na (Fig. 4), and are referred to as "trend 1". Samples in the central part of the basin exhibiting more significant oxyanion concentrations are characterized by ⁸⁷Sr/⁸⁶Sr < 0.72 and generally lower Ca/Na (Fig. 5), and are referred to as "trend 2". Boron isotope ratios (as δ^{11} B) vary significantly (-6.7‰ to 18.2‰), and the higher values of δ^{11} B are somewhat associated with lower B concentrations (Fig. 6a). Boron isotope ratios exhibit some geographic trends also in that the samples with the highest ⁸⁷Sr/⁸⁶Sr and Ca/Na (trend 1) tend to exhibit lower As and B concentrations and somewhat higher δ^{11} B than trend 2 waters (Fig. 6a–c). Sulfur isotope ratios (as δ^{34} S) vary from 2.0‰ to 13.4‰. The results indicate that trend 1 waters exhibit generally lower δ^{34} S values than trend 2 waters (Fig. 7a) and that SO²₄-dominated waters (SO²₄-/Cl⁻ > 1 and Ca/ SO²₄⁻ < 2) exhibit δ^{34} S in the narrow range of 8–10‰ (Fig. 7b and c).

4.4. Radionuclides

With the exception of samples in the mountain blocks (wells 1–3), Ra isotope activities are exceedingly low (Table 3), 1–2 orders of magnitude below the EPA maximum contaminant level. Radium isotope activities are essentially uncorrelated with salinity, pH and oxyanion-forming trace elements. Radium-224, ²²⁶Ra and ²²⁸Ra are reasonably well correlated with the divalent cations Ca ($\rho = 0.54-0.77$) and Mg ($\rho = 0.58-0.70$), but not well correlated with the chemical analog of Ra, Ba ($\rho = 0.05-0.49$). Uranium is present at low to moderate concentrations (0.3–13 µg L⁻¹) throughout the basin-fill aquifer groundwater, and concentrations are much higher in the mountain blocks (10–71 µg L⁻¹; Table 3). One mountain block water sample yielded radionuclide levels in excess of EPA drinking water standards for U (30 µg L⁻¹) and Ra (185 mBq L⁻¹ ²²⁶Ra + ²²⁸Ra).

5. Discussion

5.1. Recharge and groundwater residence time

Hydrogen and O isotope ratios of groundwater in the Willcox Basin plot along a linear trend (Fig. 2) that is along or slightly below the global meteoric water line, consistent with groundwaters



Fig. 3. Map showing δ^{18} O of water samples in relation to basin topography. Elevation data obtained from US Geological Survey (http://seamless.usgs.gov).

Table 3

Isotope results and related trace element concentrations.

Well	В	Proportion of	$\delta^{11}B$	Sr	⁸⁷ Sr/ ⁸⁶ Sr	$\delta^{18} O$	$\delta^2 H$	$\delta^{34}S_{SO4}$	³ H (TU)	U (μ g L ⁻¹)	²²⁴ Ra	²²⁶ Ra	²²⁸ Ra
	$(\mu g L^{-1})$	B as B(OH) ₃	(%)	$(\mu g L^{-1})$		(‰)	(%)	(%)			$(mBq L^{-1})$	$(mBq L^{-1})$	$(mBq L^{-1})$
Mountain blocks													
1	8.7	0.99	9.4	35	0.750097	-11.4	-79	7.7		10	1.0 ± 0.4	2.6 ± 0.6	-0.2 ± 1.1
2	77	0.99	11.4	1030	0.732472	-9.8	-72	5.0		71	220 ± 11	303 ± 8	351 ± 49
3	106	0.99	5.3	912	0.745016	-11.7	-85	10.6	0.0	27	19.5 ± 1.0	4.5 ± 0.6	33.5 ± 4.5
Willcox Basin – trend 1													
4	26	0.99	1.9	164	0.733361	-10.9	-78	6.5		4.4	20.4 ± 1.5	5.7 ± 0.7	18.9 ± 5.1
5	44	0.53	7.8	192	0.720641	-9.1	-64	5.1	0.0	1.7	5.6 ± 0.8	1.6 ± 0.6	7.9 ± 4.5
6	16	1.00	18.2	68	0.728224	-11.1	-79	7.1		0.3	5.8 ± 1.2	1.5 ± 0.5	3.4 ± 3.3
7	50	0.87	14.8	410	0.725143	-9.8	-71	6.3	0.0	14	1.3 ± 0.4	1.6 ± 0.4	1.8 ± 3.6
Willcox Basin – trend 2													
8	76	0.46	-6.7	7.4	0.715026	-11.2	-83	10.2		2.7	0.2 ± 0.1	0.4 ± 0.6	1.5 ± 3.0
9	201	0.96		65	0.711471	-9.5	-68	9.5	0.1	11	2.6 ± 0.3	0.6 ± 0.5	2.2 ± 2.3
10	99	0.98	-0.5	190	0.711904	-11.2	-80	11.1	0.1	1.6	3.0 ± 0.7	0.6 ± 0.6	3.1 ± 2.3
11	127	0.97	3.9	268	0.710778	-9.3	-66	9.2	0.1	2.0	14.5 ± 0.9	2.2 ± 0.4	7.6 ± 3.6
12	98	0.94	0.9	333	0.713142	-11.8	-85	10.8	0.0	1.4	4.2 ± 0.6	2.7 ± 0.4	2.1 ± 2.3
13	215	0.95	0.3	671	0.710594	-8.6	-62	8.8	0.4	13	21.7 ± 1.0	2.9 ± 0.3	9.9 ± 3.9
14	126	0.99	4.0	218	0.711677	-11.0	-81	8.3		3.7	3.9 ± 0.6	2.7 ± 0.6	2.6 ± 2.5
15	390	1.00	2.3	641	0.714158	-10.0	-72	2.0	0.6	11	9.5 ± 1.6	1.1 ± 0.5	5.2 ± 4.3
16	103	0.99	2.7	2270	0.710122	-9.4	-69	13.4	0.2	11	10.4 ± 1.1	48.6 ± 1.1	2.4 ± 2.7







Fig. 5. Relationship between Ca/Na and ⁸⁷Sr/⁸⁶Sr and As concentration.

in adjacent alluvial basins (Baillie et al., 2007; Earman et al., 2008; Gu et al., 2008; Adkins, 2009). Specifically, the majority of δ^{18} O values are within the range of winter precipitation reported from adjacent mountain blocks (-12.1% to -8.7%) whereas summer precipitation exhibits higher δ^{18} O values (-9.5% to -6.8%; Earman et al., 2006; Adkins, 2009). Overall, δ^{2} H and δ^{18} O values of Willcox Basin groundwaters record waters derived from local (basin floor) winter precipitation and/or mountain-front recharge of higher-elevation precipitation, as in adjacent basins (Earman et al., 2008; Adkins, 2009). There is no isotopic evidence of substantial evaporation within the basin (Fig. 2) but some indication of higher-elevation δ^{18} O values near the basin's northern and eastern edges (Fig. 3). Tritium activities consistently <1 TU in the



Fig. 6. δ^{11} B in relation to B concentration, ⁸⁷Sr/⁸⁶Sr and As concentration. Note the apparent separation between trend 1 plus the mountain blocks (low B concentration, high δ^{11} B, high ⁸⁷Sr/⁸⁶Sr, low As) and trend 2 (high B concentration, low δ^{11} B low ⁸⁷Sr/⁸⁶Sr, elevated As). Black bar represents the approximate δ^{11} B range of rhyolite and granite (Barth, 1993).



Fig. 7. δ^{34} S in relation to SO₄²⁻ concentration, SO₄²⁻/Cl⁻ ratio, and Ca/SO₄²⁻ ratio.

basin-fill sediments (Table 3) indicate that precipitation is not a source of rapid recharge on the scale of years to decades, which is consistent with the semi-arid nature of the basin. In places, the low ³H activities contradict other indications from the data, such as elevated NO_3^- concentrations in irrigated areas, which implies significant recharge from the surface. The most likely explanation is that recharge of ³H-free irrigation water derived from groundwater pumping conveys NO_3^- to the basin-fill aquifer. The slow replenishment of the basin-fill aquifer by precipitation is indicated by large water table declines in irrigated areas since the 1940s, although declines have been locally reversed as irrigation withdrawals have been reduced since the 1970s (Mann et al., 1978; Oram, 1993).

5.2. Isotopic tracing of sediment sources using Sr

As documented in previous studies, Sr concentrations and isotope ratios in groundwater are primarily derived from interaction with the host aquifer rocks (Franklyn et al., 1991; Harrington and Herczeg, 2003). Given that ⁸⁷Sr/⁸⁶Sr ratios in groundwater are not fractionated by the reaction processes themselves, the isotopic ratios represent the composition of the host aquifer rocks and in a case of multiple rock types, the Sr isotope ratio could indicate the relative mixing combinations of the different sediment sources. The Sr isotope ratios of some contributing aguifer rocks in the Willcox Basin have been previously reported: (1) \sim 1.4 Ga granitic rocks exhibiting whole-rock ⁸⁷Sr/⁸⁶Sr > 0.775 (Erickson, 1981); (2) Tertiary volcanic rocks, inferred to be contaminated by melting of Paleozoic-Mesozoic sedimentary rocks and exhibiting whole-rock ⁸⁷Sr/⁸⁶Sr of 0.708–0.716 (Bryan, 1987); and (3) Cambrian to Triassic sedimentary rocks (Fig. 1) including conglomerate, sandstone, carbonates and locally present Permian gypsum with inferred seawater-derived Sr with ⁸⁷Sr/⁸⁶Sr < 0.709 (McArthur et al., 2001). Consistent with the \sim 1.4 Ga granitic rocks, limited data from the region for the \sim 1.7 Ga rocks also indicates radiogenic whole-rock ⁸⁷Sr/⁸⁶Sr > 0.720 (Stuckless and O'Neil, 1973). From these broad ranges of isotopic ratios, it appears that the ⁸⁷Sr/⁸⁶Sr ratios of Paleozoic and Tertiary rocks may overlap: however, the Proterozoic crystalline rocks, particularly the granitic rocks, impart a distinctive radiogenic signature.

Willcox Basin samples were divided into two major trends based on patterns of Sr isotope ratios and oxyanion-forming trace elements (Section 4.3). Trend 1 waters in the basin-fill aquifer $(n = 4, {}^{87}\text{Sr}/{}^{86}\text{Sr} 0.72064 - 0.73336)$ exhibit a Sr isotope signature associated with the mountain block samples in Proterozoic crystalline rocks (n = 3, 87 Sr/ 86 Sr 0.73247–0.75010). Trend 1 samples exhibit highly radiogenic ⁸⁷Sr/⁸⁶Sr ratios for sandstone aquifers up to ~ 10 km from the mountain front (Fig. 1), derived from mixing of water from Proterozoic rock units (Frost and Toner, 2004; Uliana et al., 2007) or by weathering of geologically old K-feldspar in the aquifer sediments (Harrington and Herczeg, 2003). Because of the large distance from the crystalline rocks in which ⁸⁷Sr/⁸⁶Sr > 0.720 is observed (Fig. 1), these ratios must be the result of weathering of sediments within the basin. A radiogenic ⁸⁷Sr/⁸⁶Sr signature is made possible by (1) the large proportion of K-feldspar in the mountain block granites (Erickson, 1981); (2) the age of the crystalline mountain block rocks (Section 2.1); and (3) the apparently original (unweathered) nature of feldspars deposited in the basin.

Trend 2 with relatively non-radiogenic isotope composition $(n = 9, {}^{87}\text{Sr}){}^{86}\text{Sr} 0.71012-0.71503)$ apparently records the influence of Tertiary volcanic rocks and/or Paleozoic sedimentary rocks. The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values of Sr derived from these rocks are expected to fall within a large range (0.708-0.716) as discussed above, but are substantially less radiogenic than Proterozoic rocks contributing to trend 1. The signal of the Tertiary felsic volcanic rocks cannot be clearly distinguished from Paleozoic-source material from the Sr isotope data alone. In some instances, the proximity to dominant rock types is ambiguous; for example, sample 8 in trend 2 is also



Fig. 8. Map indicating δ^{34} S in relation to the possible gypsum source area in the Dragoon Mountains and the extent of Pleistocene lake deposits.

close to Proterozoic rocks that may contribute radiogenic Sr. Trend 2 waters include three samples (8, 10 and 12) located near the trace of the Apache Pass Fault Zone (Fig. 1), which could contribute waters to explain the large differences in temperature, major element chemistry, and 87 Sr/ 86 Sr between nearby wells (Section 2.2). In such a case, mixing of a deep, high-As water into shallow groundwater could be a significant mechanism for generating high As concentrations in addition to local water–rock interaction (Coes et al., 2002; Crossey et al., 2009; Scanlon et al., 2009).

Overall, the weak relationship between Sr concentration and 87 Sr/ 86 Sr ratios (ρ = 0.23 between 1/Sr and 87 Sr/ 86 Sr; Fig. 4) implies that Sr in the groundwater is not derived from simple mixing of water or Sr sources. Rather, the large Sr isotope variations can be explained by interaction with different rock types imparting distinctive ⁸⁷Sr/⁸⁶Sr ratios. The observed trends associated with these ⁸⁷Sr/⁸⁶Sr ratios (Fig. 4) also reflect the control of aquifer lithology on the water composition. However, the concentration of Sr in groundwater can be controlled by secondary reactions that reduce divalent cation concentrations (Section 5.4) but that would not affect the original ⁸⁷Sr/⁸⁶Sr ratios. At the center of the Willcox Basin, not directly sampled by this study, lake bed carbonate preserves the ⁸⁷Sr/⁸⁶Sr ratio of Sr in calcite-precipitating waters. Thus, this value reports a mixture of contributing Sr sources to the closed basin at the time of mineral precipitation. A reported ⁸⁷Sr/⁸⁶Sr of 0.71049 (Naiman et al., 2000) of Pleistocene Lake Cochise lake bed carbonate is consistent with the lowest ⁸⁷Sr/⁸⁶Sr value reported in this study (0.71012) observed at well 16 near the Pleistocene shoreline (Fig. 1). Thus, the radiogenic Sr derived from crystalline rocks is balanced by Sr with ⁸⁷Sr/⁸⁶Sr < 0.710 to produce values ~0.710 at the center of the basin. Sources of this non-radiogenic Sr may include volcanic rocks. Permian marine gypsum (Section 5.3) with an expected ⁸⁷Sr/⁸⁶Sr ratio of 0.707–0.708 (McArthur et al., 2001) and/or other Paleozoic sedimentary rocks with low ⁸⁷Sr/⁸⁶Sr ratios. Overall, it seems that groundwater ⁸⁷Sr/⁸⁶Sr ratios are acquired during calcite dissolution and/or silicate hydrolysis that contribute Sr relatively early along groundwater flowpaths prior to down-gradient geochemical modifications that consume divalent cations while leaving the groundwater Sr isotopic ratio unmodified.

5.3. Sulfate sources

Sulfur isotopes of SO_4^{2-} may provide information on oxyanion– forming trace element behavior by evaluating sulfide mineral oxidation as a potential source (Smedley et al., 2002) and/or by recording SO₄-reducing conditions (Krouse and Mayer, 1999), which may influence the mobility and speciation of trace elements including As (Kirk et al., 2004; Xie et al., 2009). Although other investigators have identified sulfide in the shallow clay beneath the lake bed (Schreiber et al., 1972), the primary fate for SO_4^{2-} in the oxic Willcox Basin, rather than SO₄-reduction, is gypsum precipitation in the evaporative environment of the Willcox Playa indicated by buried gypsum deposits (Vine et al., 1979); gypsum precipitation does not significantly fractionate the δ^{34} S of residual SO_4^{2-} . Because no widespread SO_4^{2-} removal mechanism such as SO_4 reduction is capable of fractionating $\delta^{34}S$ in the Willcox Basin, δ^{34} S is primarily sensitive to SO₄²⁻ sources rather than removal mechanisms. In general, the trend 2 waters exhibit higher δ^{34} S than trend 1 waters, and SO_4^{2-} concentrations and SO_4^{2-}/Cl^{-} are also generally higher in trend 2 waters inferred to contain volcanic sediment influence. The distinct group of samples with $\delta^{34}S$ near 10‰ and high SO_4^{2-}/Cl^- (Fig. 7b), consistent with the findings of Eastoe et al. (2004), Gu (2005) and Adkins (2009) in nearby basins, exhibits a marine gypsum isotope signature rather than that of oxidized volcanic sulfide, which is characterized by a lower δ^{34} S range in the region (2-4‰; Burtel, 1989), or meteoric-derived sulfate (2-8‰; Eastoe et al., 2004). Overall, the trend 2 waters inferred to interact with volcanic-source sediment do not exhibit systematically lower δ^{34} S that might be characteristic of oxidized volcanic sulfide.

Gypsum in lower Permian carbonates in the basin-bounding mountain blocks, specifically the Epitaph Dolomite, is a documented source of SO_4^{2-} with $\delta^{34}S \sim 12\%$ (Burtel, 1989) influencing regional groundwater (Eastoe et al., 2004; Adkins, 2009), and this SO_4^{2-} can be broadly redistributed in alluvial basins (Eastoe et al., 2004; Gu, 2005). In the mountain blocks bounding the Willcox Basin, the Epitaph Dolomite is present in the Dragoon Mountains west of the basin (Fig. 8; Drewes, 1987). In addition, Paleozoic sedimentary rocks underlie the basin-fill sediments at the floor of the Willcox Basin (Drewes, 1985, 1987) and could also have

contributed gypsum during the basin's history. The S isotope results of trend 2 groundwaters are consistent with a marine gypsum source, probably recycled in the lake bed deposits at the center of the basin (e.g. Eastoe et al., 2004; Gu, 2005). The extent of gypsum influence can be seen in the location of gypsum-like δ^{34} S values mainly within the Pleistocene extent of Lake Cochise rather than up-gradient portions of the basin where atmospheric values occur (Fig. 7). The anomalously low δ^{34} S value of 2.0‰ at well 15 is consistent with oxidation of biogenic sulfide minerals (Krouse and Mayer, 1999) such as those observed in the shallow lake bed (Schreiber et al., 1972) but does not represent overall basin conditions. Overall, application of S isotopes implies that dissolution of marine gypsum is a significant SO_4^{2-} source to groundwater in the central and western Willcox Basin. In the northern and eastern portions of the basin where gypsum is absent, δ^{34} S is lower (6.5– 7.7%: Fig. 4) and thus more consistent with atmospheric sources. Although volcanic sulfide minerals could be a geologic source of As, δ^{34} S does not reflect substantial oxidation of volcanic sulfide in this system. Apparently, the large contribution of S from gypsum dissolution overwhelms any contribution from oxidized volcanic sulfide, both in the Willcox Basin and near the centers of alluvial basins throughout the region, where δ^{34} S values are consistently near Permian gypsum values (Gu, 2005). Moreover, the immediate mobilization of As to groundwater seems to be caused by desorption from oxide minerals under these conditions, rather than by direct sulfide oxidation (Robertson, 1989; Smedley and Kinniburgh, 2002; Smedley et al., 2002).

5.4. Significance of the Ca/Na ratio

In addition to the initial contradiction of gypsum-like δ^{34} S values in groundwater interacting with volcanic-source material, another paradox in the S isotope data is that samples with gypsumlike δ^{34} S values exhibit the lowest Ca/Na ratios in the study area, and many exhibit Ca/SO_4^{2-} ratios below the expected ratio of 1 from gypsum dissolution (Fig. 7d). This apparent inconsistency must be due to down-gradient groundwater evolution that systematically removes divalent cations. Isotopic evidence for the reactive nature of divalent cations includes the poor correlation between Sr concentration and ⁸⁷Sr/⁸⁶Sr (Section 5.2), which implies that Sr concentrations do not simply record mixing of two principal Sr sources. Shallow, recently-recharged, and calcite-undersaturated groundwaters acquire a relatively high Ca/Na ratio from calcite dissolution in both granitic-derived (e.g. White et al., 2005) and volcanic-derived sediments (e.g. Earman et al., 2005). Subsequent groundwater evolution with increasing residence time and/or distance down-gradient may contribute Ca through gypsum dissolution, but apparently Ca is removed by processes including calcite precipitation, silicate hydrolysis linked to smectite precipitation, and/or cation exchange (Robertson, 1991; Bowser and Jones, 2002). In the Willcox Basin, Ca/Na ratios vary widely, but distinctive low values <0.2 (Fig. 5) occur near the center of the basin (samples 8, 9, 10, 12, and 14; Fig. 1). Although the lowest values of Ca/Na are seen in trend 2 waters interacting with aquifer sediment inferred to contain higher As levels, the relationships between Ca/Na and As concentration ($\rho = -0.67$; Fig. 5), δ^{34} S and Ca/Na (Fig. 7d), ⁸⁷Sr/⁸⁶Sr and Ca/Na (Fig. 5), and ⁸⁷Sr/⁸⁶Sr and Sr concentration (Fig. 4) collectively suggest that Ca/Na at least partially records hydrogeochemical processes along groundwater flowpaths and/or surface charge of sediments rather than merely fingerprinting the geologic sources of solutes within the basin. A relationship between lithologic source and the Ca/Na ratio has been observed in previous studies reviewed by Smedley and Kinniburgh (2002), in which weathered volcanic material, especially ash, yields Na-dominated waters.

5.5. Trace element and isotope behavior: implications for oxyanionforming elements

5.5.1. Arsenic

Broadly, the correlations between As, F⁻ and other oxyanionforming trace elements in the Willcox Basin are consistent with existing data sets for the Willcox Basin (Towne and Freark, 2001; USGS National Water Information System at http://waterdata.usgs.gov/nwis, accessed 17 February 2010) and other published studies of oxic, neutral to basic groundwater systems (Robertson, 1989; Del Razo et al., 1993; Smedley et al., 2002; Armienta and Segovia, 2008; Scanlon et al., 2009; Currell et al., 2011). The correlation between Ca/Na and As ($\rho = -0.67$) is consistent with behavior of As in which the presence of Ca rather than Na modifies the surface charge of As adsorption sites such as Fe oxides and promotes As adsorption in high-Ca waters (Wilkie and Hering, 1996; Smith et al., 2002; Masue et al., 2007; Jia and Demopoulos, 2005; Scanlon et al., 2009). Although the Ca/Na ratio of groundwater seems to be associated with down-gradient geochemical evolution (Section 5.4) also associated with elevated As, it is also evident that some non-volcanic aquifer materials do not impart high As to groundwater due to their low As content. In sum, although oxic conditions, neutral to slightly basic pH, and Ca/Na influence As concentrations in groundwater, it appears that both sediment source material and down-flow hydrogeochemical evolution are important contributing factors, indicated by the association of As concentration with ⁸⁷Sr/⁸⁶Sr ratios (Fig. 4) and the relatively weak overall association between pH and As concentration among the multiple rock types represented in the data set.

5.5.2. Vanadium, chromium, selenium, molybdenum, and antimony

Although the occurrence of V, Cr, Se, Mo and Sb is of less water quality significance than As in the Willcox Basin, the behavior of these oxvanions can be treated as analogous to As due to their similar chemical behavior. All of these elements occur at higher concentrations in trend 2 waters (Fig. 4), and all exhibit correlations with each other, although correlations are significantly weaker for Cr and Se. Vanadium is consistently associated with volcanicsource aquifer material and with other oxyanion-forming trace elements (Aiuppa et al., 2003; Vivona et al., 2007) and in the study area, V concentrations are higher in trend 2 waters (3.6-21.7 μ g L⁻¹) than in trend 1 waters or the mountain blocks (0.6– 4.6 μ g L⁻¹). Chromium exists primarily as soluble Cr(VI) in oxic waters, and has been observed in basin-fill aquifers sourced from mafic volcanic rocks (Izbicki et al., 2008) or fine-grained weathered volcanic material (Robertson, 1975). Chromium concentrations of up to 26.2 μ g L⁻¹ were observed in this study, but most concentrations are much lower. Selenium concentrations, although generally low throughout the study area (0.2–10.2 μ g L⁻¹), are highest in waters of trend 2, consistent with other oxyanion-forming elements (Fig. 4). Molybdenum may be elevated in felsic volcanic rocks (rhyolite; Arnórsson and Óskarsson, 2007) and is correlated with As in high-As alluvial basins of the southwestern USA (Robertson, 1989). The highest Mo concentration (11.1 μ g L⁻¹) was observed in a mountain block water sample, although otherwise, concentrations above $5\,\mu g\,L^{-1}$ were only observed in trend 2 waters consistent with other oxyanion-forming elements (Fig. 4). Antimony concentrations are low throughout the study area $(\leq 2 \mu g L^{-1}; Table 2)$ and except for one mountain block sample, the highest concentrations were observed in trend 2 waters. However, Towne and Freark (2001) reported an isolated occurrence of elevated Sb (9 μ g L⁻¹) above drinking water standards. Thus, overall, the occurrence of V, Cr, Se, Mo and Sb is similar to As in the Willcox Basin.



Fig. 9. Schematic cross-section of a generalized alluvial basin (modified from Robertson, 1991) depicting influences on observed Sr, S, B, O and H isotope ratios and the Ca/Na ratio.

5.5.3. Boron

Boron isotope data in groundwater can reflect either (1) adsorption reactions in which tetrahedral boron $(B(OH)_{4}^{-})$ with its distinctive isotopic composition is preferentially adsorbed onto clay minerals or (2) inputs of B sources with different isotopic ratios (Vengosh et al., 1994, 1999). The low-B groundwater of trend 1 and the mountain blocks exhibits higher $\delta^{11}B$ values (up to 18.2%) than waters with higher B concentrations in trend 2, forming two distinct groups (open vs. filled symbols in Fig. 6a). The associations between $\delta^{11}B$ and ${}^{87}Sr/{}^{86}Sr$ and As concentration (Fig. 6b and c) suggest that the B isotopic composition in Willcox Basin groundwater is controlled by B sources rather than processes in the aquifer. It seems that rain-sourced B with higher δ^{11} B (Vengosh and Spivack, 1999; Rose-Koga et al., 2006) controls the composition of the low-B groundwater in the trend 1 basin-fill materials. In contrast, the association of low δ^{11} B with low 87 Sr/ 86 Sr (samples with $\delta^{11}B < 5\%$ are characterized by ${}^{87}Sr/{}^{86}Sr < 0.715$ and relatively low Ca/Na) ratios implies that rhyolite weathering may affect B isotope ratios in the trend 2 waters. Thus, there are differences in B sources between trends 1 and 2, consistent with other elemental and isotopic evidence. However, given the distinct behavior of uncharged B and anionic As(V) in oxic, neutral to slightly basic waters, the application of B isotopes in this case does not provide specific information about As mobilization processes.

5.5.4. Radium and uranium

The very low Ra activities are consistent with previous studies of the Willcox Basin, in which high Ra was shown to occur only in the crystalline mountain blocks (Towne and Freark, 2001). Also, the radionuclide activities reported here are consistent with previously published results from another closed basin-fill aquifer composed of granitic-source sediment, the Carson River Basin in Nevada (Thomas et al., 1993). In that investigation, median ²²⁶Ra activity and ²²⁶Ra/²³⁸U activity ratio were low, similar to the Willcox Basin (4.4 mBq L^{-1} and 0.026, respectively) and the basin exhibits a similar pH range (\sim 6.5–9.5) as the Willcox Basin. The elevated ²²⁸Ra/²²⁶Ra ratios throughout the basin (median 3.4), except for sample 16 at the basin center exhibiting 228 Ra/ 226 Ra < 0.1 (Table 3), are also consistent with the higher mobility of U relative to Th or Ra because weathering-derived ²³⁸U may be transported toward the center of the basin and thus not contribute by decay into the precursors of ²²⁶Ra. Long-term transport of U to the center of the basin is also consistent with the U deposit hosted in lake bed deposits at the center of Willcox Basin and other alluvial basins in Arizona (Duncan and Spencer, 1993), locally contributing high U to groundwater in the center of the basin (Towne and Freark, 2001).

In contrast to the relatively soluble nature of U and oxyanions under these conditions, several co-occurring mechanisms may remove Ra from water in the aquifer: (1) adsorption to Mn and Fe oxides (Ames et al., 1983b; Herczeg et al., 1988) and clays (Ames et al., 1983a); (2) coprecipitation of Ra with BaSO₄ (Grundl and Cape, 2006); and/or (3) processes that remove divalent cations including Ra^{2+} from solution (Section 5.4). The pH-dependent adsorption-desorption behavior of Ra differs from that of As in oxic waters. The high pH of the aquifer maintains negative surface charge on Mn and Fe oxides, which makes Ra²⁺ adsorption highly effective; thus, pH-sensitive oxyanion desorption from Fe oxides (e.g. Robertson, 1989) corresponds with efficient Ra adsorption. Overall, the occurrence of all Ra isotopes (²²⁴Ra, ²²⁸Ra, ²²⁶Ra) in groundwater, including ²²⁴Ra/²²⁸Ra broadly on the order of 1 in the basin-fill aquifer (Table 3), is consistent with Ra release by alpha recoil and rapid subsequent adsorption (Krishnaswami et al., 1982).

6. Conclusions

Willcox Basin groundwater samples have been divided into two groups, trend 1 and trend 2, based on variations in ⁸⁷Sr/⁸⁶Sr and oxyanion-forming trace element concentrations. This provides a framework for assessing the relative contributions of low-As (inferred granitic) sediment sources with highly radiogenic ⁸⁷Sr/⁸⁶Sr ratios (trend 1) and high-As (inferred volcanic) sources associated with non-radiogenic ⁸⁷Sr/⁸⁶Sr values (trend 2) in imparting elevated As concentrations to groundwater. In addition to exhibiting higher concentrations of As, trend 2 waters also exhibit generally higher concentrations of other oxyanion-forming trace elements (B, V, Cr, Se, Mo, Sb) and F⁻. Strontium isotope ratios record contributions from aquifer rocks with different ⁸⁷Sr/⁸⁶Sr ratios, but do not trace Sr (and Ca) removal processes. Sulfur isotopes record atmospheric sources, apparently modified in the central and western Willcox Basin by marine gypsum dissolution. Boron isotopes primarily trace atmospheric sources and weathering of volcanicsource material during and after recharge. Thus, the consistent patterns between Sr, B, and S isotopes are largely attributable to water-rock interaction (B, S, Sr) and to some degree also meteoric sources (B, S) in which all three isotope signatures are acquired (Fig. 9). Whereas Sr isotopes provide valuable indications of high-As vs. low-As lithologic sources, S and B isotopes are not shown to be directly linked to As sources or mobilization. Hydrogeochemical modification associated with high-As, HCO3-dominated waters near the center of the basin is apparently not recorded by Sr, S or B isotope variations but is recorded by the decreasing Ca/Na ratio, which is linked to conditions favoring As(V) desorption from oxide mineral surfaces. Also, the combined use of Ra isotopes and U concentration, indicating rapid Ra removal, is consistent with inferred oxyanion desorption behavior from surfaces such as Fe oxides. However, the occurrence of low Ca/Na ratios may be more prevalent in volcanic-source material such that both lithologic source and hydrogeochemical modification influence observed Ca/Na ratios. The results of this study demonstrate that multiple tracers of water-rock interaction can provide information on the relative contributions of the aquifer's lithologic composition and hydrogeochemical processes to concentrations of oxyanion-forming trace elements in groundwater from alluvial basins. Contrasting ⁸⁷Sr/⁸⁶Sr ratios of trend 1 and trend 2 samples, which record interaction with different lithologic material rather than subsequent hydrogeochemical processes, could be a particularly useful tracer for evaluating many alluvial basins in the southwestern USA (Fig. 9), where highly radiogenic Proterozoic crystalline rocks, Paleozoic sedimentary rocks, and Tertiary-Quaternary volcanic rocks with distinct ⁸⁷Sr/⁸⁶Sr ratios contribute sediment to basin-fill aquifers. Of these, volcanic-source aquifer material is of primary concern for imparting elevated concentrations of As and other oxyanion-forming trace elements to groundwater and affecting water quality in one of the most water-scarce areas of the USA.

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