Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions

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Abstract

Arsenic (As) concentrations as high as 179 $\mu\text{g/L}$, have been observed in shallow groundwater in the Alberta's Southern Oil Sand Regions. The geology of this area of Alberta includes a thick cover (up to 200 m) of unconsolidated glacial deposits, with a number of regional interglacial sand and gravel aquifers, underlain by marine shale. Arsenic concentrations observed in 216 unconsolidated sediment samples ranged between 1 to 17 ppm. A survey of over 800 water wells sampled for As in the area found that 50% of the wells contained As concentrations exceeding drinking water guidelines of 10 $\mu\text{g/L}$. Higher As concentrations in groundwater were associated with reducing conditions. Measurements of As speciation from 175 groundwater samples indicate that As(III) was the dominant species in 74% of the wells. Speciation model calculations showed that the majority of groundwater samples were undersaturated with respect to ferrihydrite, suggesting that reductive dissolution of Fe-oxyhydroxides may be the source of some of the As in groundwater. Detailed mineralogical characterization of sediment samples collected from two formations revealed the presence of fresh framboidal pyrite in the deeper unoxidized sediments. Electron microprobe analysis employing wavelength dispersive spectrometry indicated that the framboidal pyrite has variable As content with an average As concentration of 530 ppm, reaching up to 1840 ppm. In contrast, the oxidized sediments did not contain framboidal pyrite, but exhibited spheroidal Fe-oxyhydroxide grains with elevated As concentrations. The habit and composition suggest that these Fe-oxyhydroxide grains in the oxidized sediment were an alteration product of former framboidal pyrite grains. X-ray absorption near edge spectroscopy (XANES) indicated that the oxidized sediments are dominated by As(V) species having spectral features similar to those of goethite or ferrihydrite with adsorbed As, suggesting that Fe-oxyhydroxides are the dominant As carriers. XANES

spectra collected on unoxidized sediment samples, in contrast, indicated the presence of a reduced As species (As(-I)) characteristic of arsenopyrite and arsenian pyrite. The results of the mineralogical analyses indicate that the oxidation of frambroidal pyrite during weathering may be the source of As released to shallow aquifers in this region.

1. Introduction

Arsenic occurs in the environment in oxidation states of -III, -I, 0, III and V. In sulfide minerals such as arsenian pyrite [FeS_2] and arsenopyrite [FeAsS], As is in the As(-I) oxidation state (Campbell and Nordstrom, 2014). In natural groundwater, the most prevalent oxidation states of As are oxyanions of arsenite [As(III)] and arsenate [As(V)]. Aerobic waters are dominated by As(V) species whereas As(III) is the principal species in anaerobic environments (Nordstrom, 2002). Under circumneutral pH, both species have an affinity for Fe-oxyhydroxide surfaces, but because As(III) is not as strongly adsorbed, it is more mobile in reducing aqueous environments than As(V) (Dixit and Herring, 2003). Both As(III) and As(V) are toxic (Amend et al., 2014; Leybourne et al., 2014), with As(III) being 25-60 times more toxic than As(V) (Korte and Fernando, 1991).

After contamination of drinking water by pathogenic organisms, elevated As concentrations in groundwater is the second most recognized global health hazard in drinking water (Johnston et al., 2001; van Halem et al 2009). It is estimated that over 150 million people worldwide are exposed to concentrations of geogenic arsenic in drinking water that exceed the World Health Organization (WHO) limit of $10 \mu\text{g L}^{-1}$ (Nordstrom, 2002; Smedley and Kinniburgh, 2002; Mitchell, 2014). Although Bangladesh is one of the most recognized regions of As contaminated groundwater (eg. Nickson et al., 2000; Anawar et al., 2003; Harvey et al., 2006, Van Green et al., 2008; Jung et al., 2012), concentrations of As in groundwater exceeding WHO guidelines have been measured in over 70 countries on nearly every continent or major land mass (Barringer and Reilly, 2013).

Estimates of the population in Canada exposed to groundwater As concentrations exceeding the Canadian drinking water guidelines of $10 \mu\text{g L}^{-1}$ (Health Canada, 2012) are less

documented. However, naturally occurring As has been documented at concentrations that exceed these guidelines in all provinces and one territory (Table 1). In western Canada, elevated As concentrations are typically associated with igneous and metamorphic bedrock aquifers, and associated glaciofluvial and fluvial sediments (Boyle et al., 1998; Bolton and Beckie, 2011). In eastern Canada, elevated As concentrations have been associated with metasedimentary bedrock aquifers in New Brunswick and Nova Scotia (Bottomley, 1984), igneous bedrock aquifers in Newfoundland, and sandstone aquifers in Prince Edward Island (Somers et al., 1999). Across the Prairie provinces, elevated As concentrations in groundwater are typically observed in glaciofluvial sediments (Lemay et al., 2005; Thompson et al., 1999; Moore, 2005), although groundwater obtained from some wells completed in sandstone and shale aquifers (Cheung et al., 2009) and produced-water from deep oil-field wells (White et al., 1963; Moncur, 2010) have elevated As. Anthropogenic sources of As in groundwater have been reported in many parts of Canada near facilities for wood treatment, gold mining operations (Wang and Mulligan, 2006), waste pond seepage from hydrofluoric acid production and enhanced oil recovery using thermal steam injection methods (Fennell, 2008). For example, As concentrations up to 2050 µg/L were reported for groundwater down-gradient from a Au-mine tailings impoundment in NW Ontario (Ross et al., 1999).

Table 1. Examples of natural and anthropogenic occurrences of As in groundwater across Canada.

Location	Rock Type/Aquifer	Conc. $\mu\text{g L}^{-1}$	Reference
<u>Geogenic As source to groundwater</u>			
Bowen Island, British Columbia (BC)	Metavolcanic and metasediments with sulfides	1-580	Boyle et al., 1998
Langley, BC	Glaciofluvial/marine clay	<1-276	Cavalanti de Albuquerque et al., 2012
Southern West Coast, BC	Igneous bedrock with sulfides and fluvial sediments	<1-2440	Carmichael & Clarkson, 1995; Mattu & Schreier, 2000; Bolton & Beckie, 2011
Meager Creek, BC	Geothermal hot spring water	237-303	Koch et al., 1999
Lussier, Fairmont & Radium Hot Springs, BC	Geothermal hot spring water	92, 74-88, 234 (respectively)	Moncur, 2013 unpublished data
Alberta (AB)	Glaciofluvial/ sedimentary bedrock	<1-119	Fitzgerald et al., 2001
Cold Lake-Beaver River Basin, AB	Glaciofluvial	<10-361	Stein et al., 2000; Lemay et al., 2005
Southern Athabasca Oils Sands Region, AB	Glaciofluvial	<10-30	Lemay, 2003
Central AB	Glaciofluvial/sandstone	<1-780	AHW, 2000
South-Central AB	Cretaceous sandstone/shale	<1-165	Cheung et al., 2009
Ellis Pool, AB	Deep oilfield brine	230	White et al., 1963
Saskatchewan (SK)	Glaciofluvial	<1-117	Thompson et al., 1999
Birsay, SK	Glacial till pore water	3-99	Yan et al, 2000
Virden, Manitoba (MB)	Glaciofluvial	38-44	Moore, 2005
Ontario (ON)	Various	<2.5-68	Health Canada, 2006
Quebec (QC)	Not specified	<10-330	McGuigan et al., 2010
New Brunswick	Igneous and metasediment bedrock	up to 1050	Bottomly, 1984
Prince Edward Island	Permian sandstone	<1-26	Somers et al., 1999
Nova Scotia	Metasediment bedrock with sulfides	3-5000	Meranger et al., 1984
Newfoundland	Igneous and sedimentary bedrock	up to 769	Rageh et al., 2007; Serpa et al., 2009
Carcross, Yukon	Glaciofluvial	12-27	Dayton & Knight, 2010
<u>Anthropogenic As source to groundwater</u>			
Montreal, QC	Glaciofluvial-wood preservative	1-79	Zagury et al., 2003
Cold Lake Oil Sands Region, AB	Glaciofluvial-enhanced thermal recovery of bitumen operations	5-324	CNRL, 2005; Fennell, 2008
Amherstburg, ON	Carbonate bedrock-hydrofluoric acid production	up to 206	Windsor Star, 2006
Gold mine, Balmertown, ON	Sulfide mine tailings porewater-neutral rock drainage (NRD)	300-100,000	McCreadie et al., 2000
Zn-Cu mine, Sherridon, MB	Sulfide mine tailings porewater-acid rock drainage	<10-50,000	Moncur et al., 2005
Gold mine, Yellowknife, NT	Lake sediment porewater impacted by mining operation	16-947	Andrade et al., 2010
Gold mine, Bralorne, BC	Flooded underground mine workings - NRD	up to 5898	Desbarats et al., 2014

Elevated As concentrations have been reported in many small-scale groundwater investigations in the Cold Lake-Beaver River Basin (CLBR) in east-central Alberta, but previous

studies did not clearly identify the spatial extent of this groundwater problem or identify whether the elevated concentrations were due to natural geogenic sources, or anthropogenic activities. An early study by Nriagu (1998) sampled 51 residential wells and found that 40% of the wells had As concentrations exceeding Canadian drinking water guidelines of 10 µg/L. Follow up studies of residential wells in the CLBR basin by Alberta Health and Wellness (AHW 2000) and Stein et al. (2000), found that 50% of the 59 wells and 54% of the 35 wells sampled respectively, contained As concentrations in groundwater exceeding 10 µg/L. Lemay et al. (2005) was the first to map the distribution of As concentrations in groundwater across the CLBR basin spatially and within individual formations, but did not provide information regarding the number of wells exceeding drinking water guidelines for As. A study by AHW (2014) that surveyed 152 wells in the CLBR basin found that 48% of groundwater from residential wells contained As concentrations that exceeded guidelines, with As(III) as the dominant species. Javed et al. (2014) characterized sediments from the CLBR basin and observed both arsenian pyrite and arseopyrite. Arsenic was also found to be adsorbed to sediments and bound to crystalline oxide minerals. The objective of this investigation is the integration of existing and newly collected As groundwater data, including As speciation measurements, with major ion and trace element data to understand processes controlling the spatial distribution of As concentrations in groundwater across the CLBR basin and identify areas of concern. A second objective was to determine sources and potential controls of As mobility in groundwater using geochemical modeling and detailed solid-phase and mineralogical analyses from available aquifer sediments.

2. Study area

The Alberta portion of CLBR basin is approximately 22,000 km², located 400 km northeast of Calgary (Fig. 1). The basin encompasses a portion of the Southern Oil Sands Region and the

Cold Lake Oil Sands Region (Fig. 1). Agricultural lands cover one-third of the watershed. The area also includes considerable heavy oil and gas extraction, with numerous active energy wells (Fig. 1). Commercial scale thermal in situ oil sands projects are present west and northwest of Cold Lake. Groundwater is extensively used as a source of water in the CLBR region for industrial, agricultural, municipal, and domestic purposes (AESRD, 2013).

Fig. 1. Maps show (a) distribution of active energy wells, revised after Lemay (2005). (b) regional groundwater flow and the location of water wells (symbols are differentiated by geological formation) used in this study. Inset shows the extent of the oil sands and location of the Cold Lake-Beaver River Basin in Alberta, Canada.

3. Geological and hydrogeological setting

The general stratigraphy beneath the CLBR basin is comprised of 25 to 225 m of unconsolidated sediments with the basal deposits composed of Neogene sand and gravel overlain by alternating till and sand and gravel sequences of glacial Quaternary deposits (Fig. 2). A clay-till unit blankets most of the upper surface of the CLBR basin. These sediments unconformably rest on thick (> 200 m) Cretaceous organic-rich marine shale of the Lea Park and Colorado Group (Prior et al., 2013). Neogene and Quaternary stratigraphy of the area was mapped by Andriashek and Fenton (1989), Andriashek (2003), and Parks et al. (2005). Based on their observations and lithological description of each formation or unit, twelve distinct hydrostratic units were identified as regional aquifers and aquitards (Table 2).

Fig. 2. Cross-section, A-A' from Fig. 1b, showing the distribution of stratigraphic units across the Cold Lake-Beaver River Basin (revised after Parks et al., 2005).

Bedrock incisions from preglacial and glacial drainage has produced a network of buried paleovalley and buried glaciofluvial channel aquifers throughout the CLBR basin. As a result, regional groundwater flow in aquifers is constrained by surficial topography, deep surface water bodies, and bedrock topography (Parks et al., 2005). Recharge occurs in the uplands, particularly in the north, with discharge and flowing artesian conditions occurring in the low lands near the

confluence of the Sand and Beaver Rivers, eastern reaches of the Beaver River, and near some lakes (Fig. 1). Cold Lake is approximately 100 m deep and represents both a groundwater discharge site as well as a source of recharge for hydraulically connected aquifers (Fig. 2). In the deeper Empress aquifers, flow is laterally confined by bedrock barrier boundaries, whereas shallower aquifers tend to exhibit stronger influences from topography. Cross-formational flow between shallow and deeper aquifers occurs across till sheets mostly at hydraulic windows associated with cross-cutting sands and gravels deposited during glacial and more recent erosional events (Parks et al., 2005). In general, groundwater flow in all aquifers is downward along the flanks of the CLBR watershed and laterally directed towards the Beaver River downstream of the Sand River confluence, signifying a strong influence from surficial topography (Fig. 1).

Table 2. Physical properties of the eight formations in the CLBR glacial drift deposits (revised after Parks et al., 2005). N refers to the Neogene Period.

Quaternary Period	Formation	Lithology	Hydrogeology	Area (km ²)	Volume (km ³)	Thickness (m)
	Grand Center (GC)	till	aquitard	16,000	810	1 - 150
	Sand River (SR)	sand/silt	aquifer	5,000	13	1 - 85
	Marie Creek (MC)	till	aquitard	12,000	300	1 - 100
	Ethel Lake (EL)	silt/sand/gravel	aquifer	4,600	31	1 - 65
	Bonnyville Unit 2 (BNV2)	till	aquitard	12,700	310	1 - 150
	Bonnyville (BNV)	sand/gravel	aquifer	1,100	8	1 - 65
	Bonnyville Unit 1 (BNV1)	till	aquitard	5,200	78	1 - 95
	Muriel Lake (ML)	sand/silt/gravel	aquifer	4,800	65	1 - 50
	Bronson Lake (BL)	diamicton/clay	aquitard	3,200	34	1 - 100
	Empress Unit 3 (E3)	sand/gravel	aquifer	1,600	19	1 - 110
	Empress Unit 2 (E2)	clay/silt	aquitard	1,100	13	1 - 55
Z	Empress Unit 1 (E1)	sand/gravel	aquifer	2,200	22	1 - 55

4. Methods

4.1 Groundwater Chemistry

The majority of the groundwater geochemistry data used in this study was provided by Alberta Environment and Sustainable Resource Development that included data from the Alberta Water

Well Information Database (<http://environment.alberta.ca/01314.html>), AHW (2000), Beaver River Watershed Alliance database, and a number of industry studies. The groundwater database for the CLBR basin included 527,349 entries containing groundwater geochemistry and /or water levels. This database was filtered to remove entries where depth, or latitude and longitude were missing and geochemistry data with charge balance errors exceeding 10% and industrial monitoring wells that could potentially be impacted by enhanced thermal in situ oil recovery operations. Statistical analyses such as the median, mean, maximum, minimum, and standard deviation were determined for wells that were sampled multiple times. The final data set was reduced to 1537 wells with geochemistry including pH, alkalinity and major anion and cations, 779 of which also had As concentration data. Additional groundwater chemistry was added to the data set from AHW (2014) and this study to ensure the most completed data set was interpreted. Alberta Environment provided geochemistry data from their Groundwater Observation Well Network (GOWN), including radiogenic isotopes of $^{14}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{DIC}}$ and stable isotopes of $\delta^{34}\text{S-SO}_4$. In total 816 wells with As concentrations were used for mapping.

A total of 13 groundwater wells were sampled during this study using a peristaltic pump and 6.4 mm diameter (1/4-inch) polyethylene tubing. Sample tubing was lowered into the well screen and pumped at a low-flow rate following the method of Puls and Barcelona (1996). Water levels were periodically measured during pumping to ensure that no or minimal drawdown was occurring. Measurements of pH, Eh, temperature, electrical conductivity and dissolved oxygen (DO) were made in the field using a Hydrolab with probes sealed in a flow-through cell. All probes in the Hydrolab were calibrated prior to sampling. Water samples were collected when pH and Eh values stabilized. Water samples were collected for major anions and cations, trace metals, dissolved organic carbon (DOC) from each well. All water samples were filtered with

0.45 µm polyethersulphone filters and stored in prewashed Nalgene bottles. One aliquot of water was acidified with 12 N trace-metal grade HNO₃ to a pH of <1 for cation and dissolved metals analysis, and other aliquots were left unacidified. All water samples were immediately refrigerated at 4°C until analyses. Water samples were analyzed using inductively coupled plasma – optical emission spectrometry (ICP–OES) analysis for major cations, inductively coupled plasma-mass spectrometry (ICP-MS) for trace metals, and ion chromatography (IC) for anions. Combustion and infrared detection was used for DOC analysis. Measurements of alkalinity were made in the field on filtered samples using a Hach digital titrator and bromocresol green / methyl red indicator and 0.16 N H₂SO₄.

Maps showing the spatial distribution of As concentrations in groundwater were created using ArcGIS. Shape files for all geological formations in the CLBR basin were provided by the Alberta Geological Survey. Arsenic data was mapped by individual formations/aquifers. All formation units were mapped except the Bonnyville Unit 1 and 2, Bronson Lake, Empress 2 Formations and bedrock due to limited data points.

4.2 Arsenic Speciation

There was a much smaller subset of data with speciated As analysis available from groundwater, including the AHW (2014), the GOWN wells and this study. During the AHW (2014) survey, 132 groundwater samples were speciated into As(III) and As(V) at the University of Alberta by using a HPLC-ICP-MS following the methods of Le et al. (1998) and Gong et al. (2006). An additional 34 samples from the GOWN wells and nine from this study were speciated into As(III) and As(V) in the field using a modified anion-exchange method of Ficklin (1983) followed by ICP-MS analyses.

4.3 Geochemical Modeling

The geochemical model PHREEQC 2.18 (Parkhurst and Appelo, 1999) using the WATEQ4F (Ball and Nordstrom, 1991) database was used to elucidate mineral phases that may be controlling As concentrations in the groundwater. PHREEQC is an equilibrium/mass-transfer model that provides calculations of saturation indices (SI) for discrete mineral phases. To calculate SI for this study, the minimum parameters required from a groundwater sample included pH, Eh, alkalinity ($\text{mg L}^{-1} \text{CaCO}_3$), Ca, K, Mg, Na, SO_4^{2-} , Cl, Al, Fe, As and temperature. For wells with multiple sampling events, the most recent or most complete data set was used for modeling. In total, groundwater speciation calculations were made for groundwater samples collected from 605 wells. The computer program NETPATH (Plummer et al., 1994; Parkhurst and Charlton, 2008) was used to adjust $^{14}\text{C}_{\text{DIC}}$ groundwater ages.

4.4 Solid phase analyses and mineralogy

Solid phase concentrations of As in sediments from the CLBR basin were obtained from Andriashek (2000; n=175) and Fennell (2008; n=21). In addition, we analyzed 26 sediment samples for total metal concentrations using HF/ HNO_3 extraction followed by ICP–MS. Sediments were collected at two locations in the CLBR basin (Fig. 1b) using an auger drill rig equipped with a split-spoon sampler described by Moncur (2010). Sediment samples were collected every 0.25 m over the first 3 m of drilling followed by sampling at 0.5 m intervals for the remaining depths. Samples were collected from Site 1 and Site 2 to depths of 15 m and 13.5 m, respectively (Fig. 1b). After collection, samples were immediately frozen.

Samples for mineralogical analysis were shipped frozen to the laboratory where they were air-dried, de-agglomerated, homogenized and split into representative fractions. Eleven sediment samples were analyzed from Site 1, and four sediment samples were analyzed from Site 2. Primary crystalline phases were determined for all samples by X-ray diffraction (XRD)

using a RIGAKU D/MAX 2500 rotating-anode powder diffractometer. More detailed identification of individual phases in the secondary precipitates was made using a Rigaku Rapid II rotating anode micro-XRD. For some samples, mineral species identified by XRD were confirmed by energy –dispersive spectrometry (EDS) using a JEOL JXA 8900 electron probe micro-analyzer (EPMA) to provide qualitative information about the composition of the main mineral phases observed in the polished section. Backscattered electron imaging (BSE) and quantitative wavelength-dispersive X-ray spectrometry (WDS) were used to locate and determine the compositions of the main carriers of As. X-ray absorption fine structure spectroscopy (XANES) experiments were carried out at the bending magnet beamline 20-BM at sector 20 of the Advanced Photon Source (APS), Argonne, IL, USA. XANES was used to determine the oxidation states of As mineral phases in two sediment samples collected at 5.5 and 6 m depths at Site 1 and two sediment samples collected at 1 and 11.5 m depths at Site 2 (Fig. 1b). Finely ground and homogenized samples were loaded into Teflon sample holders with Mylar windows. Experiments were carried out at room temperature in the fluorescence mode using a Canberra 13-element detector. A Au foil was used for energy calibration for As K-edge XAFS measurements. Between five to eight scans were made on each sample. Data reduction and analysis were performed with ATHENA (Ravel and Newville 2005). The least-squares fitting assessment of the XANES spectra were performed with LSFITXAFS (Paktunc, 2004).

5. Results and discussion

5.1 Sources and controls of arsenic

Results of the solid-phase As analysis of sediments from the CLBR basin are summarized in Table 3. Whole rock analyses of 216 unconsolidated sediment samples indicate that the mean As concentration was 6 ppm (min = 0.3; max = 17). These As concentrations are in the range typical

for glacial deposits (average = 9; min = 2; max = 170) (Smedley and Kinniburgh, 2002). The mean As concentration measured from the eight Lea Park Formation marine shale samples was 17 ppm (min = 8.4; max = 20). Arsenic concentrations in the glacial drift sediments are relatively constant with depth for most locations (Fig. 3), with a few exceptions, including a sharp increase in concentration within the Lea Park marine shale and elevated concentrations at a few other locations. Marine shales typically contain the highest As content in the earth's crust, following gold ores (Nordstrom, 2012). Leckie et al. (1994) found that shales from the Lea Park Formation and Upper Colorado Group that underlie the CLBR basin contained abundant pyrite.

Table 3. Total As concentrations measured in sediments from the CLBR basin, including data from Andriashek (2000), Fennell (2008) and this study. All values are in ppm and BR refers to bedrock.

Formation	n	Median	Mean	Minimum	Maximum
Grand Center	64	6.4	6.7	1.2	17
Sand River	4	3.5	3.4	2.4	4.1
Marie Creek	71	5.6	5.9	3.2	14
Bonnyville	67	7.9	6.9	1.2	14
Muriel Lake	10	1.1	1.0	0.3	1.6
Lea Park (BR)	6	18	17	8.4	20
Total – Drift	216	6.3	6.2	0.3	17
Total – Drift + BR	222	6.4	6.5	0.3	20

Fig. 3. Depth profile of total As concentrations from five bore-holes in the Cold Lake – Beaver River basin. GC – Grand Centre; MC – Marie Creek; BNV – Bonnyville; and LP – Lea Park Formations. Data from Andriashek (2000).

The As-bearing sediments in the CLBR basin were glacially deposited, except for the Empress 1 and 2 Formations that were deposited prior to glaciation. During four glaciation

events, rock was eroded from the Canadian Shield, Cretaceous age marine shales and Devonian aged carbonates and transported and deposited in the CLBR basin (Andriashek and Fenton, 1989). Most of the sediments observed in CLBR basin sediments are composed of igneous and metamorphic fragments, shale and carbonates. The primary source of As within these source-rocks is likely sulfide minerals. Marine shale from the Colorado Group, that underlies much of the CLBR basin, contained 5 to 8 wt.% pyrite (Rokosh et al., 2009). During glaciation, these sulfide minerals would have been exposed to the atmosphere. Sulfide minerals are unstable when in contact with oxygen and will oxidize (Nordstrom, 1982). For example, the oxidation of pyrite and arsenopyrite can be expressed as:

The oxidation of pyrite (eqn.1) and arsenopyrite (eqn. 2) results in formation of secondary Fe-oxyhydroxide and the release of sulfate, arsenate and H^+ . The release of H^+ may reduce the porewater pH, however sediments from the CLBR basin have a high carbonate content (Andriashek and Fenton, 1989) maintaining a circumneutral groundwater pH through buffering. Although not shown in equation 1, pyrite is a common carrier of As (Nordstrom, 2002; Majzlan et al., 2014) and will release arsenic during oxidation. Under circumneutral pH and oxidizing conditions, arsenate will adsorb to Fe-oxyhydroxide mineral phases (Dixit and Hering, 2003).

As glaciation in the CLBR basin progressed, previously deposited sediments were buried by advancing glaciation and eventually water tables within the sediments were established, limiting O_2 diffusion into the sediments. In addition, the consumption of O_2 by microbial oxidation of organic carbon [CH_2O] will lead to anoxic conditions in the groundwater (Lovley,

1987). Under reducing conditions, As can be released to groundwater through reductive dissolution of arseniferous Fe-oxyhydroxides. During the reductive dissolution, Fe reducing bacteria consume CH_2O and utilize Fe(III)-oxyhydroxide as an electron acceptor for anaerobic respiration (Hansel et al., 2003). The reduction of Fe(III)-oxyhydroxide results in the release of Fe^{2+} , HCO_3^- and sorbed ions such as arsenate to the groundwater as demonstrated by Paktunc (2013) for the mobilization of arsenic as As(III) species following reductive dissolution of goethite in a tailings impoundment. Under reducing conditions, As(V) can be reduced to As(III) (Smedley and Kinniburgh, 2002; Mukherjee et al., 2012) resulting in increased concentrations and dominance of As(III) in groundwater. Arsenic reducing bacteria such as dissimilatory arsenate respiring prokaryotes catalyze organic carbon using As(V) as an electron acceptor (Zobrist, et al., 2000). The source of organic carbon in the sediments that can stimulate Fe/As reduction can be from plant material co-deposited with sediments and from DOC produced by plant or animal degradation and transported by groundwater flow. Another source of organic carbon is from glacially redeposited organic-rich shale fragments within the till matrix and thin interbedded fine grained layers within the sand and gravel. In place Colorado Group shale has a high total organic carbon (TOC) content ranging from 0.27 to 11.04 %, with the highest values in the Upper Colorado and Second White Specks (Tu et al., 2007). Other reactants that can promote arsenate reduction include hydrogen, hydrogen sulfide, elemental sulfur and methane (Amend et al., 2014).

In the presence of dissolved SO_4^{2-} , Fe(II) and As(III), reduction may be followed by microbially-mediated (dissimilatory) sulfate reduction (DSR) where sulfate-reducing bacteria catalyze the oxidation of CH_2O reducing SO_4^{2-} to H_2S (Berner, 1985). When H_2S is produced through DSR in the presence of available Fe(II) or other metals and metalloids, a secondary

sulfide mineral will precipitate (Berner, 1985). DSR decreases the concentrations of dissolved SO_4^{2-} , Fe(II), and other elements such as As(III), and increases alkalinity and pH in the groundwater (Tuttle et al., 1969; Buschmann and Berg, 2009). Significant isotope fractionation of sulfur enrichment is another important indicator of DSR (Mayer, 2005).

To determine if As-bearing minerals were present in the CLBR basin, a detailed quantitative mineralogical characterization of the sediments was performed in two areas of the watershed (Fig. 1b). Both sites were located where the Grand Centre Formation outcrops and were approximately 22 km apart. At Site 1 a borehole was drilled to a depth of 15 m, and at Site 2, a bore-hole was drilled to a depth of 13.5 m. Sediments were visibly oxidized to depths of 5.8 m and 4.9 m at Sites 1 and 2, respectively. The results of the XRD analyses revealed similar mineralogical compositions in the sediments from Sites 1 and 2, with the crystalline phases consisting mainly of quartz, microcline, albite, calcic plagioclase, calcite, and amphibole, with various amounts of clay minerals such as kaolinite, montmorillonite and mica. No obvious mineralogical differences in the XRD analyses were observed between the brown oxidized and grey unoxidized sediments.

Small pyrite grains, typically framboidal in habit were found throughout the unoxidized sediment samples at Sites 1 and 2 (Fig. 4a and b). Although the pyrite does not represent a major mineral phase, it is common throughout the samples. The textural features of the framboidal pyrite grains suggest that pyrite is a neo-mineral formed within the sediments post deposition. Considering that pyrite is a common As carrier (Nordstrom, 2002), 19 BSE images of individual grains were taken and their compositions were analyzed by WDS to determine whether As was a significant compositional component. The As content of pyrite in samples was variable, reaching 1550 ppm in a sample at Site 1, 6 m depth, and 1840 ppm in a sample from Site 2 at an 11.5 m

depth, with averages of 460 and 590 ppm, respectively (Table 4). The presence of As in the pyrite grains analyzed suggests that pyrite is an important As carrier in these sediment samples. None of the pyrite grains examined from the unoxidized sediments showed any evidence of oxidation features. Framboidal pyrite was not observed in the sediment samples from the oxidized zone (Site 1-1 m, and Site 2-1 m), but instead spheroidal Fe-oxyhydroxide grains with minor S and variable concentrations of As were observed (Fig. 4c and d). The habit and composition strongly suggest that these Fe-oxyhydroxide grains represent pseudomorphs after framboidal pyrite grains. The As concentrations of the characterized Fe-oxyhydroxide reached values up to 670 ppm in Site 1-1 m and 2270 ppm in Site 2-1 m with averages of 200 and 770 ppm, respectively (Table 4).

Fig. 4. BSE images of representative As-bearing mineral phases observed in sediment samples showing framboidal pyrite at; (a) Site 1, 6 m depth; (b) Site 2, 11.5 m depth. Secondary Fe-oxyhydroxide pseudomorphs after framboidal pyrite at; (c) Site 1, 1 m depth; (d) Site 2, 1 m depth.

Table 4. Arsenic concentration (ppm) of Fe(III)-oxyhydroxide [FeOOH] and pyrite grains in sediments from Sites 1 and 2, determined by WDS-EPMA.

Location	Site 1	Site 1	Site 2	Site 2
Depth	1 m	6 m	1 m	11.5 m
Mineral	FeOOH	Pyrite	FeOOH	Pyrite
Sediment	oxidized	unoxidized	oxidized	unoxidized

Sample 1	<100	<100	2270	<100
Sample 2	<100	180	440	780
Sample 3	<100	190	710	570
sample 4	280	470	400	410
Sample 5	320	<100	<100	184
Sample 6	370	790		<100
Sample 7	670	<100		320
Sample 8	380	1550		
Sample 9	<100	570		1760
Sample 10	<100	810		180

K-edge XANES spectra were collected to determine the valence state (-I, III, V) in which As occurs based on the location of the absorption edges. Arsenic can occur within the structure of arsenopyrite and pyrite as As(-I), which is susceptible to oxidation particularly in the framboidal types of pyrite (Paktunc, 2008). All of the sediments with elevated concentrations of As (4.3 to 7.4 mg/kg) had spectra with the main absorption peak centred at 11874.7 eV (dashed line) indicating that the dominant species was As(V) (Fig. 5). The spectral features above the edge in Fig. 5 were similar to those of goethite or ferrihydrite with adsorbed As (Paktunc et al. 2004; 2008), suggesting that these Fe(III)-oxyhydroxides are the dominant As carriers in the sediments with elevated As concentrations. The sediment samples at 5.5 and 6 m depths along bore-hole Site 1- 1 m representing oxidized and unoxidized sediments displayed similar XANES spectra dominated by As(V). The spectra collected for oxidized and unoxidized sediment samples from 1 and 11.5 m depths along the Site 2 bore-hole displayed differences in their As K-edge. The spectrum of unweathered sample from 11.5 m depth had a shoulder on the lower energy side of the main absorption peak suggesting the presence of reduced As(-I) species in addition to As(V) (Fig. 5). The derivative value of this shoulder is 11868.5 eV which is close to those of arsenopyrite and arsenian pyrite suggesting the presence of As(-I) species in addition to As(V). The presence of As(-I) species in the unoxidized portions of the sediments were consistent with the presence of sulfide minerals such as arsenian pyrite and arsenopyrite.

Fig. 5. Normalized As K-edge XANES spectra for sediment samples collected at; (a) Site 1, 5.5 and 6 m depths (c) Site 2, 1 and 11.5 m depths; and derivatives for samples from (b) Site 1 and (c) Site 2. Vertical line is at 11874.7 eV representing the main absorption peak for As(V) and 11868.5 eV in (d) representing As(-I).

Previous mineralogical analyses of sediments from the Muriel Lake Formation (Fennell, 2008) also indicated the presence of framboidal pyrite in the sediments. In this study, SEM-microprobe analysis of the pyrite detected the presence of As, but only qualitatively at low concentrations. XANES analysis of the sediments identified As(V) as the dominant species, with minor amounts of As(III) present.

5.2 Arsenic Distribution in Groundwater

Understanding the distribution of As concentrations in aquifers is crucial for determining the placement of wells for extraction of potable water and health-risk studies. Arsenic concentrations in groundwater varied spatially across the CLBR basin and within individual formations, with no obvious trends observed along groundwater flowpaths (Fig 6). Overall, there were no obvious distribution patterns of As in groundwater except for an area west of Cold Lake where As concentration in some wells are elevated in all formations except the Grand Centre Formation. The heterogeneous nature of glacially deposited sediments likely influences the random distribution of As in both solid and aqueous phases within the CLBR basin.

Fig. 6. Spatial distribution of As in groundwater across the CLBR Basin. Arrows show groundwater flow direction in each formation (modified after Parks et al., 2005). Grey shading indicates the extent of each formation. There was insufficient data to map groundwater flow in the Marie Creek and Bonnyville Formations.

The mean concentration of As in all glaciofluvial formation groundwaters was 15 µg/L, ranging between <1 to 179 µg/L, with 50 % of the wells exceeding 10 µg/L (Table 5). Arsenic concentration in groundwater were lowest in the uppermost Grand Centre Formation with only 17 % of the wells exceeding 10 µg/L, whereas concentrations were highest in the deeper Empress 3 Formation where 70 % of the wells were >10 µg/L. There were minimal differences in As groundwater concentrations between aquitard and aquifer units. For example, average concentration of As in groundwater between the aquitard and aquifer units in the Bonnyville and Empress Formations only differed by a few micrograms per liter. In general, As concentrations in groundwater increased with depth through the unconsolidated sediments. Within the underlying shale units, all seven of the wells sampled had As concentrations that were below 10 µg/L. It was previously suggested that elevated As concentration in shallow Quaternary aquifers in Alberta could originate from the underlying pyritic shales (AHW, 2000; Fitzgerald et al., 2001). However the low As concentrations in groundwater from these deep shales suggest that they are not directly contributing to elevated concentrations (Table 5). Nevertheless, if these shales were exposed to oxygen by over pumping of a well or if fragments of these shales are present in near-surface sediments, arsenian sulfide minerals could oxidize releasing As to the groundwater.

Table 5. Arsenic concentrations in groundwater from formations in the CLBR Basin.

Formation	n	Median µg L ⁻¹	Average µg L ⁻¹	Max. µg L ⁻¹	Min. µg L ⁻¹	Wells Exceeding 10 µg L ⁻¹	% Wells Exceeding 10 µg L ⁻¹	As(III)/As _T	
								(n)	%
Grand Center	149	3	6	70	<1	23	17	23	46
Sand River	79	8	12	61	<1	32	41	27	66
Marie Creek	101	8	11	160	<1	30	33	29	65
Ethel Lake	80	11	15	100	<1	41	51	21	82
Bonnyville Unit 2	33	10	17	110	<1	16	48	14	61
Bonnyville	75	11	14	70	<1	37	51	6	85
Bonnyville Unit 1	21	11	16	50	2.0	11	52	3	88
Muriel Lake	133	17	19	140	<1	89	67	25	82
Bronson Lake	14	22	21	70	<1	8	57	4	72

Empress Unit 3	71	18	19	86	<1	50	70	8	80
Empress Unit 2	10	10	16	100	5.9	5	50	-	-
Empress Unit 1	43	11	17	179	<1	25	58	15	84
Lea Park	2	3	3	3.1	2.9	0	0	-	-
Upper Colorado	3	4	3.3	4.4	2.0	0	0	-	-
2 nd White Specks	2	-	5	9	<1	1	0	-	-
Average Glacial	816	11	15	124		27	50	175	74

Groundwater from the CLBR basin has As(III) as the principal species, accounting for 80% of the As (Table 5). Groundwater from the Grand Centre Formation had the lowest As(III) ratio making up only 46 % of the As. Overall the As(III) ratio increased with depth. At depth, over 80 % of the groundwater from aquifer units contained As(III), whereas groundwater from till units had lower percentages of As(III)/As_T, except for the Bonnyville Unit 1 Till. The dominance of As(III) over As(V) in groundwaters from the CLBR basin indicates a strongly reducing environment.

Arsenic concentrations within groundwater from the CLBR basin appear to be strongly influenced by redox conditions. Arsenic concentrations increased as the Eh decreased, with the highest As concentrations associated with the lowest Eh values (Fig. 7). The groundwater samples from reducing environments with elevated As concentrations tended to have lower concentrations of SO₄²⁻ and Fe(II). The highest As concentrations were found in groundwater with circumneutral pH conditions and with alkalinities at approximately 600 mg/L CaCO₃. The average DOC concentrations in the groundwaters across the CLBR basin was 3.1 mg/L, but the highest As concentrations were found in groundwaters with about 5 mg/L of DOC. These average groundwater DOC concentrations are not particularly high, but even at low concentrations, OC (≤1%) in the sediments can promote microbially mediated reduction reactions (Héry et al., 2010). Geochemical modelling calculations indicated that 72 % of groundwater from the wells were at equilibrium or undersaturated with respect to ferrihydrite (Fig. 7). These calculations suggest that the primary mechanism for As release from the

sediments is the reductive dissolution of Fe-oxyhydroxides. In addition to the release of As, elevated concentrations of Fe would be expected during reductive dissolution of Fe-oxyhydroxides provided that the dissolution is congruent and the Fe species remains in solution. The correlation between As and Fe concentrations in the groundwater were not strong, except for the Bronson Lake Formation ($R^2 = 0.71$). All other As to Fe relations had a $R^2 < 0.26$. This poor correlation between As and Fe may be due to scavenging of Fe during siderite [FeCO_3] precipitation. Speciation model calculations found that 80% of groundwater for the wells was at equilibrium or supersaturated with respect to siderite. Siderite is below the XRD detection limit of several percent. If present, it would be in trace quantities in the sediment. Siderite precipitation will remove Fe(II) from solution and is known to be an effective sink for As in groundwater (Mumford et al., 2012), sorbing both As(III) and As(V) (Islam et al., 2005), with the sorption of As(III) being the weaker of the two oxidation states (Jönsson and Sherman, 2008). Ferric-oxyhydroxide phases were not identified in the unoxidized sediments during the mineralogical study, yet XANES experiments revealed that over 75% of the solid-phase As concentrations in the sediments was As(V), similar to observations by Javed et al. (2014) that observed 25 to 75 % of As in other areas of the CLBR basin sediments was bound in oxides. In other aquifers with elevated groundwater As concentrations, reductive dissolution of Fe-oxyhydroxides has been proposed as the principal process for As release from alluvial and glaciofluvial sediments, for example in Southeast Asia (Nickson et al., 2000; Fendorf et al., 2010), USA Midwest (Kelly et al., 2005; Erickson and Barns, 2005), China (Guo et al., 2013) and Alaska (Munk et al., 2011). Although the groundwater chemistry, speciation modeling and mineralogy all are consistent with the prevalence of reductive dissolution of Fe-oxyhydroxides in deeper sediments from the CLBR basin, competitive desorption by phosphate or silica (Manning

and Goldberg, 1996; Holm, 2002) or desorption from clay minerals cannot be ruled out as additional processes that may be contributing to As release to groundwater.

Fig. 7. The relationship between As concentrations in groundwater and various other aqueous parameters (top two rows). Plots in the bottom row show calculated SI values for arsenolite, ferrihydrite and siderite (near equilibrium conditions $SI = -0.4$ to 0.4 , are represented by the horizontal dashed lines). Symbols are representative of the different formations included in the dataset.

There are general trends in pH and Eh conditions related to depth and geological formation (Fig. 8). The most oxidizing conditions (Eh and DO) were observed at shallow depths, in the near surface zone of the Grand Centre and Sand River Formations. Groundwater from the Grand Centre Formation had the lowest pH values which corresponded to the highest concentrations of F, Cl, Si and Ca, Mg, U, and Fe. Chemical weathering occurring in the surficial sediments is likely releasing elevated concentrations of ions to the pore water which is displaced downward into shallow groundwater, which is consistent with the mineralogical analyses of the

near-surface Grand Centre Formation sediments that showed visibly oxidized sediments and the complete consumption of sulfide minerals in the weathered zones. Groundwater sampled from 1 m below the oxidized zone in the Grand Centre Formation contained a depressed pH and elevated concentrations of major ions in the groundwater. In addition to elevated major anions and cations, elevated concentrations of NO_3^- and DOC were present in the shallow groundwater (Fig. 8). The elevated concentrations of NO_3^- and DOC are likely from anthropogenic sources such as the application of fertilizers, feed lots, and sewage seepage from septic tanks and lagoons. Elevated DOC was also observed in deeper groundwater >100 m depth (Figure 8). The source of DOC at depth is likely organic-rich shale that is dispersed throughout the unconsolidated sediments.

Fig. 8. Depth profiles of groundwater chemistry from the CLBR basin. The vertical dashed lines represent maximum allowable drinking water limits.

In addition to biogeochemical redox reactions that release As from sediments, hydrogeologic properties of the aquifer material will influence groundwater flow and residence time, affecting As concentrations (Smedley and Kinniburgh, 2002). The ^{14}C and ^3H data indicate the Grand Center and Marie Creek Formations have the youngest groundwater ages (Table 6). Tritium was not detected in any of the samples from the Ethel Lake Formation or deeper,

indicating no evidence of post 1950's water in these samples. There was a wide range in ^{14}C ages for some of the formations, but in general groundwater ages increase with depth. The large range in ages in some formations (e.g. Empress Unit 1) are not surprising since the well locations are located along a flow path, and the oldest ages are associated with the more distal reaches of the formation. These long residence times of groundwater flow in the aquifers can influence As mobilization. For example, the average As concentration in groundwater from the Grand Centre Formation was $6\ \mu\text{g L}^{-1}$ with modern aged water signifying a short groundwater flow path and residence time. Conversely, the average As concentration in the Empress Unit 1 was $17\ \mu\text{g L}^{-1}$ with groundwater ages ranging between 25,000 to 3000 years before present, indicating a long groundwater flow path and residence time. The long groundwater flow path and residence time can allow As to accumulate in the groundwater to where concentrations become hazardous (Barringer and Reilly, 2013).

Table 6. Stable isotope and radiocarbon data from groundwater in the CLBR basin. NETPATH was used to correct groundwater ages. Number of wells sampled is represented by n. VCDT refers to Vienna Canyon Diablo Troilite.

Formation	Carbon				Tritium (T.U.)	Sulfur	
	n	$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB)	$^{14}\text{C}_{\text{DIC}}$ pMC	Corr. Age (years B.P.)		n	$\delta^{34}\text{S-SO}_4$ (‰ VCDT)
Grand Center	1	-15.2	78.6	Recent	10.2	2	-5.8
Sand River		-	-	-	-	1	-0.2
Marie Creek	2	-15.2 to -14.0	50.9 - 99	1700 - recent	<0.8 - 14.4	2	-1.1
Ethel Lake	4	-14.9 to -16.1	31.5 - 61.2	6200 - 1200	<0.8	2	-4.4
Bonnyville	1	-13.2	54.6	3700	<0.8	1	-6.2
Muriel Lake	3	-20.1 to -6.8	18.1 - 59.6	14000 - 800	<0.8	3	+0.2
Bronson Lake		-	-	-	-	1	-7.9
Empress Unit 3	2	-18.7 to -15.2	9.9 - 28.5	18000 - 6700	<0.8	4	+19.5
Empress Unit 1	7	-22.7 to -13.3	5.5 - 42.4	25000 - 3000	<0.8	8	-0.7

Sulfur isotope ratio determinations on the SO_4^{2-} ion is a valuable tool for determining sources of dissolved SO_4^{2-} in groundwater. Typical values of $\delta^{34}\text{S-SO}_4$ derived from sulfide oxidation range between -30 to +10 ‰ (Mayer, 2005). With the exception of the data from the

Empress Unit 3 Formation, the $\delta^{34}\text{S-SO}_4$ results for the other formations are consistent with SO_4^{2-} originating from the oxidation of pyrite (Table 6). The depleted isotopic composition of groundwater from the formations suggests the oxidation of sulfides during recharge and glaciation contributed to SO_4^{2-} concentrations and that earlier redox conditions in the formations were potentially oxic. Within the Empress Unit 3 Formation, the $\delta^{34}\text{S-SO}_4$ value in groundwater near the recharge zone was +13.8 ‰, with SO_4^{2-} and As concentrations of 42 mg L⁻¹ and 24 µg L⁻¹, respectively. Further down-gradient along the flow-path, $\delta^{34}\text{S-SO}_4$ showed significant enrichment to +36.2 ‰ corresponding to decreased concentrations of SO_4^{2-} and As of 1.3 mg L⁻¹ and 9.6 µg L⁻¹, respectively, suggesting that DSR is occurring in the Empress Unit 3 formation and potentially limiting As concentrations in groundwater.

5.3 Long-term arsenic variations

Long-term variability of As concentrations in groundwater were evaluated using data from repeat sampling of groundwater wells between 2001 and 2009 (Fig. 9). The database included time-series data for seven of the eight formations, with only data from the Bronson Lake Formation not available. The temporal variations in As concentrations in the formations were minimal, similar to what has been reported in other temporal studies (Ayotte et al., 2014). These small variations were observed in all formations. The largest variations of As were observed in the Ethel Lake and Empress Formations, although there did not appear to be any correlation in trends between the aquifers. There also did not appear to be strong seasonal variations in any of the formations as other studies have observed in groundwater from Vietnam (Berg et al., 2001), Bangladesh (Cheng, et al., 2005), Mongolia (Guo, et al., 2013) and the United States (Ayotte et al., 2014). The shallower wells (Sand River and Ethel Lake) showed slight increases in As concentrations, whereas the deeper wells (Bonnyville, Muriel Lake, Empress) exhibited slight

decreases. Long-term trends in As concentrations could not be determined for the Grand Centre or Marie Creek wells due to their limited <3 year dataset (Ravenscroft et al., 2006). It is reasonable to conclude that natural As concentrations in the groundwater from formations in the CLBR basin are not significantly variable over the long-term. However for wells where As concentration are near maximum drinking water guidelines, the variability of As concentrations in the groundwater could be large enough to be a potential long-term risk to human health.

Fig. 9. Temporal variation of As concentrations in groundwater from wells in eight aquifers within the CLBR basin between 2000 and 2010. Horizontal dashed line represents the As drinking water standard of 10 µg/L

6. Conclusions

Glacialfluvial aquifers of the CLBR basin contained widespread elevated arsenic concentration in groundwater with 50 % of the wells exceeding 10 µg/L. The distribution of As did not show

any obvious spatial patterns or trends along groundwater flow paths. Arsenic concentrations measured from groundwater in the underlying marine shale was $<10\text{ }\mu\text{g/L}$. Speciation of the arsenic found that arsenite, the more mobile and toxic form was dominant in most of the groundwater. The highest concentrations of As was associated with reducing conditions, circumneutral pH and lower concentrations of Fe and SO_4^{2-} . Speciation modeling showed that the majority of groundwater samples were undersaturated with respect to ferrihydrite. These relations suggested that reductive dissolution of Fe-oxyhydroxides may be the source of some of the As in the groundwater.

Arsenic concentrations in glacialfluvial sediment from the CLBR basin ranged from 1 to 17 ppm, with an average of 6 ppm. Mineralogical characterization of sediment samples revealed the presence of unoxidized framboidal pyrite in the deeper sediments with an average As concentration of 530 ppm, reaching up to 1840 ppm. In contrast, the near surface oxidized sediments did not contain framboidal pyrite, but exhibited spheroidal Fe-oxyhydroxide with elevated As concentrations, interpreted to be an alteration product of former framboidal pyrite grains. XANES indicated that the oxidized sediments are dominated by As(V) species having spectral features similar to those of goethite or ferrihydrite with adsorbed As, suggesting that Fe-oxyhydroxides are the dominant As carriers. In contrast XANES spectra collected on unoxidized sediment samples indicated the presence of a reduced As species (As(-I)) characteristic of arsenopyrite and arsenian pyrite. Ferric-oxyhydroxide phases were not identified in the unoxidized sediments during the mineralogical study, however XANES experiments revealed that over 75% of the solid-phase As concentrations in the sediments was As(V) suggesting that Fe reduction of Fe-oxyhydroxides could be the main source of As to the groundwater, consistent with modeling results. Within the near-surface sediments, mineralogical analyses indicate that

the oxidation of frambroidal pyrite during weathering may be the source of As released to shallow aquifers in this region. Understanding the distribution and form of As present naturally in aquifer material and groundwater in the CLBR is important for managing water resources in the region, including the location of domestic water wells to minimize the potential health risks of As exposure.

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