

OCCURRENCE OF ARSENIC IN THE RUSH  
SPRINGS SANDSTONE AND ITS IMPLICATIONS ON  
GROUNDWATER CHEMISTRY: CADDO COUNTY,  
OKLAHOMA

By

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## **Abstract**

Arsenic is considered highly toxic; ingestion causes toxic reactions ranging from skin lesions to cancer. Groundwater in some public supply wells within the Rush Springs Sandstone aquifer in Caddo County, Oklahoma contain arsenic concentrations that exceed the maximum contaminant level (MCL) of 10 µg/L established by the U.S. Environmental Protection Agency. The Rush Springs Sandstone is a Permian-age redbed sandstone that outcrops in western Oklahoma. Iron oxide, which is prevalent in the Rush Springs Sandstone, has been associated with arsenic and its potential release into the groundwater system.

To detect possible compounds that drive desorption, concentrations of metals and nonmetals were measured on three outcrops and three cores using a handheld x-ray fluorescence analyzer. Average arsenic concentrations in the Rush Springs Sandstone were 8.20 parts per million (ppm) in the cores and 7.62 ppm in the outcrops. These values fall into the upper range of background concentrations of arsenic in sandstone yet they are not remarkably high which is supported by the dissolved arsenic in the groundwater being above the MCL though still on the lower end 10.5-18.7 µg/L. Compounds coming from the groundwater and interacting with the rock is likely controlling the arsenic release. The common fertilizer nutrient phosphorus has been linked to reactions such as

this. A majority of Caddo County's water use is dedicated to irrigation of crops that would likely utilize these types of nutrients for farming.

Introduction of competing adsorbents such as phosphorus could cause arsenic levels to increase in the groundwater and decrease in the rock.

## **Introduction**

Naturally occurring arsenic is a potential health risk and is present in detectable concentrations in groundwater across the US and the world. For example, Bangladesh has reported concentrations up to 2500 µg/l, while natural waters in Mexico have reported concentrations of up to 620 µg/l (Nordstrom, 2002). In the United States, groundwater from wells in northern Ohio contain arsenic concentrations of up to 100 µg/l (Matisoff et al., 1982). Closer to home, concentrations of up to 124 µg/l have been reported in drinking water wells in central Oklahoma (Becker et al., 2010). Exposure to arsenic in drinking water has been linked to skin damage, problems with circulatory systems and may increase the risk of cancer (U.S. Environmental Protection Agency, 2001). In 2001, the EPA reduced the Maximum Contaminate Level (MCL) of arsenic in drinking water from 50 µg/l to 10 µg/l. This regulation change put many public water-supply systems at risk for exceeding the new MCL, including some in the Rush Springs Aquifer.

The issue of naturally occurring arsenic in groundwater is not new to Oklahoma. The Garber-Wellington Aquifer located in central Oklahoma supplies groundwater to Oklahoma City metropolitan area and has been the subject of intense study with regard to arsenic concentrations (Parkhurst et al., 1996; Christenson et al., 1998; Schlottmann, 2001). The highly oxidized red rocks that make up the Garber Sandstone, underlying Wellington Formation, and overlying Hennessey Shale are known natural sources of the reported dissolved arsenic. However, specific chemical conditions are required for its release into the groundwater. For example, in the Garber-Wellington Aquifer, aqueous pH plays an important role in arsenic release. Under alkaline conditions (pH > 8.5), arsenic is released from iron oxides such as hematite and goethite to which it is naturally adsorbed. Other factors such as the geologic framework of the aquifer (i.e. permeability, rock type, and stratigraphy) as well as water type play an important role in the release of arsenic and/or other constituents that affect groundwater chemistry.

The Rush Springs Aquifer is now subject to this same concern with respect to high levels of naturally occurring arsenic in the rocks that make up the aquifer as a potential source of dissolved arsenic in groundwater. Since the EPA enacted the lower MCL, a recent study found that five out of six groundwater samples collected from the aquifer exceeded the new standard, with measured concentrations ranging from 7.1 µg/l to 18.2 µg/l



(Becker et al., 2010; Table 1). In the 1990's, Becker (1998) characterized groundwater flow in the Rush Springs and modeled flow characteristics. At that time, some water quality sampling and chemical analysis was conducted. Nitrate concentrations were the main concern, although arsenic concentrations were also measured. However, at the time of the study the MCL for arsenic in drinking water was 50 µg/l, thus detailed reporting of concentrations below that threshold were not common (i.e., 'below detection limits' or 'below MCL' was often reported). Few studies have been conducted on the Rush Springs aquifer with respect to groundwater quality (Tanaka and Davis, 1963; Becker and Runkle, 1998; Becker et al., 2010). This is beginning to change with renewed interest in the area because of a greater public awareness of water quality and rates of consumption. It has been hypothesized that the factors that control the release of arsenic in the Garber-Wellington Aquifer are also operating in the Rush Springs Aquifer. Thus, to test the hypothesis that the Rush Springs Sandstone is the source of dissolved arsenic measured in public supply wells in Caddo County, this study was conducted. The goal of this study is to characterize the chemical composition of the Rush Springs Sandstone and determine its role in controlling the chemical composition of the groundwater that flows through it.

## **Description of study site**

The Rush Springs Aquifer is located in Western Oklahoma (Figure 1). It is approximately 2,400 square miles and is bound by the Canadian River to the north, the Washita River to the west, and erosional boundaries in the east and south (Becker and Runkle, 1998). The aquifer extends into ten counties, although the largest extent of the aquifer lies in Caddo County. Caddo County is also the most populous area located within the extent of the aquifer. Thus, this study was limited to only this county. The primary land use in Caddo County is agriculture, with the top crop items being wheat, pasture land, sorghum, corn, and soybeans (2007 Census of Agriculture). The annual average precipitation in Caddo County is 32.13 inches and the average annual temperature is 61 degrees F (Oklahoma Climatological Survey, data from 1971 to 2000).

### *Geologic Setting*

The Rush Springs sandstone is a late Permian formation of Guadelupian age within the Whitehorse Group. It is a well-sorted, fine-grained, poorly-cemented "Red Bed" that is generally massive with frequent sections of cross-bedding. The red coloring of the "Red Bed" Rush Springs is due to the presence of iron minerals, generally hematite, that stains and coats the individual sand grains (Suneson and Johnson, 1996). When the section is present in its entirety it can be over 300 feet

thick. The regional dip of the Rush Springs Sandstone is 20 feet per mile to the south-southwest (Becker and Runkle, 1998). The depositional setting has been described as a nearshore marine environment associated with eolian formations (MacLachlan, 1967; Poland, in prep). Remnants of ancient dunes and dune structures are apparent across Caddo County (Poland, in prep).

The Marlow Formation, which is also part of the Whitehorse Group, underlies the Rush Springs Sandstone. It consists of interbedded sandstones, siltstones, mudstones, gypsum and dolomite. When the entire section is present, its thickness is 90 to 100 feet (Becker and Runkle, 1998). Overlying the Rush Springs Sandstone is the Permian Ochoan-aged Cloud Chief Formation, which is a massive gypsum interbedded with reddish brown shales and siltstones (Becker and Runkle, 1998). The Permian-aged Whitehorse Group Weatherford bed lies between the Rush Springs Formation and the Cloud Chief Formation, when present. It is an intermittent dolomitic/gypsiferous sandstone that creates the erosion-resistant caps on many of the buttes in northwestern Caddo County (Suneson and Johnson, 1996).

### *Hydrology*

The Rush Springs Aquifer is unconfined in Caddo County, though it becomes confined in Custer and Washita Counties to the northwest

where it is overlain by the Cloud Chief Formation (Becker and Runkle 1998). Within Caddo County the groundwater flows into streams that down cut into the Rush Springs Aquifer and intercept the water table, flowing from high altitudes to low altitudes. The aquifer porosity averages 32 percent, specific yield is 25 percent, and permeability is about 30 gallons per day per square foot (Tanaka and Davis, 1963). Yields within the aquifer are generally high, some irrigation wells will produce more than 1,000 gallons per minute (Becker et al., 2010). Fifty-two million gallons are withdrawn from the Rush Springs aquifer daily (Tortorelli, 2009). Sixty-six percent of the groundwater withdraws are for irrigation, 15 percent for public supply, and 19 percent for livestock and other uses (Tortorelli, 2009). Recharge in the aquifer is primarily due to precipitation and it discharges through streams, seeps, and rivers, mainly the Washita River (Becker and Runkle, 1998). The dominant water type in the Rush Springs Aquifer is calcium-sodium bicarbonate and the species of arsenic found in the groundwater is arsenate (As(V); Becker et al., 2010). Arsenic speciation strongly effects its solubility, reactivity, bioavailability and toxicity. Arsenate is thought to be the least toxic of the dissolved arsenic species, though it is still very harmful when ingested (Vaughan, 2006).

## *Arsenic*

Arsenic is the 74<sup>th</sup> most abundant element out of the 88 that are naturally occurring on Earth (Vaughan, 2006). It can occur in many different mineralogical assemblages and geochemical settings and is derived from many anthropogenic sources. Arsenic will mainly bond with oxides and sulfides to create such minerals. For example, realgar (AsS), orpiment (As<sub>2</sub>S<sub>3</sub>), arsenolite (As<sub>2</sub>O<sub>3</sub>), and johnbaumite (Ca<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>(OH)) are the most common arsenic minerals (O'Day, 2006). Arsenic is also present in volcanic gases and is a constituent of geothermal waters (Hem, 1989). Arsenic can exist in two different valence states: arsenite, As(III) and arsenate, As(V). In aqueous solutions, arsenite tends to be more stable in reducing conditions while arsenate has greater stability under oxidizing conditions (O'Day, 2006). Dissolved As (V) generally occurs as the arsenate ion (AsO<sub>4</sub><sup>3-</sup>). Of the two species, arsenite is slightly more toxic than arsenate (Vaughan, 2006). The arsenate and phosphorus (PO<sub>4</sub><sup>3-</sup>) ions are interchangeable in many of naturally-occurring oxide mineral assemblages (O'Day, 2006).

Arsenic is present in many hydrologic systems due to anthropogenic activities, such as wood preservation, pesticide application, glass production, and runoff of livestock feeds (Welch et al., 2000). It is also a byproduct of the burning of coal and smelting of ores (Hem, 1989).

Although the use of arsenic in many of these applications is outdated, the influence that they had on groundwater chemistry and ultimately the surrounding rocks and sediments could be substantial. For example, past use of arsenic-containing livestock feeds could represent the source of arsenic now found in sediments, although such feeds are no longer used. Mining can be an important factor in arsenic-influenced systems. The arsenic associated with pyrite in areas mined for gold may become mobile during the mining processes (Welch et al., 2000), which could cause elevated levels in the surrounding groundwater/surface water systems.

### *Agriculture*

Farming is a major use of water and land in Caddo County. In years past, peanuts were the main crop but because of economic factors, crops such as sorghum and wheat are now the dominate product. As in most other heavily farmed areas concerns about fertilizers and pesticides penetrating the groundwater or running off into the streams are always present. For example, Becker and Runkle (1998) reported dissolved nitrate concentrations of 14.3 mg/L, exceeding the MCL of 10 mg/l. Fertilizer runoff is not the only cause of the elevated nitrate levels, since human and animal waste can also be sources (Power and Schepers, 1989). However, many agricultural fertilizers contain other nutrients, such as

phosphorus and potassium. Of these, phosphorus is most important with respect to the behavior of arsenic in surface environments. If phosphorus is introduced into the groundwater system the interaction with soil and/or sediments that have adsorbed arsenate release that arsenate through ion-exchange reactions. Thus, phosphorus is removed from water, but arsenate is released (Melamed et al., 1995). Since the Rush Springs Aquifer is fairly shallow, has known communication with streams, and produces sandy soils nutrient runoff could potentially be an important issue for water quality (Wiederholt and Johnson, 2005), and ultimately arsenic release from the Rush Springs Sandstone. Phosphorus levels have never been reported for the Rush Springs aquifer.

## **Materials and Methods**

### *Site Selection and Sampling*

Six cores penetrating the Rush Springs Sandstone were collected by the US Geological Survey over twenty years ago to be used in conjunction with an aquifer modeling study by Becker (1998). This study utilized three of those cores (core 2, 4, and 5) in order to determine the chemical composition of the Rush Springs Sandstone in Caddo County with respect to arsenic. The locations for cores 2, 4, and 5 are shown on Figure 2, along with an outline of the aquifer dimensions. Each core was stored in ten foot boxes, and slabbed through those intervals where it was neither too

wet nor unconsolidated to be cut. The cores were measured and described (Figure 3-5). The cores were analyzed via XRF at three-foot intervals due to the homogeneous nature of the sandstone. Each analysis spot was scraped to obtain a fresh surface and marked in case additional analyses would be required.

Additionally, three exposed outcrops were also measured and analyzed for their geochemical composition. The measured lithologies are shown in Figure 6-8. Outcrops were chosen based on accessibility, location in the county, and amount of exposure of the Rush Springs Sandstone. The intervals for analysis were chosen to maintain a sampling interval that was comparable to the cores. XRF analyses were taken every four feet on the largest outcrop (1). However, after correcting the true height for the dip angle using a Jacob staff, the intervals were actually only 2 feet. Thus, XRF measurements on the remaining two outcrops (2 and 3) were also taken every two feet because of their relatively short exposure (~10 ft). Again, given the homogeneity of the Rush Springs Formation, such a large sampling interval is likely not an issue.

#### *X-ray Fluorescence*

A suite of elements (As, Fe, Si, S, Ca) were measured using a handheld Thermo Scientific Niton X-ray fluorescence (XRF) analyzer and are reported in Table 2. This instrument is designed to measure samples in-



situ—no sample collection is required. Samples were analyzed for a total of 4 minutes. A pressed powder sample of the USGS SCo-1 standard was analyzed for quality control during each sample run. Replicate analyses of standards yielded standard deviations (1s) that range between 6 and 21% of the mean (Table 2). Calibration factors were calculated for each element of interest by comparing the known values of the USGS SCo-1 standard and the average of the measured values. The calibration factors were then applied to the measured concentrations for each sample. Replicates of analyses for USGS SCo-1 generally agree within 10-20 %. XRF results are plotted against depth in the cores in Figures and for the outcrops in Figures 3-8.

## **Results**

After the XRF data was collected for the Rush Springs Sandstone the data was plotted along depth and corresponding metals were plotted against one another to observe relationships and any anomalous values. The main relationship analyzed is that of arsenic and iron. Iron oxide has a strong affinity for adsorbing dissolved arsenic (Korte, 1991: Fig. 9). Each core and outcrop were described and plotted into geologic lithologic logs (Figs. 3-8). Overall, very little difference was observed between the cores and outcrops. The major difference observed was the types of cements present and the degree of cementation. There were sporadic

shifts in cements throughout the cores and outcrops, calcite and gypsum were the main cements. Calcite was detected via effervescence with dilute HCl. Gypsum was detected by observations of its characteristic "sheen". The cores ranged from approximately 270 to 400 feet in length while the outcrops were much smaller due to accessibility, ranging from 10 to 40 feet tall. Nearly all of the sections observed in this study of the Rush Springs Sandstone were described as cross-bedded sandstone. All three cores penetrated the underlying Marlow Formation, where gypsiferous mudstones and shales were encountered.

The cores had an average arsenic concentration of 8.20 ppm (range: 6.18 - 14.89 ppm) and an average iron concentration of 1.07 wt % (range: 0.05 - 5.48 wt %). Overall, there was very little variation in concentrations with depth, with the exception of an anomalous spike in arsenic (14.89 ppm) in Core Two at 121 ft (Fig. 3A). There were no observed lithologic changes in this interval: the cement and grain-size was the same throughout the core although there is also a significant decrease in silica at this interval as well indicating a possible grain size or grain composition change. No concentration this high was observed in either of the other cores, although a slight increase in As concentrations does appear to occur in Cores Four and Five (Fig. 4 and 5). At depths of 121-123 ft, As concentrations increase to 9.84 ppm in Core Four and 10.19 ppm in Core Five, respectively. In Core Two, the highest concentration

was 97% higher than the concentrations in the over- and underlying analyzed intervals.

The average arsenic concentrations in the outcrops were 7.62 ppm (range: 6.89- 8.51 ppm) and the average iron concentration was of 0.66 wt % (range: 0.36 -1.32 wt %). The depth-trends of As and Fe closely follow each other indicating that the arsenic present is most likely naturally occurring and associated with the iron oxides (Fig. 6-8). This is also apparent in the cross plots of As v. Fe (Fig. 9), with nearly an  $R^2$  value close to one for each their relationship is clearly visible.

Sulfur and calcium concentrations were examined in Core Two as indicators for the presence of gypsum beds or cements. The concentrations of sulfur range from 0 - 3.4 wt % and calcium range from 0.06 -7.3 wt %, respectively. Changes in silica concentrations were utilized as proxies for changes in rock type from quartz-rich sandstones versus beds that were more dominated by clays. Si concentrations range from 1.3 - 2.8 wt % (Fig. 3B).

## **Discussion**

### *Arsenic in Sandstones*

Baseline concentrations of arsenic in sandstone range greatly. Welch et al. (1988) report concentrations in sandstones in the western

United States ranging over an order of magnitude, from 0.6 ppm to 9 ppm. Smedley and Kinniburgh (2002) report average concentrations of arsenic in sandstones in this range (4.1 ppm). The Rush Springs Sandstone is characterized by its reddish color, due to the presence of iron oxide coatings on the sand grains. Consequently, one might expect the average arsenic concentration in this unit to be near the top of the previously reported ranges. Smedley and Kinniburgh, (2002) report the range of arsenic concentrations in iron-rich sediments as 1-2900 ppm. The definition of "iron-rich" means that the average concentration is at least 15 wt. % (James, 1966). Thus, despite its red color, the Rush Springs Sandstone does not fit this criterion.

Taken together, these observations suggest that the measured arsenic concentrations in the Rush Springs Sandstone are likely the result of natural diagenetic processes, and not the result of anthropogenic processes (e.g., past use of As-containing animal feeds). They are not anomalous with respect to previously reported concentrations in other sandstone units. However, given that the reported arsenic concentrations in the Rush Springs Aquifer waters are only slightly elevated relative to the MCL, the rocks could still be the source of this arsenic. Possible mechanisms by which low levels of As could be mobilized from the Rush Springs Sandstone are described below.

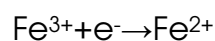
## *Mechanisms for Mobilization*

According to Smedley and Kinniburgh (2002) there are two main mechanisms that cause arsenic release from rocks: 1) the development of pH values exceeding 8.5 and 2) the presence of strongly reducing conditions. There are also lesser understood mechanisms, such as the effects of competing ions, such as phosphate (O'Day, 2006).

Arsenic stays very tightly adsorbed onto oxide minerals when pH is near neutral (Waychunas et al., 1993) and will remain so until the system is perturbed and pH increases to values above 8.5 (Smedley and Kinniburgh, 2002). This is due to the change in net surface charge of the iron-oxide from positive to negative as the pH increases above the zero-point-of-charge (Hinkle and Polette, 1998). The arsenic becomes mobile and can cause widespread contamination issues, especially when flushing rates are slow and dilution is low, such as in a confined system. Groundwater pH values can be elevated to alkaline conditions through several processes such as long residence time (Hinkle and Polette, 1998), silicate weathering (Ujević et al., 2010), and ion exchange (Parkhurst et al., 1996). Of these, ion exchange is most likely to occur under natural conditions, such as those found in the Rush Springs Aquifer. Ion exchange occurs when a geologic unit has a high capacity for cation exchange, typically because it is relatively rich in clay minerals. Ion exchange

reactions with the clays will occur, in which dissolved calcium and magnesium will substitute for sodium adsorbed to the clays (Parkhurst et al., 1996). This exchange leads to an under saturation with respect to carbonates. Thus, this will lead to increased dissolution of carbonate minerals, which can lead to an increase in aqueous pH (Parkhurst et al., 1996). Such an increase in pH can then lead to increased desorption of As from iron oxides in the surrounding aquifer.

The other most commonly-invoked mechanism for arsenic release is the presence of reducing conditions. The most common cause of a reducing environment is very rapid accumulation of and burial of organic-matter-rich sediments (Smedley and Kinniburgh, 2002). Respiration of the organic matter consumes dissolved O<sub>2</sub>, and if the rate of respiration is faster than the rate of oxygen resupply through diffusion, reducing conditions will result. Anoxic conditions in groundwater lead to the reduction of Fe(III) present in iron oxide minerals through either 1) microbially catalyzed iron reduction or 2) through thermodynamically-driven reductive dissolution. In either case, the end result is the dissolution of iron-oxyhydroxides and the subsequent release to groundwater of both Fe<sup>2+</sup> and any ions that were sorbed to the minerals, which includes As (Nickson et al., 2000). Half-reaction in which iron is reduced:



However, under reducing conditions, the arsenic itself will also be reduced from +5 (arsenate) to a +3 (arsenite) valence state (Hinkle and Polette, 1998). Arsenite is adsorbed to a lesser degree than arsenate (Welch et al., 2000; Hinkle and Polette, 1998), thus there is a potential for relatively high arsenite concentrations to persist despite common remediation techniques i.e. allowing oxidation, precipitation, and settling of the iron and in turn the arsenic that is attached to the iron (Chowdhury et al., 1999).

The last mechanism is the introduction of a competing ion into the system. For example, phosphorus is very similar to arsenic, in terms of atomic size, number of valence electrons and its ability to form several complex oxide ions (O'Day, 2006). Both As(V) and P(V) form complex ions with oxygen in a tetrahedral arrangement (arsenate,  $\text{AsO}_4^{3-}$  and phosphate,  $\text{PO}_4^{3-}$ ). Phosphorus is a common nutrient in fertilizers and a byproduct of fecal matter, both of which can be common in an area that is mainly cropland and farms. When arsenic (as arsenate) is deposited simultaneously with phosphorus it generally stays much more mobile than it would without the phosphate present (Melamed et al., 1995; Jain and Loeppert, 2000; O'Day, 2006). An example of this type of setting was analyzed by Campos (2002). It was suggested that arsenic and

phosphorus was introduced into the soil and subsequently into the groundwater through phosphate fertilizers that were derived from phosphate rock that also contained arsenic thus introducing both with a single application. This simultaneous application was causing the phosphorus to be preferred over the arsenic for adsorption and subsequently causing arsenic levels to be elevated in the groundwater. There is also a preference for phosphorus adsorption over arsenic when phosphate is introduced into a system that already has arsenate adsorbed on oxides (Welch et al., 2000). In a study done by Kent and Fox (2004) it was found that As(V) adsorbed to Fe oxide responds to the introduction of phosphate under oxic to sub oxic conditions at a pH of 5-7 causing a competition for adsorption sites and resulting in the preference of phosphate and the release of arsenate. In a lab experiment within this study it was found that the adsorbed phosphate comprised greater than 90 percent of the total phosphate analyzed (Kent and Fox, 2004).

Applying such mechanisms to the Rush Springs Aquifer is difficult. The measured pH in groundwaters throughout the study site is near neutral (7.3; Table 1) ruling out pH-dependent reactions which occur under alkaline conditions. Also, given the geology of the Rush Springs Sandstone, there is little opportunity for cation exchange to occur and cause such shifts in pH—there are no clays present in the Rush Springs Sandstone. The very high dissolved oxygen content in the groundwater



(Table 1) does not support the presence of a reducing environment. There is no organic carbon present in the Rush Springs Sandstone. Eliminating the more common causes of arsenic desorption from this system the arsenic mobility is likely caused by one of the lesser known mechanisms.

Assuming that the arsenic measured in the public supply wells in Caddo County is coming from the Rush Springs Sandstone, it is likely being mobilized through a competing ion mechanism, with phosphorus being the most likely competitor. It is known that farming has affected the groundwater in the Rush Springs Aquifer. For example, mean nitrate concentrations of 14.3 mg/L were previously reported by Becker and Runkle (1998). This exceeds the Environmental Protection Agencies maximum allowable level of 10 mg/l. While dissolved phosphorus concentrations have not been measured in these waters, it is very likely that they are present through the same mechanisms that lead to high nitrate concentrations (e.g., runoff of fertilizers, etc.). Low levels of phosphorus input to the system could lead to desorption of arsenic from the Rush Springs Sandstone, leading to the slightly elevated concentrations observed by Becker et al. (2010). In Kent and Fox (2004), an average of 1.0 mg/L of phosphorus led to an average dissolved As concentration of 2.2 µg/L. Therefore, since we have As concentrations of 10.5-18.7 µg/L, it is possible that phosphorus concentrations are

significantly higher within the Rush Springs Aquifer. Agriculturally treated soils are a significant source of phosphorus; Campos (2002) reports a value of 518.0 ppm of P in a fertilizer treated soil. Such value is likely to lead to increased phosphorus in water that comes in contact with the soil i.e. runoff.

### *Comparison to the Garber-Wellington Aquifer*

In the Garber-Wellington Aquifer, which is East of the Rush Springs Aquifer, pH and dissolved oxygen play an important role in arsenic release. The Garber-Wellington Aquifer is also Permian in age and shares a similar "red" appearance as the Rush Springs. However, the Garber-Wellington is older and has more geologic variation vertically and horizontally than the Rush Springs. The Garber-Wellington consists of siltstone and mudstone interbedded with cross-bedded sandstone and sandstone lenses (Christenson, 1998). The arsenic contamination of the groundwater in the Garber-Wellington is fairly well understood, because it provides water for a much more populated area than the Rush Springs Aquifer. Also, the measured dissolved arsenic concentrations were well above the MCL (22-124  $\mu\text{L}$  (Becker et al., 2010). In the Garber-Wellington Aquifer, there are areas where the pH exceeds 8.5, but the dissolved oxygen stays at high levels (8.6 –10.7 mg/L). Even though reducing conditions are not realized, the alkaline conditions lead to dangerously

high dissolved arsenic concentrations. The alkaline conditions are caused by ion exchange reactions with the clays, the sodium ions from the clay exchange with the calcium and magnesium in the water which then under saturates the water with respect to Ca and Mg (Parkhurst et al., 1996). This leads to dissolution of the dolomite present deeper in the aquifer. However, the extent of this mechanism is limited by the availability of clays and the decreased solubility of carbonate minerals at pH values above 8.5 (Schlottman, 2001).

Preliminary discussions have suggested that due to the gross similarity of lithologies between the Rush Springs Sandstone and the Garber-Wellington Formation, these same mechanisms may lead to the slightly elevated arsenic concentrations reported for the Rush Springs Aquifer. These geologic concerns are mainly caused by the presence of the Marlow Formation beneath the Rush Springs Formation. The Marlow Formation is abundant in clay minerals and some wells within the aquifer were drilled deep enough that Marlow Formation may be contributing, minimally, to the groundwater and its chemistry. However, while the Marlow Formation mainly acts as a confining unit for the Rush Springs Aquifer (Becker and Runkle, 1998), it is possible to get water from the formation. This water has been reported as being of very poor quality and "gyppy" (Tanaka and Davis, 1963). The data collected by Becker et al. (2010) showed that the deeper (320-375 ft) wells produced water that was

slightly higher (15.7-18.2  $\mu\text{g/l}$ ) in total dissolved arsenic than the other (10.5  $\mu\text{g/l}$ ). This observation could be indicative of possible hydraulic communication between the Marlow Formation and the Rush Springs Aquifer. The arsenic concentrations in the Marlow Formation are higher than those in the Rush Springs Sandstone (Fig. 3A, 4, and 5). This difference is likely a result of grain size differences between the Marlow, which is very fine sand and silt, and the Rush Springs, which is fine sand. The smaller grains in the Marlow give a greater surface area for the iron to cover thus a greater area for the arsenic to adsorb onto. The clay-sized particles in the Marlow Formation are not responsible for a pH-increasing ion exchange reaction as in the Garber-Wellington, since pH values measured in the the Rush Springs Formations are only 7.2-7.4. Also, there is no dolomite present in the Rush Springs and little in the Marlow Formation to act as a source of excess calcium or magnesium. In order to determine better how the Marlow affects the groundwater in the Rush Springs Aquifer samples would need to be acquired throughout a well that is known to penetrate the Rush Springs Sandstone along with the Marlow Formation. However, the data from this study does not support this possibility well, and an additional mechanism must be considered.

## Conclusions

Arsenic concentrations measured in core and outcrop samples of the Rush Springs Sandstone ranged from 6.89 -14.89 pp. While not remarkably high, they are still at or above the top of the range of previously reported arsenic concentrations in other sandstones. These findings agree with the previously reported values of dissolved arsenic in the groundwater. They exceed the EPA's MCL for arsenic of 10 µg/l ranging from 10.5 – 18.7 µg/l. Even though concentrations are not as high as other areas such as Bangladesh, it is still vital to understand where and how the arsenic is being introduced into drinking water. The most common explanations for desorption of arsenic from oxides, increased pH (> 8.5) and a reducing groundwater environment are not applicable to the Rush Springs Aquifer. Thus, the mostly likely mechanism causing the arsenic to be released into the groundwater system is a competing ion reaction. In this case phosphorus is the most likely ion to compete with arsenic for adsorption to iron oxides in the Rush Springs Sandstone. Widespread application of fertilizers on the vast cropland in Caddo County is a likely source for a nutrient, such as phosphorus, to be introduced into the groundwater system.

In order to prove that this is the mechanism for arsenic mobility, extensive groundwater sampling will have to be conducted and analyzed

for nutrients such as phosphorus. Along with this, other studies should be conducted in order to truly understand the geochemical processes that are taking place in the Rush Springs Aquifer. Some being, down hole sampling of groundwater where the well is known to penetrate the Marlow Formation, soil sampling and analysis from agricultural areas for arsenic and phosphates, and water quality sampling along the small streams that are in communication with the aquifer. Finally, expanding the study area to the entire aquifer would provide much more insight into the workings of this aquifer system.

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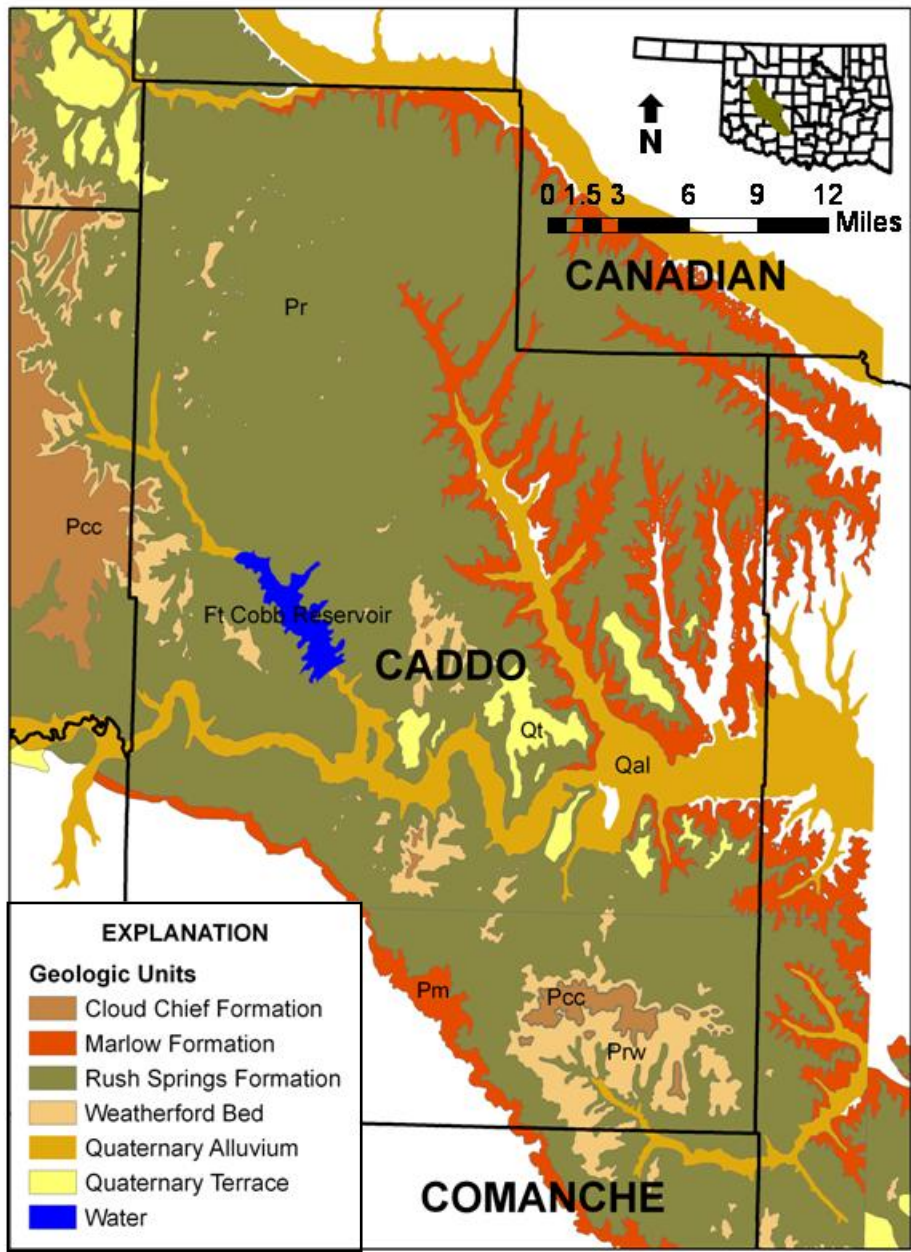


Figure 1. Map of Caddo County displaying geologic units within the boundaries of the Rush Springs Aquifer (geology from Heran et al, 2003, aquifer outline from Becker and Runkle, 1998).

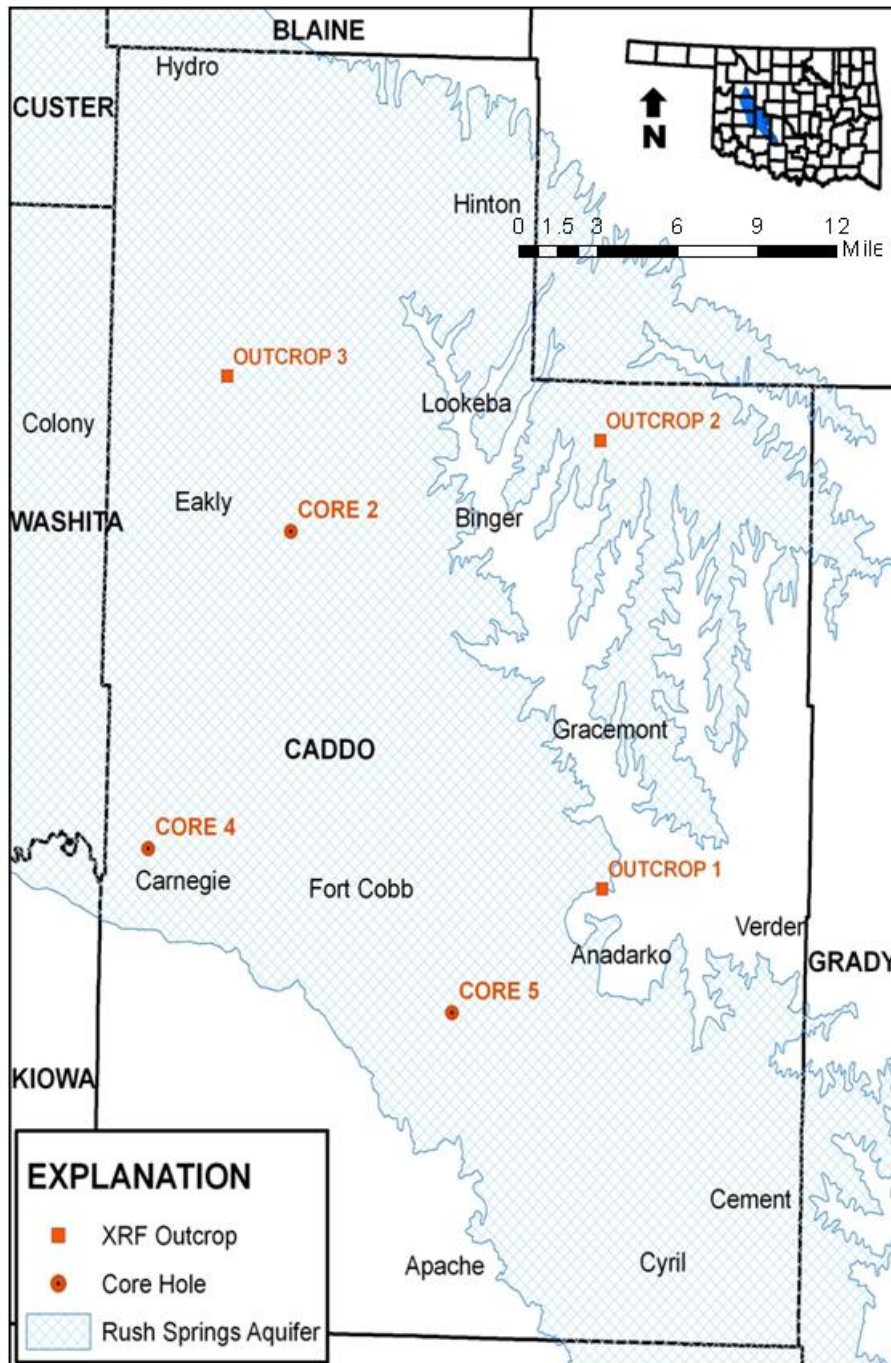


Figure 2. Map of Caddo County displaying aquifer boundaries, core hole locations, and outcrop analysis sites (aquifer outline from Becker and Runkle 1998).

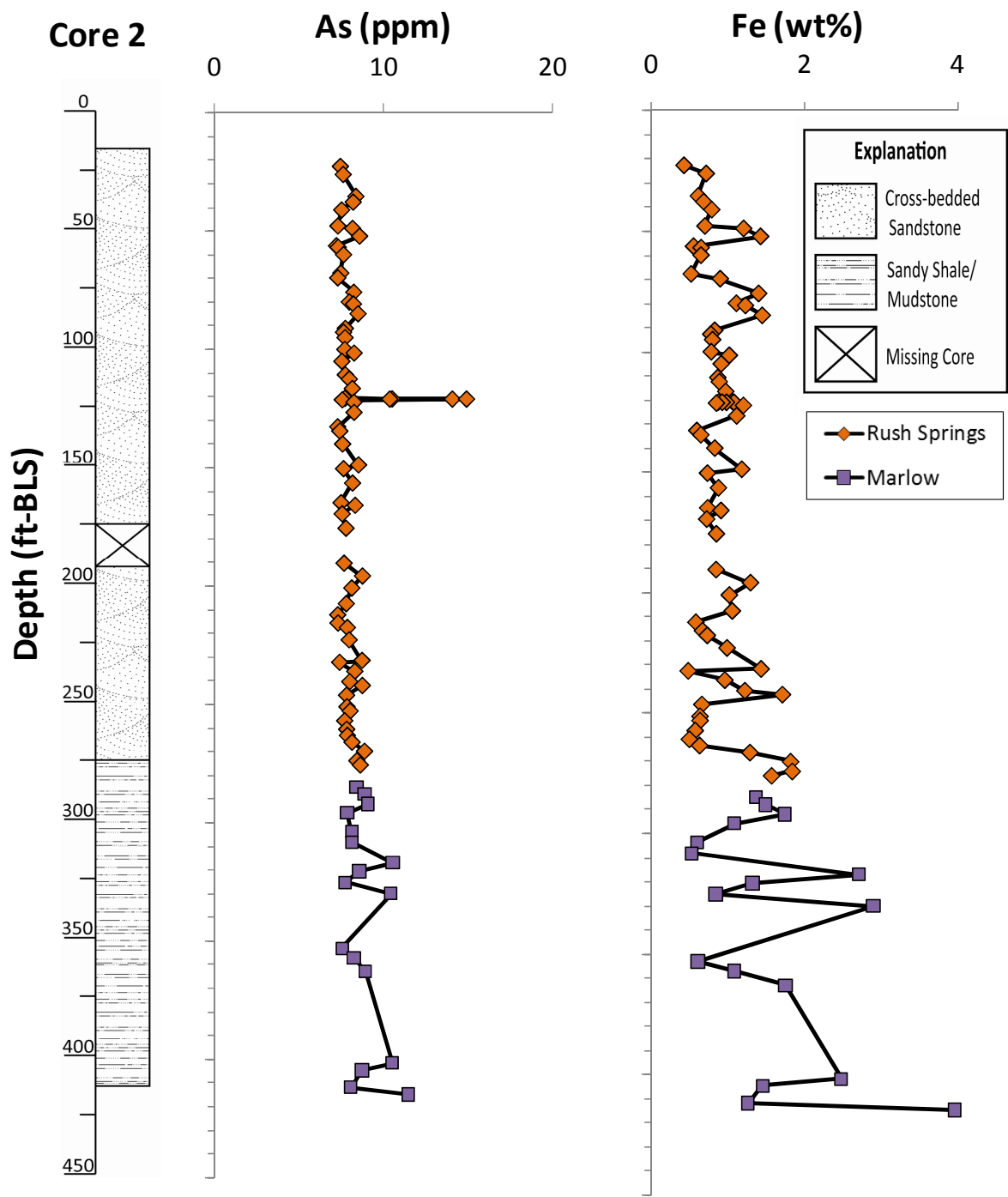


Figure 3A. Lithologic section depicting the Rush Springs Sandstone and Marlow Formation of core 2 plotted against the XRF values of arsenic and iron.

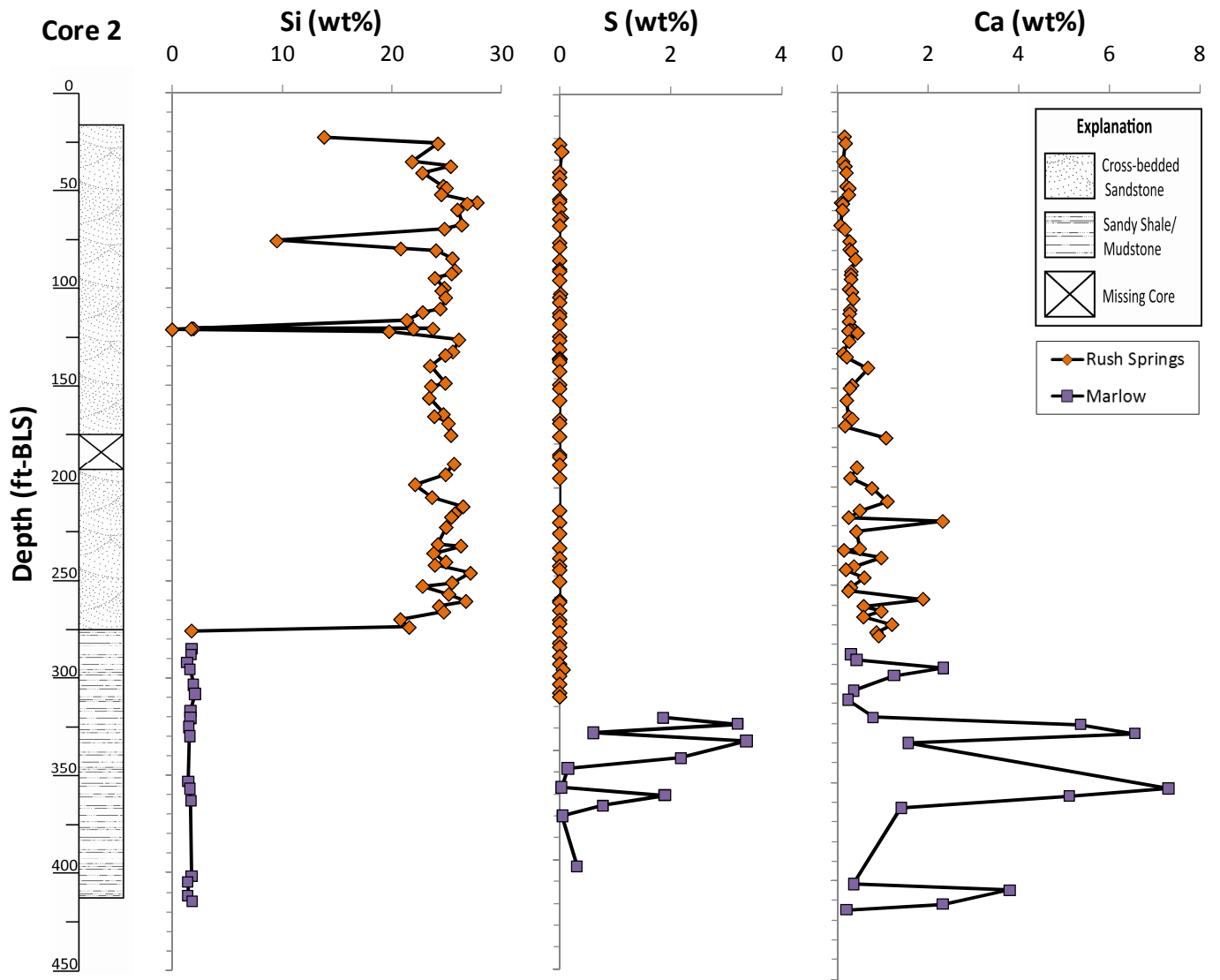


Figure 3B. Lithologic section depicting the Rush Springs Sandstone and Marlow Formation of core 2 plotted against the XRF values of sulfur, silica, and calcium.

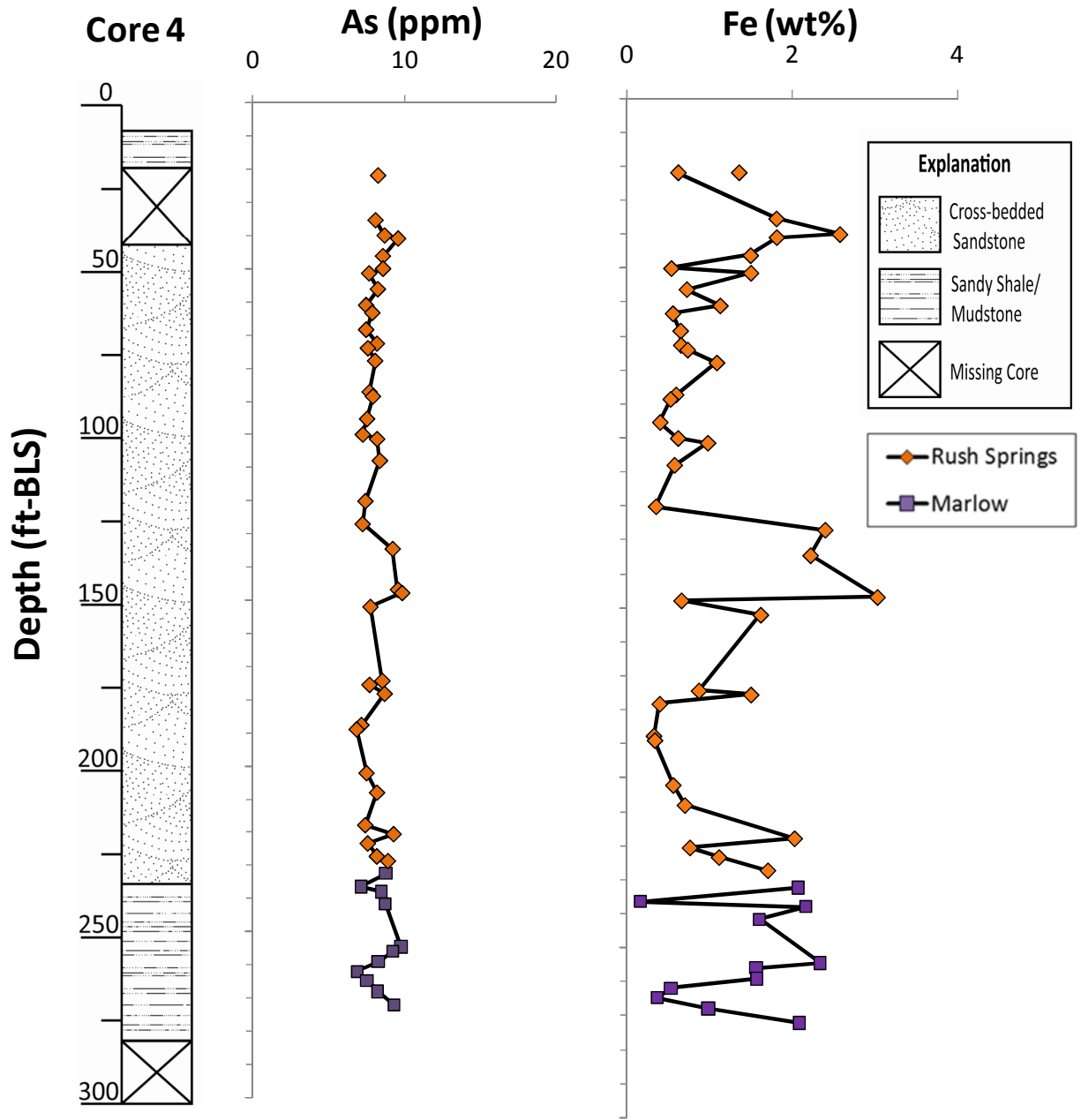


Figure 4. Lithologic section depicting the Rush Springs Sandstone and Marlow Formation of core 4 plotted against the XRF values of arsenic and iron.

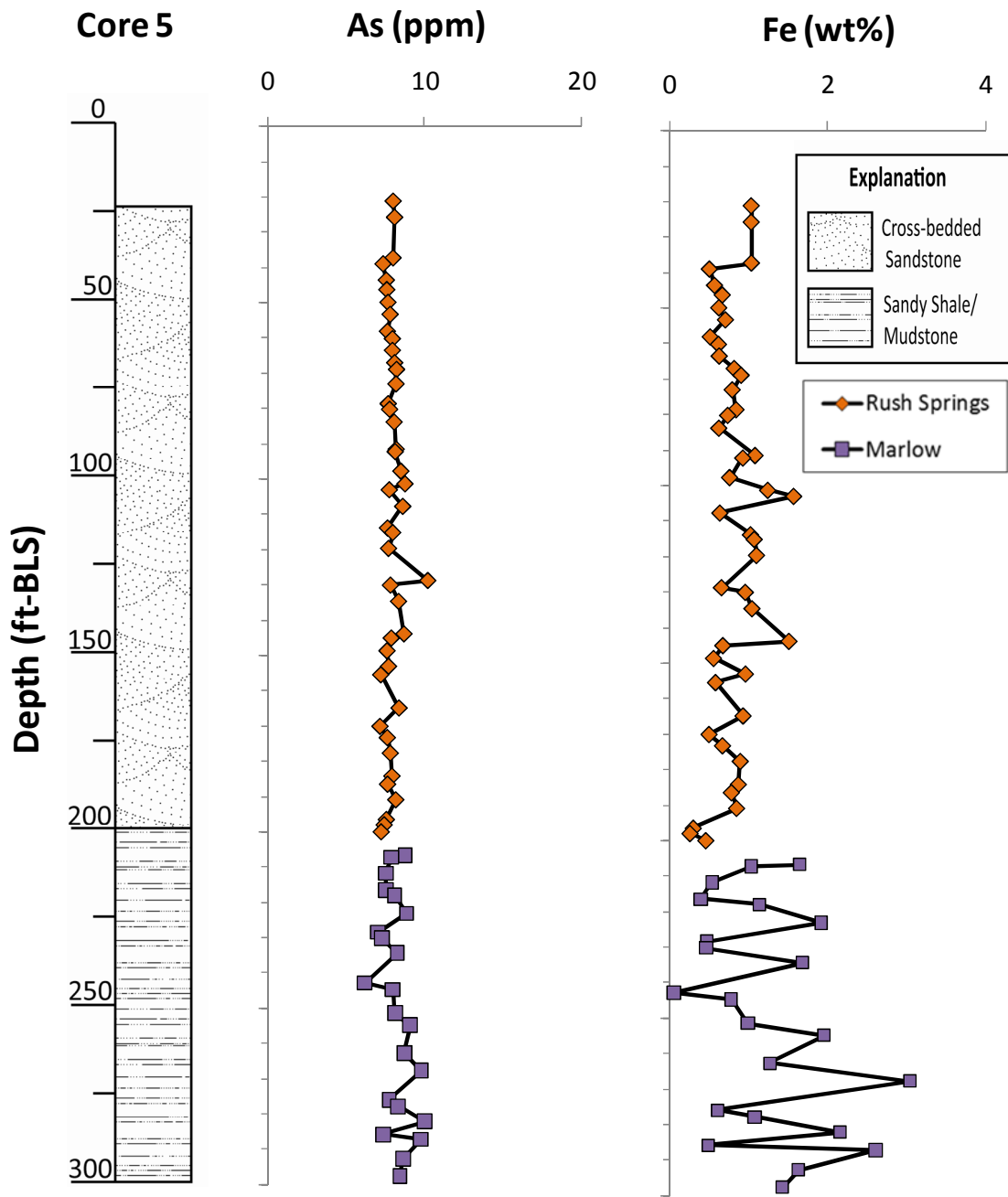


Figure 5. Lithologic section depicting the Rush Springs Sandstone and Marlow Formation of core 5 plotted against the XRF values of arsenic and iron.



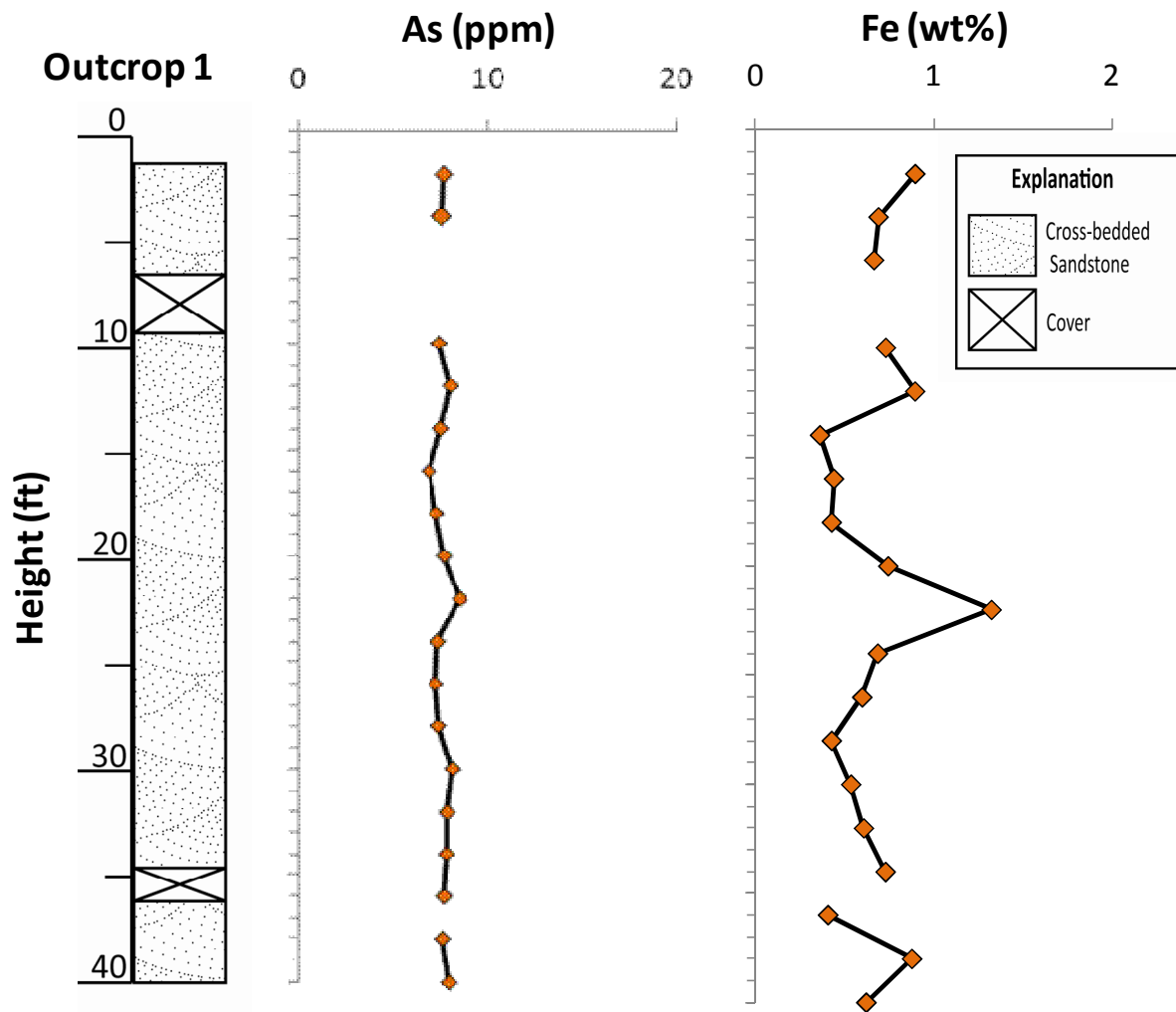


Figure 6. Lithologic section depicting the Rush Springs Sandstone of outcrop 1 plotted against the XRF values of arsenic and iron.

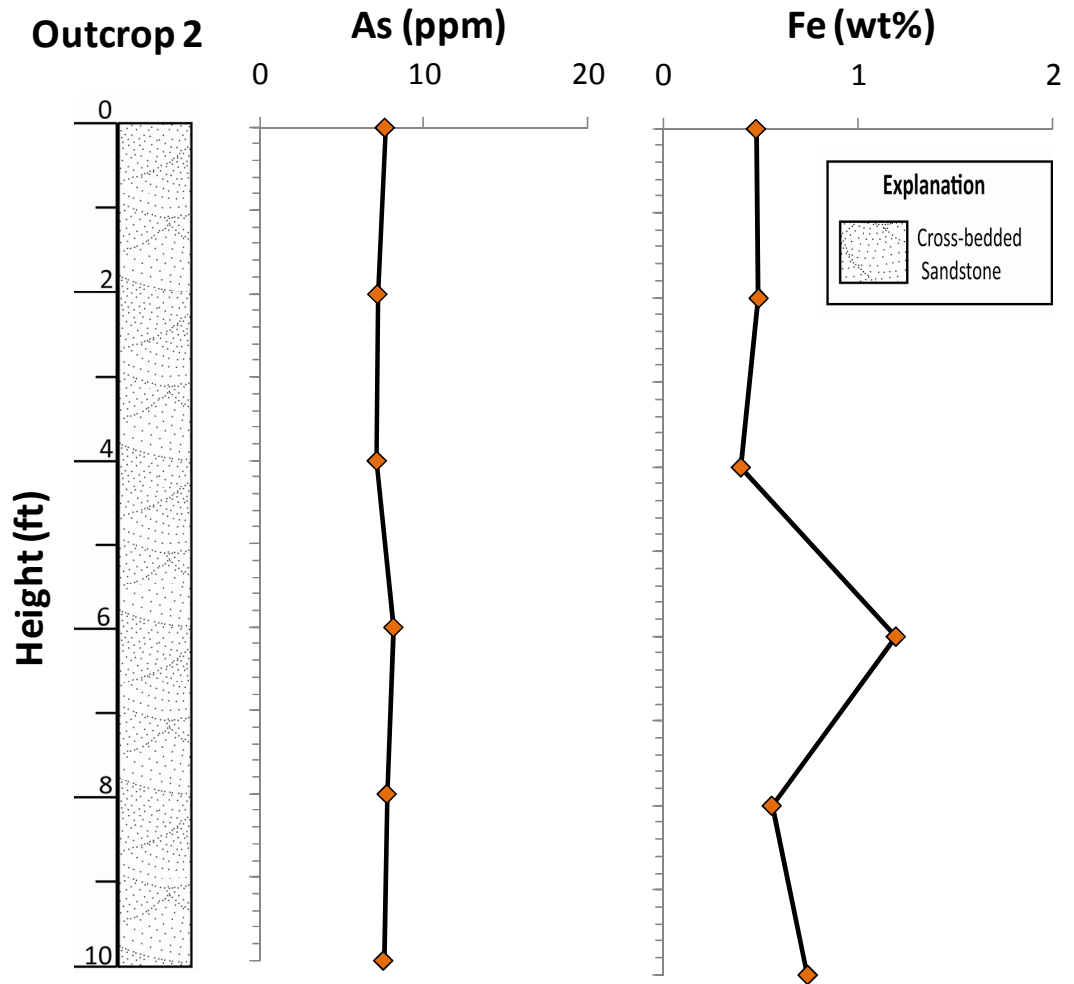


Figure 7. Lithologic section depicting the Rush Springs Sandstone of outcrop 2 plotted against the XRF values of arsenic and iron.

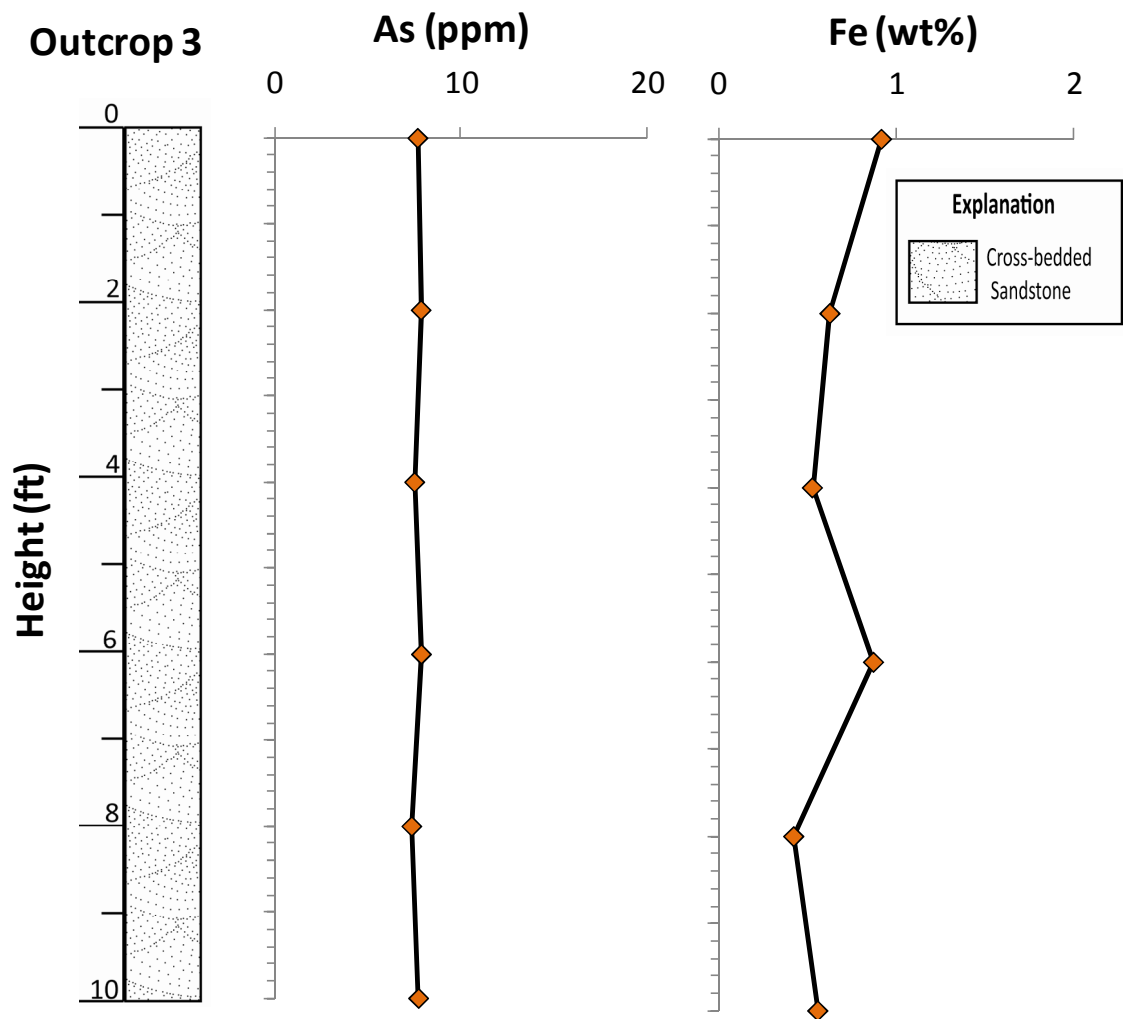


Figure 8. Lithologic section depicting the Rush Springs Sandstone of outcrop 3 plotted against the XRF values of arsenic and iron.

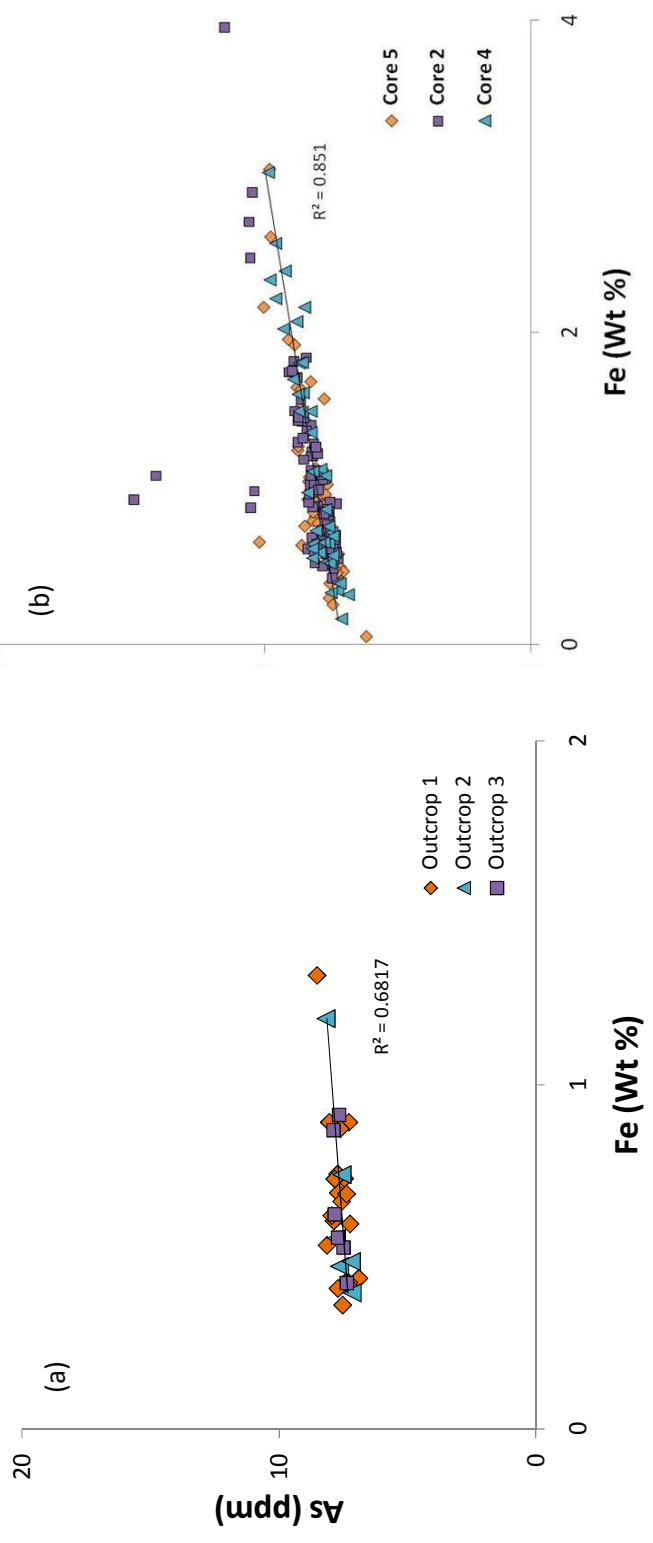


Figure 9. Crossplots of XRF analyzed arsenic v. iron from both the (a) outcrops and the (b) cores.

Table 1. Summary of general groundwater chemistry adapted from Becker et al., 2010.

<b>Parameter Measured</b>	<b>Range Detected</b>
Dissolved Oxygen (mg/L)	8.6-10.7
Alkalinity (mg/L)	157-290
Temperature (°C)	16.8-18.1
Total Dissolved Solids (mg/L)	191-937
pH	7.2-7.4
Dissolved Arsenic (µg/L)	10.5-18.7
Arsenate (µg/L)	9.3-17.2

Table 2. Summary of measurements of the USGS SCo-1 Standard (Corrected values display the number 2 along with the elemental symbol in the

<b>Element</b>	<b>Certificate Concentration</b>	<b>Measured Concentration*</b>	<b>Standard Deviation†</b>	<b>Calibration Factor</b>
As (ppm)	12	28.1 (7)	6.2	0.43
Fe (wt%)	3.59	3.78 (7)	14.5	0.95
S (ppm)	630	773 (1)	n/a	0.82
Ca (wt%)	1.87	1.42 (7)	20.8	1.32

\*value in parenthesis is number of replicates

†standard deviation is 1s value reported as percent of mean

## Appendix

## Core2

Depth (ft)	As	Fe	Fe wt%	Si	S	Ca	As-2	Fe-2	Fe wt%-2	Si wt%	S wt%	Ca wt%
22.6	17.5	4484.7	0.4	138475.5		1071.2	7.5	4256.0	0.4	13.8		0.1
26.0	17.9	7548.8	0.8	242354.6	489.5	1260.0	7.6	7163.8	0.7	24.2	0.04	0.2
35.3	19.6	6457.9	0.6	218743.4		867.2	8.4	6128.6	0.6	21.9		0.1
37.7	19.2	7213.1	0.7	253964.1		1246.7	8.2	6845.2	0.7	25.4		0.2
41.0	17.6	8325.3	0.8	228182.4		1397.4	7.5	7900.7	0.8	22.8		0.2
47.8	17.1	7382.3	0.7	247145.2		1403.3	7.3	7005.8	0.7	24.7		0.2
48.8	19.2	12718.2	1.3	249989.0		1873.0	8.2	12069.6	1.2	25.0		0.2
52.1	20.1	15065.2	1.5	245289.3		1791.6	8.6	14296.9	1.4	24.5		0.2
56.2	16.9	5798.6	0.6	278131.0	392.9	520.7	7.2	5502.8	0.6	27.8	0.03	0.1
56.8	17.2	6852.2	0.7	268934.7		804.7	7.3	6502.7	0.7	26.9		0.1
59.9	17.9	6834.3	0.7	260041.8		768.3	7.6	6485.8	0.6	26.0		0.1
67.7	17.5	5468.9	0.5	264035.9		430.3	7.5	5190.0	0.5	26.4		0.1
69.7	17.1	9487.6	0.9	248224.8		1159.5	7.3	9003.7	0.9	24.8		0.2
75.8	19.3	14793.6	1.5	95404.0		1933.8	8.2	14039.2	1.4	9.5		0.3
79.9	18.7	11720.9	1.2	208304.1		1931.8	8.0	11123.1	1.1	20.8		0.3
80.8	19.3	12983.2	1.3	240535.0		2287.7	8.2	12321.0	1.2	24.1		0.3
84.9	19.9	15289.8	1.5	255416.7		2937.1	8.5	14510.0	1.5	25.5		0.4
91.1	18.1	8728.2	0.9	257871.9	201.0	2236.1	7.7	8283.1	0.8	25.8	0.02	0.3
92.7	17.9	8188.7	0.8	254645.1		2179.5	7.6	7771.1	0.8	25.5		0.3
95.0	18.1	8426.8	0.8	239399.7		2178.1	7.7	7997.0	0.8	23.9		0.3
100.0	18.1	8245.7	0.8	248081.8		1825.6	7.7	7825.2	0.8	24.8		0.2
101.5	19.4	10745.3	1.1	245694.1		2326.8	8.3	10197.3	1.0	24.6		0.3
105.0	17.7	9623.1	1.0	249331.3		2562.8	7.5	9132.4	0.9	24.9		0.3
110.7	18.1	9145.3	0.9	244338.4		2051.5	7.7	8678.9	0.9	24.4		0.3
112.5	18.7	9359.9	0.9	228373.4		1934.3	8.0	8882.5	0.9	22.8		0.3
116.5	19.1	10249.8	1.0	213868.3		1836.1	8.2	9727.0	1.0	21.4		0.2
120.7	18.1	11163.1	1.1	18075.5		1959.7	7.7	10593.8	1.1	1.8		0.3
120.9	24.6	9229.4	0.9	19477.6		2112.0	10.5	8758.7	0.9	1.9		0.3
121.0	32.9	11377.9	1.1	219829.1		2807.6	14.1	10797.6	1.1	22.0		0.4
121.0	24.3	10351.6	1.0	237643.8		2758.3	10.4	9823.7	1.0	23.8		0.4
121.0	34.9	9761.8	1.0	17331.8		2112.5	14.9	9263.9	0.9	1.7		0.3

## Core2

Depth (ft)	As	Fe	Fe wt%	Si	S	Ca	As-2	Fe-2	Fe wt%-2	Si wt%	S wt%	Ca wt%
121.3	17.7	8970.3	0.9			1752.8	7.6	8512.9	0.9	0.0		0.2
122.3	19.3	12691.5	1.3	197696.4		3282.5	8.3	12044.3	1.2	19.8		0.4
126.6	19.4	11759.8	1.2	261264.4		1879.3	8.3	11160.0	1.1	26.1		0.2
132.7	17.1	6248.6	0.6	255819.8		853.7	7.3	5929.9	0.6	25.6		0.1
134.5	17.4	6810.8	0.7	249096.4		1445.0	7.4	6463.5	0.6	24.9		0.2
140.0	17.8	8742.2	0.9	235221.6		5038.5	7.6	8296.3	0.8	23.5		0.7
148.8	20.0	12470.0	1.2	249012.5		2369.6	8.5	11834.0	1.2	24.9		0.3
150.4	17.9	7719.8	0.8	236048.1		2005.2	7.6	7326.1	0.7	23.6		0.3
156.5	19.1	9252.0	0.9	234321.6		1459.4	8.2	8780.1	0.9	23.4		0.2
164.8	17.6	7756.5	0.8	247224.5		1826.2	7.5	7360.9	0.7	24.7		0.2
165.9	19.5	9589.1	1.0	238916.7		2388.1	8.3	9100.1	0.9	23.9		0.3
169.5	17.7	7616.9	0.8	251750.6		1195.9	7.6	7228.4	0.7	25.2		0.2
175.6	18.2	8958.3	0.9	254094.2		8057.5	7.8	8501.4	0.9	25.4		1.1
190.5	18.0	8947.0	0.9	256492.0		3209.1	7.7	8490.7	0.8	25.6		0.4
195.9	20.5	13641.8	1.4	248967.8		2128.4	8.8	12946.1	1.3	24.9		0.3
201.0	19.0	10752.6	1.1	221010.7		5714.6	8.1	10204.2	1.0	22.1		0.8
207.6	18.3	11150.2	1.1	236552.3		8305.4	7.8	10581.6	1.1	23.7		1.1
212.3	17.1	6182.5	0.6	264814.6		3692.9	7.3	5867.2	0.6	26.5		0.5
215.8	17.1	7091.8	0.7	257333.8		1859.6	7.3	6730.1	0.7	25.7		0.2
217.7	18.4	7732.1	0.8	254167.4		17534.7	7.9	7337.8	0.7	25.4		2.3
222.9	18.7	10445.0	1.0	249410.9		3128.6	8.0	9912.3	1.0	24.9		0.4
231.6	20.5	15097.2	1.5	241930.7		3668.2	8.7	14327.3	1.4	24.2		0.5
232.4	17.3	5134.4	0.5	262797.1		1058.3	7.4	4872.6	0.5	26.3		0.1
236.2	19.4	10131.7	1.0	237919.8		7288.7	8.3	9615.0	1.0	23.8		1.0
240.6	18.7	12883.1	1.3	249062.3		2714.3	8.0	12226.1	1.2	24.9		0.4
242.2	20.5	18006.8	1.8	239155.3		1382.6	8.7	17088.5	1.7	23.9		0.2
246.3	18.3	7000.4	0.7	271511.4		4450.6	7.8	6643.4	0.7	27.2		0.6
251.2	18.4	6749.9	0.7	254816.6		2204.5	7.8	6405.7	0.6	25.5		0.3
253.0	18.8	6754.3	0.7	227882.6		1786.6	8.0	6409.9	0.6	22.8		0.2
257.1	18.0	6085.0	0.6	251803.0		14268.8	7.7	5774.7	0.6	25.2		1.9
260.7	18.3	5294.6	0.5	267323.4		4348.4	7.8	5024.5	0.5	26.7		0.6
263.3	18.4	6698.1	0.7	243038.1	759.3	7285.4	7.9	6356.5	0.6	24.3	0.06	1.0



Core2

Depth (ft)	As	Fe	Fe wt%	Si	S	Ca	As-2	Fe-2	Fe wt%-2	Si wt%	S wt%	Ca wt%
266.2	19.1	13568.1	1.4	247171.0		4299.7	8.1	12876.1	1.3	24.7		0.6
270.0	20.8	19127.3	1.9	207721.3		9076.0	8.9	18151.8	1.8	20.8		1.2
274.0	19.7	19352.0	1.9	215610.0		6483.8	8.4	18365.0	1.8	21.6		0.9
275.8	20.2	16530.5	1.7	17274.0		6843.8	8.6	15687.4	1.6	1.7		0.9
285.0	19.7	14416.0	1.4	17264.2		2201.5	8.4	13680.8	1.4	1.7		0.3
288.0	20.8	15744.1	1.6	17041.0		3144.5	8.9	14941.1	1.5	1.7		0.4
292.0	21.3	18370.6	1.8	12995.1		17681.0	9.1	17433.7	1.7	1.3		2.3
295.8	18.4	11444.1	1.1	15721.0		9431.5	7.9	10860.5	1.1	1.6		1.2
303.6	19.0	6308.3	0.6	18904.2		2669.7	8.1	5986.5	0.6	1.9		0.4
308.2	19.0	5530.4	0.6	20239.1		1684.1	8.1	5248.3	0.5	2.0		0.2
317.0	24.7	28514.6	2.9	16321.8		5928.0	10.6	27060.4	2.7	1.6		0.8
320.6	20.0	13906.6	1.4	16371.1	22753.7	40540.9	8.6	13197.4	1.3	1.6	1.85	5.4
325.2	18.1	8821.6	0.9	14313.0	39223.9	49676.2	7.7	8371.7	0.8	1.4	3.20	6.6
330.0	24.5	30523.8	3.1	15569.8	7380.4	11747.9	10.4	28967.1	2.9	1.6	0.60	1.6
353.1	17.7	6414.1	0.6	14082.3	41223.8	55282.8	7.6	6087.0	0.6	1.4	3.36	7.3
357.0	19.3	11422.2	1.1	15346.6	26687.0	38668.2	8.2	10839.6	1.1	1.5	2.17	5.1
363.0	20.9	18447.1	1.8	16459.6	1716.1	10581.2	8.9	17506.3	1.8	1.6	0.14	1.4
401.7	24.6	26095.0	2.6	17327.1	326.9	2669.6	10.5	24764.1	2.5	1.7	0.03	0.4
404.7	20.4	15330.6	1.5	13927.3	23209.7	28754.8	8.7	14548.7	1.5	1.4	1.89	3.8
411.9	18.9	13309.3	1.3	13895.3	9483.4	17577.1	8.1	12630.5	1.3	1.4	0.77	2.3
414.8	26.9	41636.0	4.2	18020.3	543.5	1423.1	11.5	39512.5	4.0	1.8	0.04	0.2

## Core4

Depth (ft)	As	Fe	Fe wt%	As-2	Fe-2	Fe wt%-2
21.8	19.3	14288.7	1.4	8.3	13560.0	1.4
35.4	19.0	6455.2	0.6	8.1	6126.0	0.6
40	20.4	18980.1	1.9	8.7	18012.1	1.8
40.9	22.4	27054.9	2.7	9.6	25675.1	2.6
46.2	20.1	19014.2	1.9	8.6	18044.5	1.8
50	20.1	15669.7	1.6	8.6	14870.5	1.5
51.4	18.0	5574.2	0.6	7.7	5289.9	0.5
56.2	19.3	15720.0	1.6	8.2	14918.3	1.5
61	17.5	7543.1	0.8	7.5	7158.4	0.7
63.3	18.5	11801.9	1.2	7.9	11200.0	1.1
68.4	17.5	5778.3	0.6	7.5	5483.6	0.5
72.6	19.2	6756.1	0.7	8.2	6411.5	0.6
74	17.8	6805.4	0.7	7.6	6458.3	0.6
77.8	18.9	7654.9	0.8	8.1	7264.5	0.7
87.2	18.1	11372.4	1.1	7.7	10792.4	1.1
88.5	18.6	6177.9	0.6	7.9	5862.8	0.6
95.3	17.7	5471.7	0.5	7.5	5192.7	0.5
100	17.0	4150.3	0.4	7.3	3938.6	0.4
101.4	19.2	6440.1	0.6	8.2	6111.6	0.6
107.9	19.6	10230.7	1.0	8.4	9708.9	1.0
120.1	17.4	5982.5	0.6	7.4	5677.4	0.6
127	17.0	3620.2	0.4	7.3	3435.5	0.3
134.5	21.6	25185.1	2.5	9.2	23900.7	2.4
146.8	22.4	23319.8	2.3	9.6	22130.5	2.2
147.8	23.1	31842.4	3.2	9.8	30218.4	3.0
152	18.2	6863.2	0.7	7.8	6513.2	0.7
174.3	20.0	16965.7	1.7	8.5	16100.4	1.6
175.5	18.0	9097.3	0.9	7.7	8633.3	0.9
178.2	20.4	15732.8	1.6	8.7	14930.5	1.5
187.6	16.8	4091.7	0.4	7.2	3883.0	0.4
188.9	16.1	3342.2	0.3	6.9	3171.8	0.3
202.1	17.6	3474.1	0.3	7.5	3296.9	0.3
208	19.2	5807.4	0.6	8.2	5511.3	0.6

## Core4

Depth (ft)	As	Fe	Fe wt%	As-2	Fe-2	Fe wt%-2
217.8	17.4	7296.2	0.7	7.4	6924.1	0.7
220.5	21.7	21281.3	2.1	9.3	20196.0	2.0
223.3	17.8	7939.4	0.8	7.6	7534.5	0.8
227.2	19.2	11654.1	1.2	8.2	11059.7	1.1
228.6	20.9	17875.2	1.8	8.9	16963.6	1.7
232.4	20.6	21776.1	2.2	8.8	20665.5	2.1
236.4	16.7	1709.1	0.2	7.1	1621.9	0.2
238	19.9	22737.3	2.3	8.5	21577.7	2.2
241.7	20.5	16870.9	1.7	8.7	16010.5	1.6
254.5	22.9	24591.7	2.5	9.8	23337.5	2.3

## Core5

Depth (ft)	As	Fe	Fe wt%	As-2	Fe-2	Fe wt%-2
21.2	18.7	10877.7	1.1	8.0	10322.9	1.0
25.8	19.0	10877.7	1.1	8.1	10322.9	1.0
37.3	18.7	10902.7	1.1	8.0	10346.6	1.0
39.0	17.3	5281.0	0.5	7.4	5011.6	0.5
43.6	17.7	5963.5	0.6	7.6	5659.3	0.6
46.3	17.8	7005.7	0.7	7.6	6648.4	0.7
49.9	18.0	6546.2	0.7	7.7	6212.4	0.6
53.3	18.3	7425.0	0.7	7.8	7046.3	0.7
58.1	17.9	5386.5	0.5	7.6	5111.8	0.5
60.2	18.6	6491.9	0.6	8.0	6160.8	0.6
63.5	18.6	6593.5	0.7	8.0	6257.3	0.6
67.0	19.0	8603.9	0.9	8.1	8165.1	0.8
68.9	19.2	9527.4	1.0	8.2	9041.5	0.9
73.0	19.2	8338.7	0.8	8.2	7913.4	0.8
78.6	18.0	8855.3	0.9	7.7	8403.6	0.8
80.2	18.2	7728.6	0.8	7.8	7334.5	0.7
83.8	18.9	6547.0	0.7	8.1	6213.1	0.6
91.5	19.2	11393.5	1.1	8.2	10812.4	1.1
92.2	19.0	9758.7	1.0	8.1	9261.0	0.9
97.7	19.9	7983.9	0.8	8.5	7576.7	0.8
101.3	20.5	13085.4	1.3	8.7	12418.0	1.2
103.0	18.2	16561.1	1.7	7.8	15716.4	1.6
107.7	20.2	6683.9	0.7	8.6	6343.0	0.6
113.8	17.9	10782.2	1.1	7.6	10232.3	1.0
115.1	18.7	11276.3	1.1	8.0	10701.2	1.1
119.6	18.1	11578.4	1.2	7.7	10987.9	1.1
128.7	23.9	6900.8	0.7	10.2	6548.8	0.7
130.0	18.3	10085.9	1.0	7.8	9571.5	1.0
134.6	19.5	10979.5	1.1	8.3	10419.5	1.0
143.8	20.3	15929.1	1.6	8.7	15116.7	1.5
145.0	18.5	7083.4	0.7	7.9	6722.1	0.7
148.6	17.8	5833.7	0.6	7.6	5536.2	0.6
153.0	18.1	10109.7	1.0	7.7	9594.1	1.0

## Core5

Depth (ft)	As	Fe	Fe wt%	As-2	Fe-2	Fe wt%-2
155.4	16.9	6101.0	0.6	7.2	5789.8	0.6
164.8	19.6	9790.1	1.0	8.4	9290.8	0.9
170.0	16.8	5227.1	0.5	7.2	4960.5	0.5
173.2	17.9	7038.1	0.7	7.6	6679.1	0.7
177.6	18.3	9412.8	0.9	7.8	8932.8	0.9
184.1	18.6	9152.7	0.9	7.9	8685.9	0.9
186.4	17.9	8228.3	0.8	7.6	7808.7	0.8
190.8	19.1	8919.4	0.9	8.2	8464.5	0.8
196.4	17.7	3129.1	0.3	7.6	2969.5	0.3
197.9	17.4	2687.3	0.3	7.4	2550.2	0.3
199.9	17.0	4797.8	0.5	7.2	4553.1	0.5
206.7	20.6	17331.5	1.7	8.8	16447.6	1.6
207.2	18.5	10867.8	1.1	7.9	10313.6	1.0
211.8	17.6	5613.8	0.6	7.5	5327.5	0.5
216.5	17.7	4116.2	0.4	7.5	3906.3	0.4
218.0	18.9	11901.9	1.2	8.1	11294.9	1.1
223.1	20.8	20199.5	2.0	8.9	19169.3	1.9
228.5	16.5	4932.1	0.5	7.0	4680.6	0.5
230.2	17.1	4828.8	0.5	7.3	4582.5	0.5
234.4	19.4	17723.3	1.8	8.3	16819.4	1.7
242.8	14.5	528.0	0.1	6.2	501.1	0.1
244.7	18.7	8169.5	0.8	8.0	7752.9	0.8
251.4	19.0	10375.7	1.0	8.1	9846.5	1.0
254.8	21.3	20573.8	2.1	9.1	19524.6	2.0
262.7	20.4	13362.6	1.3	8.7	12681.1	1.3
267.8	23.0	32046.5	3.2	9.8	30412.2	3.0
276.0	18.2	6300.2	0.6	7.8	5978.9	0.6
277.8	19.5	11279.2	1.1	8.3	10703.9	1.1
282.2	23.5	22742.5	2.3	10.0	21582.6	2.2
285.8	17.2	5088.0	0.5	7.4	4828.5	0.5
287.2	22.9	27485.2	2.7	9.8	26083.4	2.6
292.8	20.2	17197.1	1.7	8.6	16320.0	1.6
297.7	19.7	15039.2	1.5	8.4	14272.2	1.4

### Outcrop 1

Depth	As	Fe	Fe wt %	As-2	Fe-2	Fe wt%-2
2.0	17.1	9406.7	0.9	7.3	8926.9	0.9
4.0	18.0	7244.4	0.7	7.7	6874.9	0.7
6.0	17.7	6979.1	0.7	7.6	6623.1	0.7
10.0	17.4	7680.8	0.8	7.4	7289.1	0.7
12.0	18.8	9406.2	0.9	8.0	8926.4	0.9
14.0	17.6	3801.1	0.4	7.5	3607.3	0.4
16.0	16.1	4622.4	0.5	6.9	4386.7	0.4
18.0	17.1	4490.3	0.4	7.3	4261.3	0.4
20.0	18.1	7819.1	0.8	7.7	7420.3	0.7
22.0	19.9	13910.0	1.4	8.5	13200.6	1.3
24.0	17.3	7209.2	0.7	7.4	6841.5	0.7
26.0	16.9	6288.3	0.6	7.2	5967.6	0.6
28.0	17.3	4492.1	0.4	7.4	4263.0	0.4
30.0	19.0	5633.7	0.6	8.1	5346.4	0.5
32.0	18.4	6382.6	0.6	7.9	6057.0	0.6
34.0	18.3	7667.1	0.8	7.8	7276.0	0.7
36.0	18.0	4312.1	0.4	7.7	4092.2	0.4
38.0	17.8	9211.0	0.9	7.6	8741.2	0.9
40.0	18.6	6544.5	0.7	7.9	6210.7	0.6

### Outcrop 2

Depth	As	Fe	Fe wt %	As-2	Fe-2	Fe wt%-2
0.0	17.9	5002.7	0.5	7.6	4747.5	0.5
2.0	16.8	5146.6	0.5	7.2	4884.1	0.5
4.0	16.8	4186.6	0.4	7.2	3973.1	0.4
6.0	19.1	12567.9	1.3	8.2	11927.0	1.2
8.0	18.2	5856.7	0.6	7.8	5558.0	0.6
10.0	17.7	7799.2	0.8	7.5	7401.4	0.7

### Outcrop 3

Depth	As	Fe	Fe wt %	As-2	Fe-2	Fe wt%-2
0.0	18.0	9625.2	1.0	7.7	9134.3	0.9
2.0	18.4	6592.8	0.7	7.8	6256.5	0.6
4.0	17.6	5559.7	0.6	7.5	5276.2	0.5
6.0	18.4	9155.6	0.9	7.9	8688.7	0.9
8.0	17.2	4461.4	0.4	7.3	4233.9	0.4
10.0	18.1	5877.0	0.6	7.7	5577.3	0.6

## VITA

Jessica Shirley Magers

Candidate for the Degree of

Master of Science

Thesis: OCCURRENCE OF ARSENIC IN THE RUSH SPRINGS SANDSTONE AND ITS IMPLICATIONS ON GROUNDWATER CHEMISTRY: CADDO COUNTY, OKLAHOMA

Major Field: Geology

Biographical: Born in Alexandria, LA on January 24, 1987.

### Education:

Completed the requirements for the Master of Science in Geology at Oklahoma State University, Stillwater, Oklahoma in July 2011.

Completed the requirements for the Bachelor of Science in Geology at Oklahoma State University, Stillwater, Oklahoma in May 2009.

### Experience:

Teaching Assistant at Oklahoma State University 2007-2011

Hydrologist at U.S. Geological Survey 2008-2011

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Name: Jessica Shirley Magers

Date of Degree: July, 2011

Institution: Oklahoma State University

Location: Stillwater, Oklahoma

Title of Study: OCCURRENCE OF ARSENIC IN THE RUSH SPRINGS SANDSTONE  
AND ITS IMPLICATIONS ON GROUNDWATER CHEMISTRY:  
CADDO COUNTY, OKLAHOMA

Pages in Study: 40

Candidate for the Degree of Master of Science

Major Field: Geology

Scope and Method of Study: Three cores and three outcrops of the Rush Springs Sandstone were analyzed for As, Fe, Ca, S, and Si using a handheld Thermo Scientific Niton X-ray fluorescence (XRF) analyzer. The Rush Springs Sandstone is a Permian aged 'red-bed' fine grained eolian sandstone. It is the major water bearing unit within the Rush Springs Aquifer and is thickest in Caddo County. Dissolved arsenic exceeding the EPA maximum contaminate level was detected in the groundwater of this area. Arsenic concentrations within the sandstone were determined and plotted alongside iron concentrations to provide insight into the arsenic origin, naturally occurring or anthropogenic, and the possibility of it desorbing from the iron and influencing the groundwater chemistry.

Findings and Conclusions: The XRF data collected along with the previous studies on the water chemistry within the Rush Springs Aquifer suggests that the arsenic is naturally occurring within the sandstone and is likely being desorbed by the introduction of a competing ion. Other explanations were considered for desorption i.e. increase in pH and reducing conditions, neither of which fit the study area. In this case the likely competitor is that of phosphorus. It shares a similar chemical structure and is preferred over arsenic when bonding to iron. Agriculture in Caddo County is wide spread giving a source of the phosphorus that may be introduced into the groundwater causing arsenic to be released.