

Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water–rock interaction

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Accepted 6 November 2005

Abstract

Arsenic (As) is being released from the Suwannee Limestone, Upper Floridan aquifer, during aquifer storage and recovery (ASR) cycle testing with concentrations of up to 130 $\mu\text{g/L}$ in the recovered water. To determine the abundance and mineralogical association of As in the Suwannee Limestone matrix we have conducted a detailed mineralogical and geochemical study of 306 core samples. In addition to random sampling of core material, we also collected “targeted” samples of core material that contained organic material, hydrous ferric oxide, pyrite, phosphate minerals and clays. Bulk As concentrations were determined by acid digestion followed by hydride generation-atomic fluorescence spectrometry (HG-AFS). Specific mineral phases were analyzed using scanning electron microscopy (SEM) and electron-probe microanalyses (EPMA). The average As concentration for all 306 samples is 3.5 ppm, but only 1.7 ppm after exclusion of the “targeted” samples. The average for the “targeted” samples is 9.5 ppm.

The detailed lithologic, mineralogical, and geochemical study of As in the Upper Floridan aquifer, Suwannee Limestone shows that: (1) Arsenic is present in the Suwannee Limestone in low concentrations, but is concentrated in minor mineral phases, particularly pseudo-framboidal pyrite. (2) Pyrite is generally As-rich and can contain concentrations between 100 and 11,200 ppm As (average 2300 ppm, $n=25$). (3) Compared to pyrite, other trace minerals contain much less As. (4) Pyrite is ubiquitous throughout the Suwannee Limestone, but is most abundant in high porosity zones. (5) Previously suggested hydrous ferric oxide, clay minerals and apatite are not an important source of As.

This study also provided some insight into the question whether the interaction (reaction) of water with an aquifer matrix that contains only a few part per million As is capable of producing high-As concentrations in groundwater. Our findings indicate that it can be relatively easy to generate a high-As groundwater despite a low bulk As concentration in the aquifer matrix. A change in physico-chemical conditions that selectively affects the stability of As-bearing minerals is sufficient to increase As concentrations by several orders of magnitude.

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Keywords: Arsenic; Aquifer storage and recovery (ASR); Pyrite; Suwannee Limestone; Floridan aquifer

1. Introduction

The principal public health concern for arsenic (As) is the occurrence of high-As groundwater, because As is a known carcinogen and can lead to a wide range of

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health problems in humans (Smedley and Kinniburgh, 2002). New findings about the environmental and human toxicity of As (Jain and Ali, 2000), combined with widespread As contamination in Argentina, Bangladesh, Chile, China, Mexico, India, Thailand, Taiwan and Vietnam (e.g., Meng et al., 2001; Plant et al., 2004), have sparked an increasing interest in the study of As sources and how As is released from the aquifer matrix. Two scenarios can be responsible: (1) anthropogenic As contamination of groundwater through agriculture (e.g., As in herbicides and pesticides) and industry (e.g., semi-conductors and wood treatment) and (2) contamination of groundwater by natural As due to a change of physico-chemical and biological conditions, whether anthropogenic or naturally induced. The second scenario has not received as much attention as the first, because natural background As concentrations are generally low. Clearly there are crucial exceptions such as in Bangladesh where mean As concentrations in alluvial sand are 2.9 ppm, in

alluvial mud/clay 6.5 ppm and in river bed sediments 5.9 ppm (Datta and Subramanian, 1997; BGS and DPHE, 2001). This raises the question if the interaction (reaction) of water with an aquifer matrix that contains only a few part per million As is capable of producing high-As concentrations in groundwater.

Recent developments in central Florida have provided us with the opportunity to answer this question. This study began as a result of elevated As concentrations being discovered in recovered water from aquifer storage and recovery (ASR) systems in west-central Florida. Aquifer storage and recovery is the process of artificially recharging and storing treated surface water in a confined aquifer, then recovering that water at a time of need, such as during a drought or dry season. The Florida Geological Survey (FGS) reported As values in recovered water of up to 130 $\mu\text{g/L}$ from several ASR sites (Arthur et al., 2001). This is surprising, because the injected water was virtually As free (Pichler et al., 2004) and the storage zone consists of limestone,

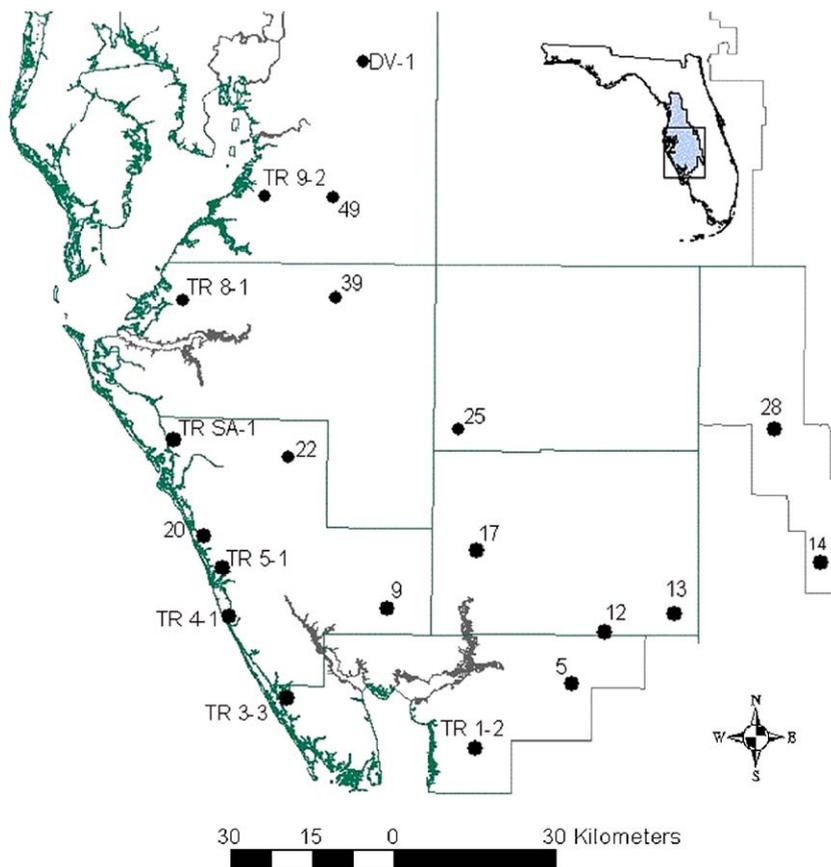


Fig. 1. General location map of the study area. Black circles indicate the location and Regional Observation Monitor Well Program (ROMP) well number of the cores that were sampled. The study area was limited to the southern half of the Southwest Florida Water Management District between Tampa and Ft. Myers (shown in shaded area in upper-right inset).

which is generally low in As; Baur and Onishi (1969) reported a global mean of 2.6 ppm for limestone. The possibility of anthropogenic contamination is unlikely, because the storage zone is separated from surface water by an aquitard. This leaves only water–aquifer matrix interaction as a likely source for the As. Thus the As contamination of ASR water in central Florida affords us with a large scale experiment to investigate if a low-As aquifer matrix can produce a high-As groundwater.

If water–matrix interaction is responsible, understanding As mobilization due to water–rock interactions that take place during ASR is vital because this technology continues to be increasingly important for providing water to the growing global population. More than 100 ASR facilities operate worldwide, and over 37 ASR facilities are under construction or operating in Florida (Pyne, 1994; Arthur et al., 2002). Detailed knowledge about its mineralogical association is particularly important for the evaluation of As mobility based on thermodynamic data, which is the common approach for geochemical modeling (e.g., Langmuir et al., 1999). Only geochemical models/calculations that use the correct mineral phase(s) provide the necessary confidence on which to base decisions that may affect development of ASR facilities in Florida and worldwide.

2. Hydrogeology of the study area

The study area is located in central Florida between Tampa and Ft. Myers (Fig. 1). Here, a multilayered aquifer system exists, which can be subdivided into three distinct hydrostratigraphic units based on lithology and position. They are from the top down: the Surficial aquifer system, the Intermediate aquifer system or confining unit and the Floridan aquifer system (Fig. 2). The Floridan aquifer system consists of a vertically continuous sequence of carbonate rocks of generally high permeability that are hydraulically connected to varying degrees, and is subdivided into the Upper Floridan aquifer, the Middle confining unit and the Lower Floridan aquifer (Miller, 1986). The Suwannee Limestone is the uppermost unit of the Floridan aquifer system, and is confined in the study area by the Hawthorn Group, a sequence of interbedded carbonates, sands and clays of low permeability (Scott, 1988).

The lithology of the Suwannee Limestone in the study area consists primarily of limestone, which has been described as a wackestone mud to pelletal, foraminiferal grainstone (e.g. Gilboy, 1985; Hammes, 1992; Green et al., 1995; Williams et al., 2002). It contains minor amounts of phosphatic quartz sand and

Geologic Age	Lithostratigraphic Unit		Hydrostratigraphic Unit
Pleistocene	Surficial Sediments		Surficial Aquifer System
Pliocene			
Miocene	Hawthorn Group	Peace River Formation	Intermediate Aquifer System/ Intermediate Confining Unit
		Arcadia Formation	
Tampa Member Nocatee Member			
Oligocene	Suwannee Limestone		Upper Floridan Aquifer System
Eocene	Ocala Limestone		
	Avon Park Formation		

Fig. 2. Lithostratigraphic and hydrostratigraphic column for the study area. Note the location of the Suwannee Limestone (modified from Williams et al., 2002)

clay intermixed with limestone near the top of the formation, and a small layer (3 to 6 m) of dolostone in the lower third (Miller, 1986; Green et al., 1995). Chert nodules, organic material, and pyrite are also present in minor amounts (Miller, 1986; Green et al., 1995). Mollusk molds and casts are common in the upper part, but are generally less abundant lower in the section (Miller, 1986). These zones provide areas of high moldic porosity, which are important for aquifer storage and recovery (ASR) (Ellison, pers. comm., 2001). Elsewhere, intergranular porosity is common and can be high enough to allow ASR. In our study area the thickness of the Suwannee Limestone is generally between 50 and 100 m; detailed measurements are given in Appendix A.

3. Methods

A combination of petrographic and geochemical techniques was used to evaluate the abundance and mineralogical association of As in 306 samples from 20 Suwannee Limestone cores. The core was originally collected as part of the Regional Observation Monitor Well Program (ROMP) by the Southwest Florida Water Management District (SWFWMD), and is stored at the Florida Geological Survey (FGS) in Tallahassee. Each core was sampled at an even spacing to ensure representation of the entire Suwannee interval. Targeted samples were taken from sections likely to have higher As concentrations than the bulk carbonate matrix, such as areas with visible trace minerals, minor constituents, or organic material. The core was also sampled immediately adjacent to the targeted areas for comparison. Fractures have the potential for preferential flow during ASR injection and recovery and thus fracture surfaces were sampled along with the adjacent matrix.

We have applied methods first utilized by Pichler et al. (2001), which include a combination of lithologic and petrographic techniques, along with bulk rock chemical analysis, scanning electron microscopy, and electron-probe microanalysis, to constrain the location of the As with each consecutive step. X-ray diffraction generally requires ~1% to 5% modal abundance for element/mineral detection and was therefore not applied, considering the very low expected concentrations of the As in bulk Suwannee Limestone, e.g., Arthur et al. (2002) reported a maximum of 11 ppm As for the Suwannee Limestone.

Hand samples were first examined and described in the field and laboratory, and polished thin sections of selected samples were examined in transmitted and

reflected light for mineralogical determinations. For bulk rock chemical analysis, each sample was powdered and dissolved using a digestion method modified from van der Veen et al. (1985). Our method consisted of weighing 0.5 g of homogenized, powdered sample into a Teflon pressure decomposition vessel (bomb). After adding 10 mL aqua regia (a 3:1 mixture of hydrochloric (HCl) and nitric acid (HNO₃)), each bomb was closed and allowed to remain at room temperature for 24 h. During this time the sample was periodically shaken to insure complete digestion of As-bearing phases. The sample solutions were transferred into 50 mL centrifuge tubes, and de-ionized (DI) water was added to the 50 mL mark of each sample. Residuals were removed by passing the solution through a 0.45 μm filter. A limestone standard from the Japanese Geological Survey (JLs-1) with a well established As concentration was digested and analyzed with each batch of samples for quality control. Blanks of aqua regia were included throughout the entire digestion procedure to assess possible contamination during sample preparation. All reagents were analytical grade or higher and de-ionized (DI) water was better than 17.9 mΩ.

The concentration of As was determined by hydride generation-atomic fluorescence spectrometry (HG-AFS) on a PSA 10.055 Millennium Excalibur system at the Center for Water Analysis, University of South Florida. In preparation for the HG-AFS analysis, 10 mL of sample solution was mixed with 15 mL concentrated HCl, 1 mL saturated potassium iodide (KI) solution, and diluted with DI water to a volume of 50 mL. The accuracy and precision of the measurements and acid digestion was verified by analysis of the JGS JLs-1 reference material and sample duplicates, which indicate a precision of better than 5%. Reagent-acid blanks were tested and showed no detectable As. Background signal drift was consistently less than 1%.

Analyses of iron (Fe), calcium (Ca), magnesium (Mg), manganese (Mn), silica (Si), sulfur (S), and phosphorus (P) were carried out using a Perkin Elmer Optima 2000 DV inductively coupled plasma-optical emission spectrometer (ICP-OES) for those samples high in As in order to assess elemental correlations. The analyses of several duplicates indicate a precision of better than 5%. The accuracy of the measurements and acid digestion was verified by analysis of the JGS JLs-1 reference material. Acid blanks were tested and showed no detectable contamination of analyzed elements. Background signal drift was consistently less than 1%.

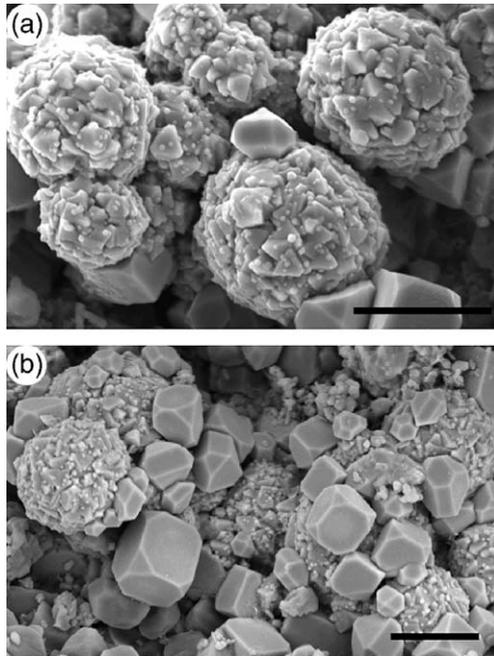


Fig. 3. (a) Scanning electron photograph of framboidal pyrite found in the Suwannee Limestone. (b) Scanning electron photograph of both framboidal pyrite and single euhedral crystals of pyrite (the scale bar in the lower right corner of each figure represents 20 μm).

To better constrain the mineral phases containing As, those samples highest in bulk As were selected for scanning electron microscopy (SEM) using a JEOL JSM-5900-LV, and electron-probe microanalysis (EPMA or Electron Microprobe) using a JEOL 8200 microprobe at the Florida International University and the University of New Mexico, respectively. The JEOL JSM-5900-LV has Energy Dispersive Spectrometry (EDX) capabilities, which allows elemental detection down to a concentration of about 1000 ppm (Beasley, pers. comm., 2002). For the EDX analyses of As, however we had to use the 10.6 keV peak rather than that at 1.26 keV to avoid the overlap with Mg, which was present in all of our samples. Unfortunately, the detection limit of that peak is more likely in the 2000 to 3000 ppm range. To obtain quantitative elemental compositions, polished thin sections were analyzed by electron microprobe, which has a detection limit for As of approximately 100 ppm (Beasley, pers. comm., 2002). Operating conditions were 20 kV accelerating voltage, a 20 nA current, and a spot size of approximately 10 μm . In addition to spot analysis we generated several chemical maps to explore As distribution between individual minerals and matrix.

4. Results

4.1. Petrography and mineralogy

The majority of samples is largely composed of pure, pelletal limestone, and can be classified as mudstones or grainstones using the Dunham classification scheme (Dunham, 1962). Minor siliciclastic samples are composed of clay, silt and sand, often with minor amounts of phosphate nodules. Siliciclastics were found mainly at the top of the Suwannee Limestone, near the contact with the Hawthorn Group, but were also observed together with carbonate cement near the bottom of the section. Areas containing a green smectitic clay were mainly present near the top of the Suwannee Limestone. In addition several minor mineral phases, including dolomite, chert, secondary calcite and pyrite are also present. We observed dolomite in the lower portions of the Suwannee Limestone in several cores, and chert nodules were occasionally encountered throughout the entire section. Organic matter is heterogeneously dispersed throughout the Suwannee Limestone, but was most commonly observed in low porosity zones. Pyrite is ubiquitous in the Suwannee Limestone and generally present in the form of pseudo-framboids, or framboid-shaped pyrite aggregates (Fig. 3a and b). True framboids are defined as spheroidal to sub-

Table 1

Mean concentrations of As in part per million (mg/kg) for 20 cores from the Suwannee Limestone in central Florida

ROMP Well	Average	Minimum	Maximum	σ	(n)
TR 9-2*	4.94	0.23	54.10	13.0	17
TR 3-3	2.77	0.06	48.73	9.9	24
DV-1	5.51	0.47	42.59	11.2	13
TR 1-2	6.19	0.33	36.65	9.8	21
9	10.45	0.15	33.96	13.6	10
25	3.66	0.14	32.99	8.0	16
TR 8-1	3.80	0.26	26.77	7.0	15
TR 5-1	3.47	0.03	26.35	7.4	20
5	4.43	0.15	19.70	5.2	24
TR 4-1	4.13	0.17	17.81	6.6	14
20	3.10	0.19	16.93	4.3	19
17	2.65	0.28	16.85	3.3	26
TR SA-1	1.71	0.17	15.87	4.3	13
39	2.50	0.01	14.39	3.4	16
49	2.22	0.29	12.30	3.1	15
28	2.43	0.45	9.48	2.6	11
14	2.16	0.42	6.97	2.7	5
12	1.69	0.61	3.69	1.2	13
13	1.10	0.02	2.73	1.0	8
22	0.55	0.00	2.54	0.8	8

*Well numbers correspond to those in Fig. 1.

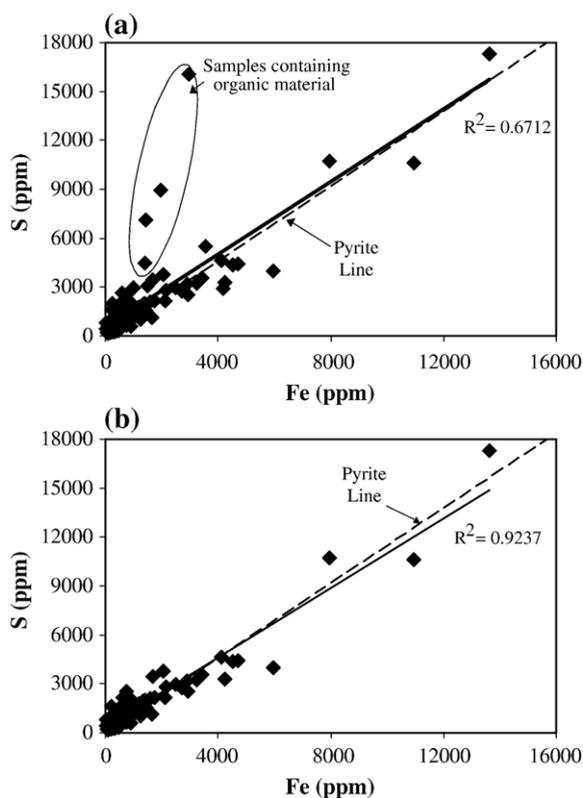


Fig. 4. (a) Fe vs. S for all samples analyzed by ICP-OES ($n=120$). Samples containing abundant organic material have higher S concentrations and are circled. The “Pyrite Line” (dashed) represents $\text{Fe}=2\text{S}$, i.e., FeS_2 . Note the good agreement between the linear best fit (solid black line) and the pyrite line. (b) Fe vs. S after those samples containing organic material were removed. Note increase in r^2 .

spheroidal clusters of equidimensional and equimorphic, discrete microcrystals (Ohfuji and Rickard, 2005). The majority of pyrite in the Suwannee Limestone is considered pseudo-framboidal because they consist of octahedral to cuboidal microcrystals that have intergrown, causing massive internal structure (Fig. 3a and b). Few true framboids (<1%) were observed in samples containing layers of quartz sand. Small euhedral pyrites were observed adjacent to pseudo-framboids (Fig. 3b). Framboids and pseudo-framboids were examined by SEM and are approximately 10 to 20 μm in diameter. Pseudo-framboidal pyrite was unevenly distributed, occurring with smectite, organic material, quartz and phosphatic sand, but mostly associated with secondary calcite in moldic, high porosity zones. Hydrous ferric oxides (HFO) or Fe-oxyhydroxides were only observed in 3 out of 306 samples as alteration halos around pyrite.

Thin sections were made for those 20 samples highest in As (Table 2). The sections were investi-

gated with reflected and transmitted light, and contained predominantly calcite, with minor mineral phases identified as quartz, pyrite, apatite, dolomite, and chert. Pseudo-framboidal pyrite was observed in more than 80% of the thin sections, and was the most abundant minor mineral phase next to quartz. Organic material was also examined in thin section and found to contain abundant pseudo-framboidal pyrite.

4.2. Bulk rock chemical composition

4.2.1. Arsenic abundance and distribution

Bulk rock chemical analyses by HG-AFS show that As concentrations in the Suwannee Limestone range from 0.01 to 54.1 ppm, with a mean of 3.5 ppm (Table 1; Appendix 1). This value includes interval and targeted samples and should therefore be considered with caution. The mean As concentration of interval samples is 1.7 ppm, while the mean of targeted samples is 9.5 ppm.

The distribution of As in the Suwannee Limestone is heterogeneous, but somewhat predictable. Samples

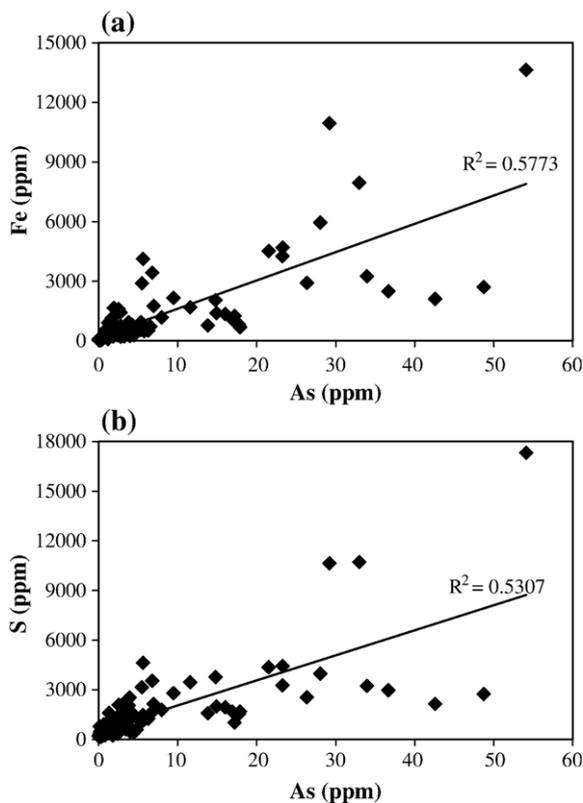


Fig. 5. (a) As vs. Fe for the complete data set. (b) As vs. S for the data set after samples containing abundant organic material were removed.

composed of relatively pure limestone (i.e., no visible minor mineral phases) consistently contained As concentrations below the global average of 2.6 ppm (Baur and Onishi, 1969). Most of the samples were low in As; 90% of the samples had less than 10 ppm As, and approximately 50% of our samples had less than 1 ppm (Appendix 1). High As concentrations are most often correlated with the abundance of non-carbonate minerals, whether primarily deposited as siliciclastics, phosphates, or organic material, or secondary, diagenetic input, such as framboidal or pseudo-framboidal pyrite. Interval samples only showed high As when associated with minor constituents, and targeted samples comprised almost the entire suite of samples with high As concentrations.

The results for all 120 samples that were analyzed by ICP-OES for S, Fe, Ca, Mg, Mn, Si, P, and Sr, along with their respective As data are presented in Appendix 2. The 25 samples highest in As arranged from highest to lowest concentration are presented in Table 1. A significant degree of linear correlation exists between Fe and S, with an r^2 value of 0.67 for the entire data set (Fig. 4a). The correlation improved after those samples consisting of mostly organic

material were removed from the plot ($r^2=0.92$, Fig. 4b). Plants incorporate S, which is left behind during decomposition. Thus, high S concentrations are expected for those samples that contain organic matter, justifying their removal from the correlation plot.

The strongest correlation we found for As in the Suwannee Limestone is with Fe and S, with correlation coefficients (r^2) of 0.57 and 0.53, respectively (Fig. 5a and b, Table 2). The correlation coefficients (r^2) between As and other elements are as follows: Ca=0.14, Mg=0.001, Mn=0.003, Si=0.15, P=0.05, and Sr=0.0008.

4.2.2. Arsenic on fracture surfaces and in adjacent matrix

Thirteen samples of fracture surfaces were taken along with their non-fractured (matrix) counterparts from the same depth intervals. Total As concentrations were determined for both fracture surfaces and adjacent matrix by HG-AFS analysis.

The fractured areas were sampled because it was thought that iron oxyhydroxide might be coating fracture surfaces and thus could be releasing As during

Table 2
Chemical composition of those Suwannee Limestone samples highest in arsenic

ROMP Well	Depth (m)	As (ppm)	S (ppm)	Fe (ppm)	Ca (ppm)	Mg (ppm)	Mn (ppm)	Si (ppm)	P (ppm)
TR 9-2	116	54	17,320	13,640	124,800	4200	11	1324	31
TR 3-3	233	49	2748	2708	82,800	8120	5	284	82
DV-1	76	43	2154	2106	392,500	1977	32	153	77
TR 1-2	400	37	2976	2492	335,200	5480	20	186	121
9	181	34	3237	3249	133,750	5281	6	2612	29
25	179	33	10,720	7960	360,800	3876	17	80	95
TR 1-2	294	29	10,640	10,960	108,000	7720	26	500	2296
9	190	28	3972	5953	105,100	75,100	17	413	323
TR 8-1*	165	27	8920	1964	314,000	3936	20	304	57
TR 5-1	183	26	2548	2920	263,600	9000	16	3712	1908
5	258	23	4443	4703	321,450	2798	15	355	2420
9	190	23	3276	4255	9785	15,385	1	590	132
TR 5-1	173	22	4360	4520	244,000	12,560	11	2508	104
17	213	18	1684	684	378,000	4760	8	184	93
9	248	18	1546	813	395,100	4304	4	42	82
5	267	17	1017	1255	8872	14,033	0	418	646
20	160	17	1688	1076	384,400	2952	19	156	66
TR SA-1	219	16	1942	1351	230,500	115,400	30	219	761
39	201	15	2004	1397	374,850	3894	7	62	34
TR 1-2	276	15	3772	2048	408,000	1112	11	102	74
TR 1-2	402	14	1584	776	408,000	3720	5	218	81
49*	162	12	16,040	2956	13,360	3832	10	1232	604
TR 8-1*	166	12	2972	992	385,600	6400	24	428	53
20	254	12	3456	1680	377,200	4280	8	325	4320
TR 9-2*	119	11	3088	1496	369,600	3104	10	255	70

*These samples contain appreciable amounts of organic material.

Table 3

Arsenic concentration of fracture surfaces compared to surrounding limestone matrix (concentrations are in part per million)

ROMP Well	Depth (m)	As fracture	As matrix	Deviation in %
TR 1-2	431	1.69	1.82	2.1
12	249	1.26	1.11	1.9
14	206	0.42	0.72	2.7
20	262	1.25	1.58	2.3
28	157	1.34	1.33	2.0
39	213	2.87	4.27	2.5
TR 5-1	148	1.09	0.93	1.9
5	283	8.43	7.57	1.9
5	294	0.63	0.74	2.2
5	299	0.15	0.40	3.6
TR 8-1	125	1.23	1.00	1.8
TR 3-3	279	0.73	0.56	1.8
TR 3-3	280	1.35	1.16	1.9

ASR. However, secondary mineral growth on fracture surfaces was limited to calcite or dolomite. No hydrous ferric oxide was observed during sampling, and the comparison between fracture surfaces and the associ-

ated non-fractured matrix sample showed no significant differences in As concentration (Table 3).

4.3. Arsenic abundance in individual minerals

After determination of bulk chemical composition, those samples high in As were targeted for a more detailed investigation with the purpose to determine the exact locations of As, i.e., to determine its mineralogical association. Scanning electron microscope analysis confirmed the presence of those minerals that were identified by transmitted and reflected light microscopy. Of all minerals that were analyzed by EDX, As was only detected in pyrite. However, As was not detected in all pyrites and the height of the 10.6 keV peak was found to vary significantly. This indicates that As is not homogeneously distributed in pyrite. The reason for this phenomenon is unclear, because there is no noticeable spatial pattern of As-rich vs. As-poor pyrites, nor was it possible to distinguish between different generations of pyrite. Based on the EDX analyses it emerged that pyrite

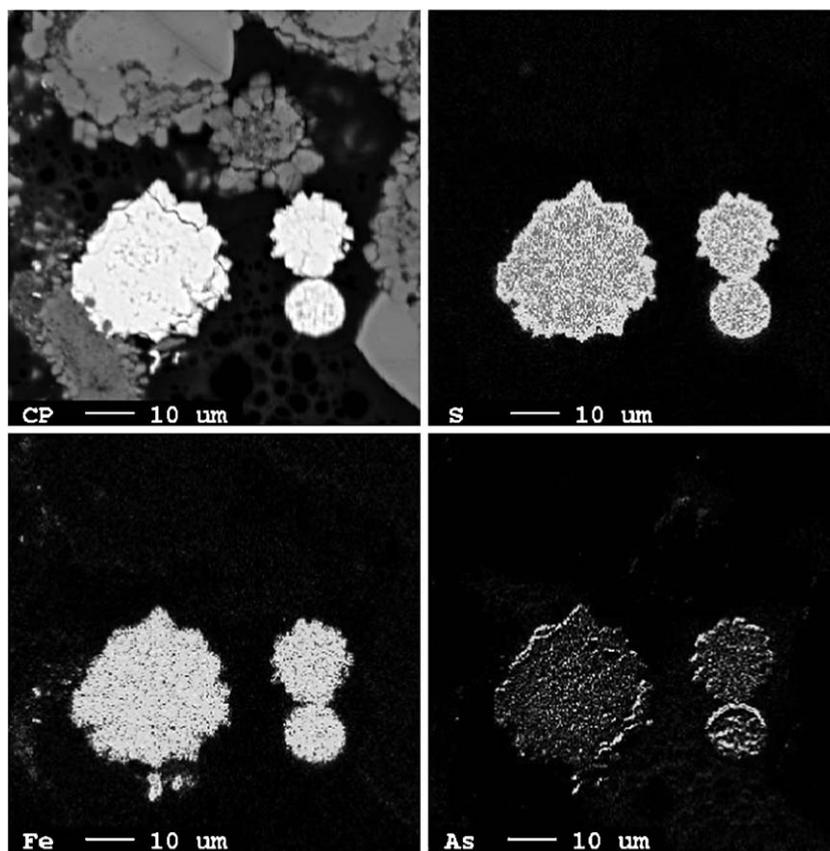


Fig. 6. Backscatter image (upper left) and S, Fe, and As element maps of framboidal pyrite and surrounding matrix in the Suwannee Limestone. The abundance of S, Fe, and As is shown in the upper right, lower left, and lower right, respectively. Note: the dark areas in the backscatter image are epoxy, while the light grey is carbonate.

Table 4
Electron microprobe data for pyrite (values in weight percent)

No.	S	Fe	As	Hg	Pb	Cu	Zn	Total
1	51.5	45.2	0.32	0.00	0.00	0.02	0.11	97.1
2	52.6	45.0	0.17	0.00	0.00	0.01	0.08	97.8
3	51.9	45.0	0.33	0.00	0.00	0.00	0.06	97.3
4	52.2	44.6	0.12	0.00	0.04	0.02	0.05	97.0
5	51.6	44.6	0.19	0.01	0.00	0.00	0.04	96.4
6	52.3	44.9	0.14	0.00	0.00	0.02	0.06	97.5
7	53.2	45.7	0.14	0.00	0.02	0.03	0.03	99.1
8	51.1	43.2	1.00	0.00	0.07	0.10	0.09	95.6
9	49.3	44.4	0.08	0.00	0.00	0.00	0.03	93.8
10	52.8	45.0	0.18	0.00	0.00	0.00	0.02	97.9
11	53.4	45.6	0.05	0.00	0.00	0.01	0.01	99.1
12	53.0	45.5	0.07	0.00	0.03	0.00	0.00	98.6
13	50.3	42.6	0.10	0.00	0.00	0.01	0.03	93.1
14	50.2	42.4	0.12	0.00	0.04	0.00	0.03	92.7
15	52.5	44.9	0.49	0.00	0.01	0.00	0.08	98.0
16	53.3	45.3	0.09	0.00	0.01	0.00	0.04	98.7
17	53.1	45.5	0.07	0.00	0.01	0.01	0.03	98.7
18	50.9	44.1	0.04	0.00	0.01	0.00	0.00	95.0
19	42.0	37.8	0.01	0.00	0.00	0.03	0.05	79.9
20	50.5	44.4	0.14	0.00	0.01	0.00	0.00	95.1
21	37.7	42.4	1.12	0.00	0.00	0.01	0.00	81.2
22	24.2	50.4	0.17	0.00	0.00	0.05	0.02	74.8
23	28.5	48.5	0.15	0.00	0.00	0.04	0.03	77.3
24	17.5	48.7	0.23	0.00	0.00	0.03	0.01	66.5
25	34.7	46.4	0.19	0.00	0.00	0.18	0.06	81.5
Minimum	17.5	37.8	0.01	0.00	0.00	0.00	0.00	66.5
Maximum	53.4	50.4	1.12	0.01	0.07	0.18	0.11	99.1
Mean	46.8	44.9	0.23	0.00	0.01	0.02	0.04	92.0
%RSD	10.1	2.4	0.27	0.00	0.02	0.04	0.03	9.2

is the only mineral that contains appreciable amounts of As, i.e. in concentration above the detection limit of EDX (~1000–3000 ppm).

Similar to SEM-EDX analyses, the electron microprobe analyses of clays, pyrite, apatite, calcite, dolomite, quartz and organic material did not reveal appreciable amounts of As in minerals other than pyrite. An example of elemental mapping is presented in Fig. 6, which clearly demonstrates the As enrichment in pyrite when compared to the matrix. The mean concentration of As in pyrite is 0.23 wt.% or 2300 ppm ($n=25$), with a range from 100 to as high as 11,200 ppm (Table 4). These are some of the highest (if not the highest) reported values for As in framboidal or pseudo-framboidal pyrite. Prior studies of pyrite framboids have documented As concentrations of as much as 1000 ppm, substituting for sulfur in the FeS_2 crystal structure (Thomas and Saunders, 1998). Our data indicate that As in pseudo-framboidal pyrite from the Suwannee Limestone can be as much as 10-times this value.

The heterogeneous distribution of As within pyrite that was indicated by SEM-EDX analysis could also be confirmed by electron microprobe analyses.

5. Discussion

Based on the data presented above it becomes apparent that pyrite is responsible for harboring most of the As in the Suwannee Limestone. The question that remains is if we can quantify its role. Assuming that Fe and S in our bulk rock analyses are exclusively derived from the breakdown of pyrite we can calculate its abundance in the aquifer matrix. This approach is warranted by the strong linear correlation between Fe and S and its closeness to the pyrite line ($\text{Fe}=2\text{S}$), which indicates the relative concentrations of Fe and S in pyrite in part per million (Fig. 4). The calculated value of pyrite abundance multiplied by the mean As concentration in pyrite provides an estimate of bulk As concentration, which now can be compared to the actual concentration of As that was measured by AFS (Fig. 7). In those samples that plot above the equal concentration line pyrite alone cannot account for the amount of As that was measured in the bulk sample. On the other hand in those samples that plot on or below the equal concentration line, As in pyrite can account for the amount of As that was measured in the bulk sample. Only a few samples high in clay content plot above the equal concentration line. This confirms that pyrite is the dominant As-bearing phase in the Suwannee Limestone, with clay minerals being a distant second.

Indirect evidence for the role of pyrite is provided through the aquifer storage and recovery (ASR) process itself. As mentioned earlier the injected water is virtually As-free, while the recovered water can contain up to 130 $\mu\text{g/L}$ As. Knowing that the bulk of As in the

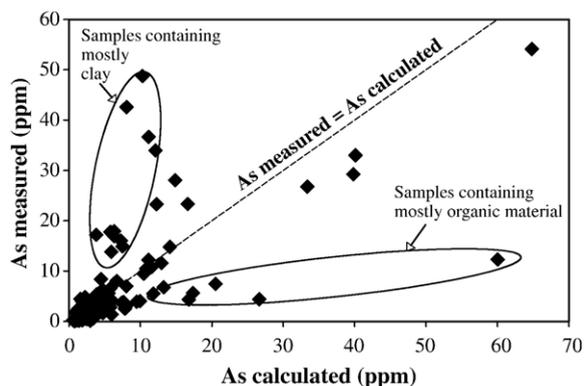


Fig. 7. Plot of As measured vs. As calculated, based on As abundance in pyrite. The dotted line represents the ideal case of As measured = As calculated. Data points that fall above this line contain more bulk As than expected, considering pyrite as the only source of As, and are made up of mostly samples containing clay. Data points below the line are due to high S contents in organic material and therefore have higher calculated As values.

Suwannee Limestone is contained in pyrite, a logical next step is to consider the chemical reactions taking place during ASR recharge into the Suwannee Limestone. In aqueous solutions pyrite is generally stable under reducing, oxygen-depleted conditions within a pH range from 4 to 9 and an Eh range from -0.4 to 0.1 (e.g., Garrels and Christ, 1965). These physico-chemical conditions exist in our study area (Sprinkle, 1989), hence the abundance of pristine pyrite in our samples. A change towards oxygen-rich conditions causes the rapid breakdown of pyrite as seen in the formation of acid mine drainage (e.g., van Geen et al., 1999). Thus, the breakdown of pyrite and mobilization of As from the aquifer matrix during ASR could be caused by introducing oxygen into the Suwannee Limestone. In Florida the operators of ASR facilities are required by Florida Law (Florida Administrative Code, Chapter 62-528, Underground Injection Control) to inject treated (potable) water for storage. As a result the recharge water is extremely oxygen-rich, because it is treated with ozone (O_3) prior to injection (Tampa Bay Water Department, Lowe, pers. comm., 2002). Mericki (2004) reports that dissolved oxygen (DO) is reduced during cycle testing at ASR systems in west-central Florida, from atmospheric equilibrium 8 mg/L to approximately 2 mg/L. A simplified chemical reaction for the uptake of oxygen is the breakdown of pyrite: $FeS_2 + 7/2 O_2 = Fe^{2+} + 2 SO_4^{2-} + 2 H^+$. This reaction then releases iron (Fe^{2+}), sulfate (SO_4^{2-}) and As (in the case of As-rich pyrite) into the recharge water. While the increase in As and Fe has been observed in recovered water, along with a subsequent decrease in DO (Arthur et al., 2002; Mericki, 2004), it is not possible to detect an increase in sulfate, because of its high background concentration in the Upper Floridan aquifer, which conceals any changes in SO_4^{2-} content (Sacks et al., 1995). The decomposition of organic matter could be an alternative oxygen-consuming reaction in the Suwannee Limestone, however, in our study area organic material was observed in only a few samples.

Hydrous ferric oxide (HFO), in particular ferrihydrite, can have As concentrations greater than 5 wt.% (e.g., Pichler et al., 1999). Thus, the release of As from HFO was originally considered a possible source for the high values in recovered ASR water (CH2MHill, 2000; Arthur et al., 2002). Hydrous ferric oxide, however, was encountered in only three samples, where it occurred as an oxidation halo around pseudo-framboidal pyrite. Its absence is not surprising when considering that the physico-chemical conditions of the Upper Floridan aquifer in the study area are generally oxygen-poor

(Sprinkle, 1989), because HFO is generally only stable in an oxygen-rich environment (e.g., Pichler et al., 1999). Thus, the HFO halos around the framboids are interpreted to be the result of pyrite oxidation during and after the drilling and coring process. Nevertheless, HFO should not be categorically dismissed as a source of As. In unconfined aquifers, for example HFO can be stable if oxidizing conditions exist. There, a change from oxidizing to reducing would cause the breakdown of HFO and thus release previously adsorbed As.

5.1. Implications for the interpretation of As concentrations in bulk rock

This study is the first to determine the specific location of As in limestone, whereas other reported concentrations for As in limestone were a byproduct of more comprehensive bulk rock chemical analyses (Baur and Onishi, 1969). According to Taylor and McLennan (1985) the abundance of As in the upper continental crust is approximately 1.5 ppm. This value is somewhat controversial, because most of the individual rock types that were analyzed for As have higher values. The averages for the common igneous rocks, basalt and granite are 8.3 and 7.6 ppm, respectively (Taylor, 1964). The average for shale and its related materials, such as loess and mud, is approximately 10.6 ppm (Li, 2000). The average composition for sandstone is too difficult to determine, but the value for the commonly used geostandard GSR-4 is 9.1 ppm (Govindaraju, 1994). The average value for limestone/dolomite is 2.6 ppm (Baur and Onishi, 1969). Thus, the As concentration in the upper continental crust is most likely above 1.5 ppm, but should not be in excess of 10 ppm. While the average concentrations are known, next to nothing is known about how the bulk of As is present in the individual rocks that comprise the upper continental crust.

The average of 3.5 ppm for the entire data set from this study is about one third higher than the reported global average for As in limestone of 2.6 ppm (Baur and Onishi, 1969). The sampling strategy that was applied for this study is the likely cause for this difference. Those samples that were “targeted” have a mean As concentration of 9.5 ppm, while the interval samples have only a mean As concentrations of 1.7 ppm. Thus, minor mineral phases, which contain relatively high As concentrations, have a dominating effect on the abundance of As in the Suwannee Limestone. The global average for As in limestone could be assumed to be a value based on pure limestone without siliciclastics or secondary (diagenetic) inputs. There has been no

determination of the distribution coefficient for As between various waters and calcium carbonate, and recent data for aragonite and calcite that precipitated from a hydrothermal fluid show that As concentrations in the carbonates are low (<2 ppm, Pichler and Veizer, 2004) despite a very high concentration in the fluid (>1 mg/L; Pichler et al., 1999). This confirms our findings for the Suwannee Limestone, and suggests that As in excess of 2 ppm is not associated with the calcium carbonate, but rather with impurities, such as trace minerals and organic matter that are common in limestone (e.g., Tucker and Wright, 1990). Thus, the determination of trace element abundances has to incorporate careful sampling of minor mineral phases as well as bulk rock.

It is also noteworthy that the As in the Suwannee Limestone (and possibly many other sedimentary rocks) seems to be of a post-depositional origin. The microcrystals making up the framboids are colloid-sized, which indicates that their formation is post-depositional (diagenetic) because they are stable in fresh water, but unstable in seawater (Wilkin and Barnes, 1997). Therefore, their location in fossil molds suggests post-depositional processes. Single euhedral pyrite crystals are also observed, possibly suggesting two stages of crystallization.

6. Summary and conclusions

Our detailed lithologic, mineralogical, and geochemical study of As in the Upper Floridan aquifer, Suwannee Limestone shows that:

1. Arsenic is present in the Suwannee Limestone at low concentrations, but is concentrated in minor mineral phases, particularly pseudo-framboidal pyrite.
2. Pyrite is generally As-rich and can contain concentrations between 100 and 11,200 ppm As (average 2300 ppm, $n=25$).
3. Compared to pyrite, other trace minerals contain much less As.
4. Pseudo-framboidal pyrite is ubiquitous throughout the Suwannee Limestone, but is most abundant in moldic, high porosity zones.
5. Hydrous ferric oxide (HFO) or Fe-oxyhydroxide, clay minerals and apatite are not an important source of As.

The average As concentration for all 306 samples that were collected is 3.5 ppm, which is higher than the global average for limestone. This is a result of the emphasis that was placed on finding the exact location

of As. In addition to random sampling, we also collected targeted samples that were chosen, because they had the potential for elevated As. The average As concentration without the targeted samples is only 1.7 ppm, while the average for the targeted samples is 9.5 ppm. This confirms that secondary trace minerals rather than the carbonate matrix are responsible for elevated As values in limestone. This has implications for the determination of As in rocks that undergo post-depositional alteration (diagenesis).

With respect to the operation of ASR facilities that intend to store water in limestone it is important to carry out a detailed mineralogical/chemical investigation of the aquifer matrix prior to operation. If As-rich pyrite is present, the injection of oxygen-rich water, compared to native groundwater, will most likely cause the release of As. The As problem for ASR in the Suwannee Limestone is enhanced considering that pyrite is most abundant in the high porosity zones that are the prime storage zones. Based on our observations, samples from the high porosity zones in the Suwannee Limestone do not contain minerals other than pyrite and calcium carbonate. This study also indicates that if the pyrite dissolution hypothesis is accepted, the current injection practices in Florida may need to be reconsidered (Florida Administrative Code, Chapter 62-528, Underground Injection Control).

Although not thoroughly discussed in the text, this study indicates that it is possible to generate a high-As groundwater due to water–rock interaction with an aquifer matrix low in As. Groundwater in the Upper Floridan aquifer is in equilibrium with pyrite and contains generally less than 1 $\mu\text{g/L}$ As (Pichler et al., 2004; Pichler, unpubl. data). The water that is injected for storage is treated according to the US EPA drinking water standards and generally contains less than 1–2 $\mu\text{g/L}$ As (Arthur et al., 2001). Thus the release of As from the aquifer matrix is the possible explanation for As concentrations of up to 130 $\mu\text{g/L}$ in the recovered ASR water. A change in physico-chemical conditions that has an effect on the stability of As-bearing minerals is sufficient to increase As concentrations by several orders of magnitude.

Acknowledgements

Funding for this study was provided through a grant to TP from the Southwest Florida Water Management District. The Florida Geological Survey supplied the core material for this study. We thank John Arthur and Gregg Jones for their constructive comments and continued discussion. Tom Beasley and Mike Spilde

are thanked for their help with the SEM and EMP analyses. Comments from Matthew Eick and an anonymous reviewer helped to improve the manuscript. [DR]

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2005.11.018](https://doi.org/10.1016/j.chemgeo.2005.11.018).

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