



## Determination of arsenic concentration and distribution in the Floridan Aquifer System

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### ABSTRACT

Here we report on the different sampling strategies for almost seven years of sampling rocks/sediments for the determination of As within the Intermediate Aquifer System (IAS) and upper Floridan Aquifer System (FAS), a very large and productive limestone aquifer spanning from Georgia into Florida. In the FAS, As contamination has become a recurring problem during aquifer storage and recovery (ASR), particularly in central and south Florida.

To investigate these phenomena, samples from solid drill cores and rock cuttings were collected from the Hawthorn Group, Suwannee Limestone, Ocala Limestone and Avon Park Formation. Samples were taken along drill cores and rock cuttings (referred to as 'interval' samples) or from particular drill core sections and rock cuttings (referred to as 'targeted' samples) likely to contain elevated concentrations of As as indicated by the presence of pyrite, hydrous ferric oxide, organic matter, clay minerals, fracture surfaces, and high permeable (moldic) zones.

Arsenic was present in all of the stratigraphic units at low concentrations, close to the global average for As in limestone of 2.6 mg/kg. The highest As concentration was 69 mg/kg. In all units, however, the average bulk As concentration in the targeted samples was substantially higher than that in the interval samples. Based on direct spot measurements by electron microprobe and indirect calculations, pyrite was identified as the main source of As in the FAS. Concentrations in pyrite ranged from less than 100 mg/kg to more than 11,000 mg/kg. Because pyrite is heterogeneously distributed, both vertically and horizontally in the sampled stratigraphic units, the same was observed for the distribution of As. However, As concentrations generally decreased with depth, i.e., highest As values in the Hawthorn Group and lowest As values in the Ocala Limestone and Avon Park Formation. Compared to pyrite, other trace minerals contained much less As.

The average As concentrations of the two types of sample media (solid cores and rock cuttings) were quite similar. These results indicate that if simply the average bulk rock As concentration of a geologic unit is the desired outcome of an investigation, either interval or targeted sampling of rock cuttings, seems to be sufficient. This is particularly important when time and money are a factor. This approach could work equally well for any other trace element. Structural sedimentary information, such as fractures, etc., is likely lost, however, when sampling rock cuttings. Thus, if this information is required, solid core samples need to be collected by hollow core diamond drilling.

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### 1. Introduction

Numerous occurrences of elevated arsenic (As) concentrations in groundwater were reported during the past 20 to 30 years. With few exceptions, the source of As was geogenic, i.e., naturally occurring in the aquifer matrix. The release of As from the aquifer matrix was generally thought to be caused by anthropogenic perturbations of the physico-chemical conditions in the aquifer. There are many publications in the

scientific literature addressing this issue, including several excellent reviews (e.g., Amini et al., 2008; Ferguson and Gavis, 1972; Korte and Fernando, 1991; McNeill et al., 2002; Smedley and Kinniburgh, 2002). This type of As contamination is a public health issue worldwide. In particular the ongoing catastrophic problems in Bangladesh and West Bengal have been front-page stories in newspapers and scientific journals (e.g., Ahmed et al., 2006).

Like in Bangladesh, there are many other locations where similar geogenic As contamination occurs independent of aquifer matrices, whether fluvial sediments, marine shale or carbonate rocks. However, little is known about geogenic As contamination in limestone/carbonate aquifers. A thorough literature search provided only five published

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works on this matter (Armienta and Segovia, 2008; Gbadebo, 2005; Romero et al., 2004; Simsek et al., 2008; Vesper and White, 2003). Limestones, typically considered excellent aquifers due to low bulk concentrations of As compared to sandstones and shales, are possibly problematic because karstification allows contaminants to be transported over large distances, thus posing a potential threat to public and private water supplies (e.g., Ducci et al., 2008; Katz, 2004; Kovacova and Malik, 2007; McMahon et al., 2008; Obeidat et al., 2008; Zhou and Beck, 2008). Groundwater can flow through conduits so that there is little opportunity for filtration or sorption of contaminants onto aquifer material. Thus, it is important to assess and understand geogenic As contamination in limestone aquifers, where anthropogenic perturbations could cause the release of As from a limestone matrix far from the area where elevated As values eventually occur. In addition, although limestone aquifers generally contain low concentrations of As, recent data suggest that high concentrations of As can be released due to anthropogenic perturbations (e.g., Price and Pichler, 2006). Considering this, it is important to understand the distribution and association of As in a limestone aquifer, e.g., to know if As is associated with a certain mineral or distributed mainly within the matrix porosity or the fracture porosity. Detailed knowledge about the precise mineralogical phases involved is particularly important for geochemical modeling to predict the mobilization of geogenic As from an aquifer matrix (e.g., Pichler et al., 2001).

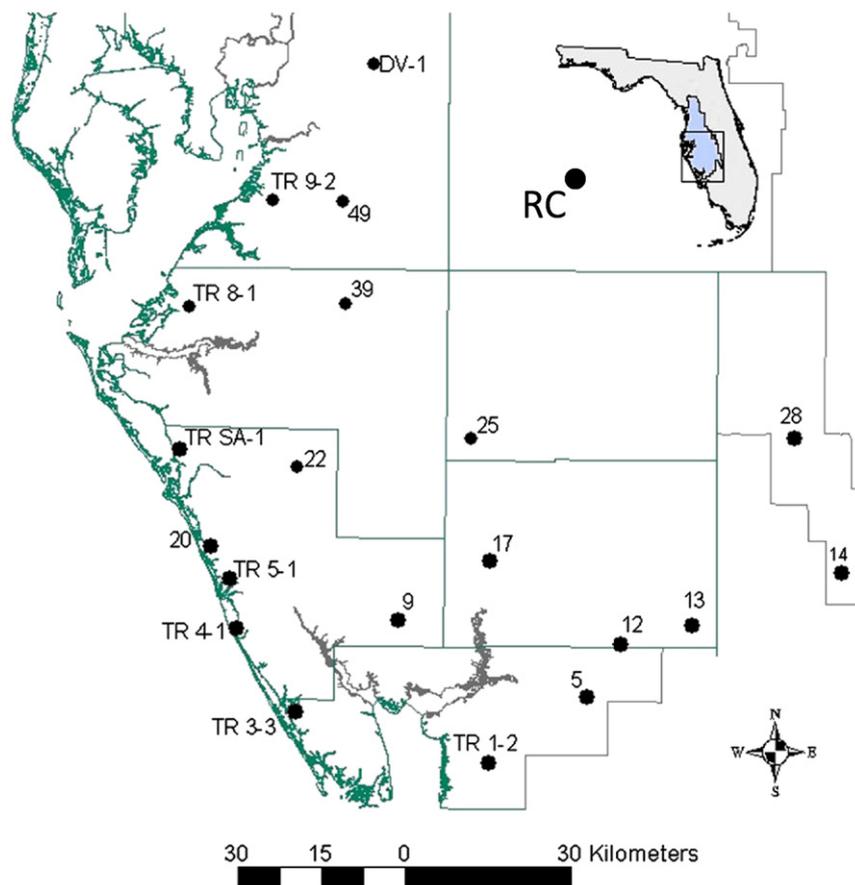
Here we address the issues discussed above by assessing different sampling strategies utilized during seven years of sampling rocks for the determination of As concentration and distribution within the Floridan Aquifer System (FAS), which is a very large and productive limestone aquifer spanning from Georgia into Florida (Dippold and Pichler, 2008; Lazareva and Pichler, 2007; Price and Pichler, 2006). In the FAS, geogenic

As contamination has become a recurring problem. The practice of aquifer storage and recovery (ASR) caused mobilization of As from the aquifer matrix, which exceeded the maximum allowable contaminant level (MCL) for As in drinking water set by the US Environmental Protection Agency (Arthur et al., 2003, 2005). Furthermore, there were numerous occurrences of elevated As concentrations in public and private water supply wells (Pichler and Sueltenfuß, 2010). In this paper, we compare published data for the Hawthorn Group (Lazareva and Pichler, 2007) and Suwannee Limestone (Price and Pichler, 2006) to new data for the Ocala Limestone and Avon Park Formation. This combination of data allows us to describe the occurrence and distribution of As in the complete section of the Intermediate and Upper Floridan Aquifer, and to evaluate the best sampling strategy across various applications.

## 2. Geology and hydrogeology of the study area

The study area is located in central Florida (Fig. 1). In this area the subsurface can be subdivided into three distinct hydrostratigraphic units, which generally thicken from the north to the south. They are from top to bottom, the Surficial Aquifer System (SAS), the Intermediate Aquifer System (IAS) or confining unit and the Floridan Aquifer System (FAS) (Fig. 2). Due to good permeability and confinement, the upper portion of the FAS is the preferred target for ASR.

The upper part of the FAS consists generally of limestone, which was deposited in a shallow marine environment. From top to bottom, the sequence of rocks in the upper FAS consists of the Suwannee Limestone, the Ocala Limestone, and the limestones and dolomites of the Avon Park Formation. Carbonate deposition was at first interrupted periodically, and later completely, with the influx of siliciclastic sediments eroded



**Fig. 1.** General location map of the study area. Numbered black circles indicate the locations of Regional Observation Monitor Well Program (ROMP) 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 the upper-right inset). The location where the rock cuttings were collected is indicated by RC.

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

Fig. 2. Lithostratigraphic and hydrostratigraphic column of the study area. The lithostratigraphic units, which were part of this study are shaded. Modified from Miller (1986).

from the Appalachian Mountains. Thus, the IAS, which confines the FAS in the study area, consists of interbedded carbonates, sands, silts and clays of the Hawthorn Group (Miller, 1986). The Hawthorn Group was deposited in a shallow marine to non-marine fluvial and deltaic environment, which prograded over the older carbonate platform and caused an increase in siliciclastic sediments towards the top of the section. With respect to As distribution, rock type and minor (accessory) mineral phases are important, as well as the presence of fracture zones. These attributes are briefly described for each rock type in the following sections.

### 2.1. The Hawthorn Group

The Miocene Hawthorn Group is subdivided into a lower section comprising the undifferentiated Tampa and Nocatee Members of the Arcadia Formation and the upper section of the Peace River Formation (Fig. 2) (Scott, 1988, 1990). The Tampa Member of the Arcadia Formation is predominantly carbonate with variable amounts of dolostone, clay, quartz sand and minor occurrences of francolite (a carbonate-rich variety of apatite), while the Nocatee Member is characterized by less carbonate and more siliciclastic material (Scott, 1988; Wingard et al., 1993). The Peace River Formation unconformably overlies the Arcadia Formation (Fig. 2) and consists mainly of greenish gray sandy clays and some carbonates, which are comprised of interbedded limestone and dolostone (Green et al., 1995). Mainly in its framboidal form, pyrite was found unevenly distributed throughout the Hawthorn Group (Lazareva and Pichler, 2007).

### 2.2. The Suwannee Limestone

The Oligocene Suwannee Limestone in the study area consists primarily of limestone, which was described as a wackestone (mud to pelletal) and foraminiferal grainstone (Gilboy, 1985; Green et al., 1995; Hammes, 1992). It contains minor amounts of phosphatic quartz sand and clay intermixed with limestone near the top of the formation (representing the influx of siliciclastic sediments as the Georgia Straights closed), and a thin layer (3 m to 6 m) of dolostone in the lower third of the formation. Chert nodules, organic material, and pyrite are also present in minor amounts (Green et al., 1995; Miller, 1986). Mollusk molds and casts are common in the upper part, but become generally less abundant with depth (Miller, 1986). Thus, the upper part

of the Suwannee Limestone is characterized by high moldic porosity, which is important for ASR. In other parts of the Suwannee Limestone intergranular porosity is common. Fractures are present in parts of the Suwannee Limestone, which allow fracture flow of groundwater.

### 2.3. The Ocala Limestone

The Upper Eocene Ocala Limestone in the study area is a chalky, fine- to coarse-grained limestone, containing trace amounts of organic material, clay and variable amounts of dolomite. Siliciclastics are rare. However, chert occurs throughout the formation and is generally more common where the unit occurs at or near land surface. Trace amounts of organics and clay likely represent post-depositional filling (Green et al., 1995). Pyrite is also present as a trace mineral, but to a lesser extent than in the overlying Suwannee Limestone or underlying Avon Park Formation.

### 2.4. The Avon Park Formation

The Lower Eocene Avon Park Formation (APF) is comprised of interbedded limestone and dolomite in the upper portions, changing with depth to thick beds of continuous dolomite with increasing amounts of evaporites towards the base. The limestone is a recrystallized fossiliferous packstone, fine- to coarse-grained, cream to brown in color, with variable amounts of organic-rich peat laminations and numerous sea grass fossil beds near the top of the formation (Tihansky, 2005). The limestone is sometimes interbedded with dark brown to tan fossiliferous dolostones, which are very hard and sucrosic in texture and highly fractured (Arthur et al., 2008). Moving deeper in the Avon Park Formation, the rocks become almost entirely dolomitic, and interstitial void spaces are filled with evaporites. The evaporites occur in the dolomite as interstitial gypsum and anhydrite and are interbedded in the lower two thirds of the formation, increasing with depth and resulting in reduced porosity (Tihansky, 2005). Arthur et al. (2008) identified chert, pyrite, gypsum, and quartz as accessory minerals throughout the Avon Park Formation.

## 3. Methods

In order to evaluate the abundance and mineralogical association of As in the IAS and FAS, samples from the Hawthorn Group, Suwannee Limestone, Ocala Limestone and Avon Park Formation were analyzed using a combination of petrographic and geochemical techniques. Solid cores from the Hawthorn Group, Suwannee Limestone and Avon Park Formation have been drilled as part of the Regional Observation Monitor Well Program (ROMP) of the Southwest Florida Water Management District (SWFWMD) and are stored at the Florida Geological Survey (FGS) core repository in Tallahassee, Florida. The locations of the cores were chosen to obtain good spatial coverage of the area between Tampa and Ft. Myers (Fig. 1). From those solid cores, we collected samples at fixed intervals (referred to as 'interval' samples) or only at particular locations (referred to as 'targeted' samples). In addition to the core samples, a set of samples from the Suwannee Limestone, Ocala Limestone and Avon Park Formation was collected as rock drill cuttings during the installation of an exploratory aquifer recharge well at the Hines Energy Complex southeast of Tampa (RC in Fig. 1).

### 3.1. Core samples

Each core was sampled at an even spacing to ensure representation of the stratigraphic units. For example, if the total thickness of the Suwannee Limestone would be 30 m in a certain core, a sample would be collected every 3 m. In addition to these interval samples, targeted samples were taken along each core from sections with visible pyrite, hydrous ferric oxide, clays or organic material. These sections were suspected to have As concentrations higher than the bulk carbonate

matrix. Since fractures can enhance groundwater flow, particularly during ASR, fracture surfaces were also part of the targeted samples. A similar logic of collecting interval and targeted samples was applied to the core sections from the Avon Park Formation. The only difference was that in highly permeable zones in the upper parts of the Avon Park Formation, approximately double the amount of interval samples were collected. These zones were determined based on drill log data. The reason behind the tighter spacing was to get better information for future ASR operation in the Avon Park Formation (Dippold, 2009).

When a core was poorly indurated or crumbly, a small piece was broken off by hand and placed in a Ziploc® bag. If a core sample was too hard to break by hand, a rock hammer or rock saw was used. All instruments were thoroughly rinsed with de-ionized (DI) water at 17.9  $\mu\Omega$  or better.

### 3.2. Rock cuttings

During drilling of the exploratory aquifer recharge well (RC in Fig. 1), rock cuttings, approximately 0.5 cm to 3 cm in size, were collected continuously into 5 L buckets, which then were filled with nitrogen and closed with an airtight lid until time of analysis. The rock cuttings were brought to the surface with the reverse air circulation method and bottom-up times were taken into account during logging to ensure correlation between borehole depth and rock cuttings. Each bucket represented an interval of approximately 3 m.

In the laboratory, rock cuttings from each interval were removed from the buckets and spread evenly on a flat surface for visual examination, aided by hand lens and stereomicroscope. To ensure representation of the stratigraphic units two samples were collected randomly from each bucket. These samples can be directly compared to the interval samples (see above). Additionally, one to three targeted samples were taken per bucket. Targeted samples were chosen based on the same criteria applied during collection of the core samples, i.e., the presence of hydrous ferric oxides, clays, pyrite and organic matter.

### 3.3. Chemical analyses

For bulk rock chemical analysis, each sample was powdered and dissolved using a digestion method modified from van der Veen et al. (1985). Mortar and pestle were cleaned with pure quartz sand and rinsed with distilled water between samples to prevent cross contamination. A dilute solution of HNO<sub>3</sub> was used instead of distilled water during preparation of the fine glauconitic clays of the Hawthorn Group. This was necessary to quantitatively remove all clay residue from the mortar. An electronic scale was used to weigh out  $0.5 \pm 0.005$  g of powdered sample into Teflon vials for digestion. Digestion was performed with 10 mL aqua regia, a 3:1 mixture of HCl and HNO<sub>3</sub>. Digestion batches included internal and external standards, blanks, and duplicate samples for quality control and assurance.

The Suwannee samples were sealed and remained at room temperature for 24 h with periodic agitation to assist in digestion. The elevated temperatures in a hot block can speed up the digestion and thus, a hot block was used for the Hawthorn Group, Ocala Limestone and Avon Park samples. The Ocala and Hawthorn samples were capped with a ribbed plastic watch glass to prevent the escape of water vapor and potentially arsine gas and placed on a hot block at 95 °C for 30 min (Tatro et al., 1999). The Avon Park samples were capped in the same manner and placed on a hot block for 30 min at 80 °C. Once cooled, the digestates were diluted to a volume of 50 mL with DI water. Since the aqua regia digestion did not break down silicate minerals, such as clay, feldspar and quartz, the digestates were filtered through a 0.45  $\mu\text{m}$  membrane to remove the residuals. The Hawthorn samples, which contained the highest amount of residuals, were centrifuged first and then filtered to minimize filter clogging. Centrifugation was not necessary for the Suwannee Limestone and Avon Park samples and they were filtered after a settling period of 24 h.

Following digestion and filtration, the samples were analyzed for selected major and trace elements by inductively coupled plasma-optical emission spectrometry (ICP-OES) and atomic fluorescence spectrometry (AFS). 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 added to 15 mL concentrated HCl, 1 mL saturated potassium iodide (KI) solution and diluted with DI water to a volume of 50 mL. All reagents used in sample preparation were trace metal grade or better.

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%. Arsenic recovery was verified by spiking approximately 5% of the samples during digestion. Recovery was generally better than 10% indicating the reliability of our digestion method. Reagent-acid blanks were tested and showed no detectable As, i.e., concentrations were consistently below 0.05  $\mu\text{g/L}$ . Background signal drift was consistently less than 5%.

The analyses of iron (Fe), calcium (Ca), magnesium (Mg), silica (Si), sulfur (S) phosphorus (P) and aluminum (Al) were carried out using a Perkin Elmer Optima 2000 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). Two mL of the filtered digestate were diluted with 8 mL of DI water into 15 mL conical tubes in preparation for analysis. The accuracy of the measurements and acid digestion was verified by analysis of the JGS JLS-1 reference material and sample duplicates. Acid blanks were tested and showed no detectable contamination of analyzed elements. Background signal drift was consistently less than 1% and the analyses of duplicates indicated a precision of better than 5%.

Samples with bulk concentrations of As significantly above the global average for limestone of 2.6 mg/kg were selected for further analyses to better constrain the mineral phases containing As. This included the preparation of carbon-coated sample fragments and polished thin sections for the microanalysis by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), respectively. During SEM analyses, where elemental compositions can be determined through energy dispersive spectrometry (EDS), the high Mg content of the samples required the use of the 10.6 keV peak, which for As has a detection limit of 2000 to 3000 mg/kg. Thus, the SEM was not suitable for detailed As work, but rather was useful for examining the bulk sample matrix and for identifying clays and major matrix minerals.

Thin sections of selected samples were analyzed by EPMA to identify trace As concentrations in discrete minerals. In all studies pyrite was the main focus. In addition to spot analyses, elemental maps were produced to show the concentrations of Sr, S, Fe, As, Ca, Mg, K, Si, and Al within and around pyrite.

## 4. Results

### 4.1. Core samples

Arsenic concentrations in all Hawthorn samples varied from 0.1 to 69 mg/kg with an average of 5.6 mg/kg ( $n = 356$ ,  $\sigma = 7.1$ ). The data for each individual core are presented in Table 1, where values are presented for the carbonaceous Arcadia Formation, followed by values in brackets for the entire Hawthorn Group, including the non-carbonaceous Peace River Formation. Values from the Hawthorn Group were differentiated, because lithologically only the Arcadia Formation is similar to the Suwannee Limestone, Ocala Limestone and Avon Park Formation. The interval samples had an average of 5 mg/kg ( $n = 285$ ,  $\sigma = 5.8$ ) and the targeted samples had an average of 8.3 mg/kg ( $n = 77$ ,  $\sigma = 10.5$ ). Average As concentrations for the individual units of the Hawthorn Group varied from 9 mg/kg in the Peace River Formation to 3 mg/kg in the Tampa Member of the Arcadia Formation (Lazareva and Pichler, 2007). Based on EPMA

**Table 1**

Average, minimum and maximum As concentrations (mg/kg) in the undifferentiated Arcadia Formation, Suwannee Limestone and Avon Park Formation sorted by individual cores.

Well	Geology	Average	Minimum	Maximum	$\sigma$	(n)
5	Arcadia	5.8 (6.4)	1.1	25.9	6.0	25
9	Arcadia	4.8 (6.5)	0.4	17.9	5.4	20
12	Arcadia	5.4 (6.1)	0.2	69.0	14.2	23
13	Arcadia	5.1 (5.3)	0.5	18.7	4.8	22
17	Arcadia	5.1 (5.6)	0.8	11.1	3.6	17
20	Arcadia	5.9 (6.2)	0.2	36.0	10.6	18
22	Arcadia	4.4 (5.2)	0.2	14.0	4.5	13
25	Arcadia	8.7 (10.7)	1.5	27.9	7.5	11
39	Arcadia	4.7 (4.9)	0.3	12.1	4.0	17
49	Arcadia	6.3 (6.8)	0.5	28.5	7.4	15
DV-1	Arcadia	4.6 (4.4)	0.4	14.2	5.3	6
TR-3-3	Arcadia	4.0 (4.9)	0.3	12.3	3.5	32
TR-4-1	Arcadia	4.5 (4.5)	0.3	33.1	6.7	28
TR-5-1	Arcadia	5.6	0.4	18.1	5.7	18
TR-9-2	Arcadia	3.6 (3.6)	0.6	8.3	2.9	10
TR-SA-1	Arcadia	4.6 (4.6)	0.1	26.2	5.8	24
5	Suwannee	4.4	0.2	19.7	5.2	24
9	Suwannee	10.5	0.2	34.0	13.6	10
12	Suwannee	1.7	0.6	3.7	1.2	13
13	Suwannee	1.1	<0.1	2.7	1.0	8
14	Suwannee	2.2	0.4	7.0	2.7	5
17	Suwannee	2.7	0.3	16.9	3.3	26
20	Suwannee	3.1	0.2	16.9	4.3	19
22	Suwannee	0.6	<0.1	2.5	0.8	8
25	Suwannee	3.7	0.1	33.0	8.0	16
28	Suwannee	2.4	0.5	9.5	2.6	11
39	Suwannee	2.5	<0.1	14.4	3.4	16
49	Suwannee	2.2	0.3	12.3	3.1	15
DV-1	Suwannee	5.5	0.5	42.6	11.2	13
TR-1-2	Suwannee	6.2	0.3	36.7	9.8	21
TR-3-3	Suwannee	2.8	0.1	48.7	9.9	24
TR-4-1	Suwannee	4.1	0.2	17.8	6.6	14
TR-5-1	Suwannee	3.5	<0.1	26.4	7.4	20
TR-8-1	Suwannee	3.8	0.3	26.8	7.0	15
TR-9-2	Suwannee	4.9	0.2	54.1	13.0	17
TR-SA-1	Suwannee	1.7	0.2	15.9	4.3	13
5	Avon Park	3.2	0.2	20.7	4.8	23
9	Avon Park	1.5	0.3	7.7	1.5	23
13	Avon Park	2.7	0.1	22.9	4.7	34
14	Avon Park	0.8	<0.1	4.2	0.9	26
20	Avon Park	3.4	<0.1	27.5	5.8	37
22	Avon Park	3.1	0.1	18.4	5.0	35
25	Avon Park	3.1	<0.1	30.8	7.0	19
28	Avon Park	3.5	<0.1	20.5	5.6	23
39	Avon Park	3.3	<0.1	30.4	7.4	17
49	Avon Park	0.7	<0.1	3.1	0.7	26
DV-1	Avon Park	1.7	<0.1	7.5	1.9	29
TR-4-1	Avon Park	1.3	0.4	2.1	0.5	19
TR-9-2	Avon Park	1.4	<0.1	11.0	2.3	33
TR-SA-1	Avon Park	1.4	<0.1	5.0	1.4	29
RC	Suwannee	3.0	<0.1	16.2	4.2	104
RC	Ocala	1.5	<0.1	14.7	2.9	70
RC	Avon Park	2.9	0.6	14.2	3.0	35

Note: Values in brackets are for the complete Hawthorn Group, including the non-carbonaceous Peace River Formation. RC = Rock Cuttings. Data for the Suwannee Limestone are from Price and Pichler (2006) and data for the Hawthorn Group are from Lazareva and Pichler (2007). Data for RC and Avon Park are from this study. Data for parametric and non-parametric statistical tests can be found in Lazareva (2004) and Dippold (2009).

analyses, pyrite was identified as the main source of As in the Hawthorn Group.

Pyrite was heterogeneously distributed in the Hawthorn Group and its As concentration varied from less than 100 mg/kg to a maximum of 8260 mg/kg (Lazareva and Pichler, 2007). The average As concentration obtained from all pyrite measurements in the Hawthorn Group was 1272 mg/kg ( $n = 126$ ,  $\sigma = 379$ ). In the Arcadia Formation As concentrations in pyrite ranged from less than 100 mg/kg to a maximum of 8260 mg/kg and the average was 1437 mg/kg ( $n = 48$ ,  $\sigma = 1569$ ). In the Tampa Member As concentrations in pyrite varied from less than 100 mg/kg to a maximum of 3220 mg/kg and the average was 1004 mg/kg ( $n = 39$ ,  $\sigma = 770$ ). In the Nocatee Member As concentra-

tions in pyrite varied from less than 100 mg/kg to a maximum of 5710 mg/kg and the average was 2884 mg/kg ( $n = 9$ ,  $\sigma = 1869$ ). In the Peace River Formation As concentrations in pyrite varied from less than 100 mg/kg to a maximum of 4160 mg/kg and the average was 772 mg/kg ( $n = 30$ ,  $\sigma = 1082$ ).

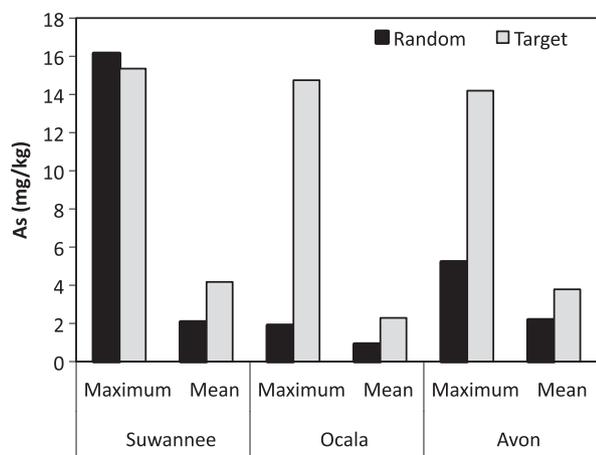
Arsenic concentrations in all Suwannee Limestone bulk rock samples varied from 0.1 to 54.1 mg/kg with an average of 3.5 mg/kg ( $n = 306$ ,  $\sigma = 7.4$ ) (Table 1). The interval samples had an average of 1.7 mg/kg ( $n = 235$ ,  $\sigma = 2.8$ ) and the targeted samples had an average of 9.5 mg/kg ( $n = 71$ ,  $\sigma = 12.5$ ). Price and Pichler (2006) reported the presence of pyrite throughout the Suwannee Limestone, but noted that it was most abundant in high porosity zones and along fractures. Pyrite was generally As-rich and had concentrations between 100 mg/kg and 11,200 mg/kg As (Price and Pichler, 2006). The average As concentration for all pyrite measurements in the Suwannee Limestone was 2300 mg/kg ( $n = 25$ ,  $\sigma = 2700$ ).

Arsenic concentrations in the Avon Park Formation were determined for 373 samples and they were slightly lower than those in the Hawthorn Group and Suwannee Limestone. The As concentrations in all samples ranged from <0.1 mg/kg to 30.8 mg/kg with an average of 2.2 mg/kg and a standard deviation of 4.2 mg/kg. The statistical breakdown of the bulk analyses by individual core is presented in Table 1 and all data are presented in Appendix A. The average As concentrations were slightly elevated due to the targeted samples; the interval samples had lower average As concentrations. Interval samples, which were taken at a tighter spacing from the high permeability zones had an average of 1.0 mg/kg As. The remaining interval samples had an average of 1.3 mg/kg As and the targeted samples had an average of 3.2 mg/kg As. Bulk elemental analyses by ICP-OES for Ca, Mg, Al, S, Si, Fe, P and Sr were consistent with the lithologic observations. Calcium was the most abundant element, followed by Mg. Aluminum and Si had limited abundance, indicating the presence of relatively pure carbonates, but concentrations increased in the fine-grained "muddy" samples confirming the presence of clay minerals. The molar S/Fe ratio in the bulk samples was higher than that of pyrite, which indicated an additional source of S. Lithologic descriptions of hand samples and bulk As data were used as bases to select 31 samples for EMPA. Most of those samples belonged to the targeted category and contained pyrite, clay or organic laminations. A total of 228 pyrite minerals were analyzed. Arsenic values in pyrite from the Avon Park Formation ranged from less than 100 mg/kg to 5820 mg/kg with an average of concentration of 945 mg/kg ( $\sigma = 1026$ ).

#### 4.2. Rock cuttings

In total there were 20 buckets of rock cuttings from the Ocala Limestone, 29 from the Suwannee Limestone and 10 from the Avon Park Formation, each representing approximately 3-m intervals. The concentration of As in the Suwannee Limestone, Ocala Limestone and the Avon Park Formation varied widely from 0.02 mg/kg to 15.4 mg/kg, from 0.1 mg/kg to 14.7 mg/kg, and from 0.7 mg/kg to 14.2 mg/kg, respectively (Figs. 3 and 4; Table 2). The highest As values were found in those samples containing pyrite, clays, and phosphate, regardless of the stratigraphic unit. Mean and maximum concentrations of As were higher in the majority of targeted samples versus the random samples, although the maximum As concentration in the Suwannee Limestone was found as an interval sample (16.1 mg/kg).

In rock cuttings from the Suwannee Limestone the average As concentrations were 2.9 mg/kg, 2.1 mg/kg and 4.2 mg/kg, in all samples, interval samples and targeted samples, respectively. In rock cuttings from the Ocala Limestone the average As concentrations were 1.5 mg/kg, 0.9 mg/kg and 2.3 mg/kg, in all samples, interval samples and targeted samples, respectively. In rock cuttings from the Avon Park Formation the average As concentrations were 2.9 mg/kg, 2.2 mg/kg and 3.8 mg/kg, in all samples, interval samples and targeted samples,



**Fig. 3.** Maximum and average As values in the Suwannee Limestone, Ocala Limestone and Avon Park Formation for random and targeted samples, which were collected as rock cuttings.

respectively. More statistical data are provided in Table 2. In rock cuttings from the Ocala Limestone and APF the average and maximum As concentration were higher in the targeted samples than in the interval samples, whereas in the rock cuttings from the Suwannee Limestone interval and targeted samples had approximately the same average and maximum As concentrations (Fig. 3).

## 5. Discussion

If a geographic area or population of interest is too large to be analyzed as a whole, its parts can be sampled and analyzed. If a set of samples is representative of the whole, then results can be extrapolated. However, the larger the heterogeneity of the whole or the sample, the less accurate the extrapolation of results will be. Heterogeneity can be overcome or addressed by investigating a larger number of samples, although this is generally limited by factors such as accessibility, time, money, etc. In sampling geologic media one faces exactly the same problem. To determine the distribution of As in, for example, well-sorted sandstone would be much easier than in a conglomerate. In a mature quartz sandstone, a few tens of grams of sample may be representative of the whole; whereas in a conglomerate a few tens of grams of sample may not be even representative of one cobble or boulder. The same is true for a well-sorted carbonaceous sediment versus a carbonaceous sediment formed in a changing depositional environment. In order to know precisely the abundance of As, or any other chemical element for that matter, in a geologic formation one would have to homogenize the whole formation and then take a sample – obviously this is not possible. Nevertheless, information about the abundance and distribution of chemical elements can be crucial for mineral exploration, mining and environmental assessment. The need for this type of information led to the development of statistical tools (Krige, 1951; Matheron, 1963), which are rather complex and not easy to apply by an inexperienced user.

In our study we relied mainly on a dual sampling approach – taking random (interval) samples and targeted samples, based on purely qualitative characteristics suggesting the presence of elevated As concentrations in rocks. This approach was applied in three previous studies and produced comparable results (Dippold, 2009; Lazareva and Pichler, 2007; Price and Pichler, 2006). With this approach, we found that in the study area targeted samples had higher average As concentrations than interval samples. A difference in number, however, does not necessarily imply a statistically significant difference. Application of t-tests confirmed the statistical difference between the average As concentrations in interval and targeted rock cutting samples from the Suwannee Limestone, but not for samples from the Ocala Limestone and

Avon Park Formation. The average concentrations of As in interval and targeted samples collected from solid core were significantly different in the Hawthorn Group, Suwannee Limestone and Avon Park Formation. This suggests that it is easier to target high As samples while sampling solid core.

Rather than just the average concentration of As in the study area, there were more important questions to be addressed, such as: (1) how is As spatially distributed in the study area; (2) with which minerals are high As concentrations associated; and (3) which sampling approach is most preferable.

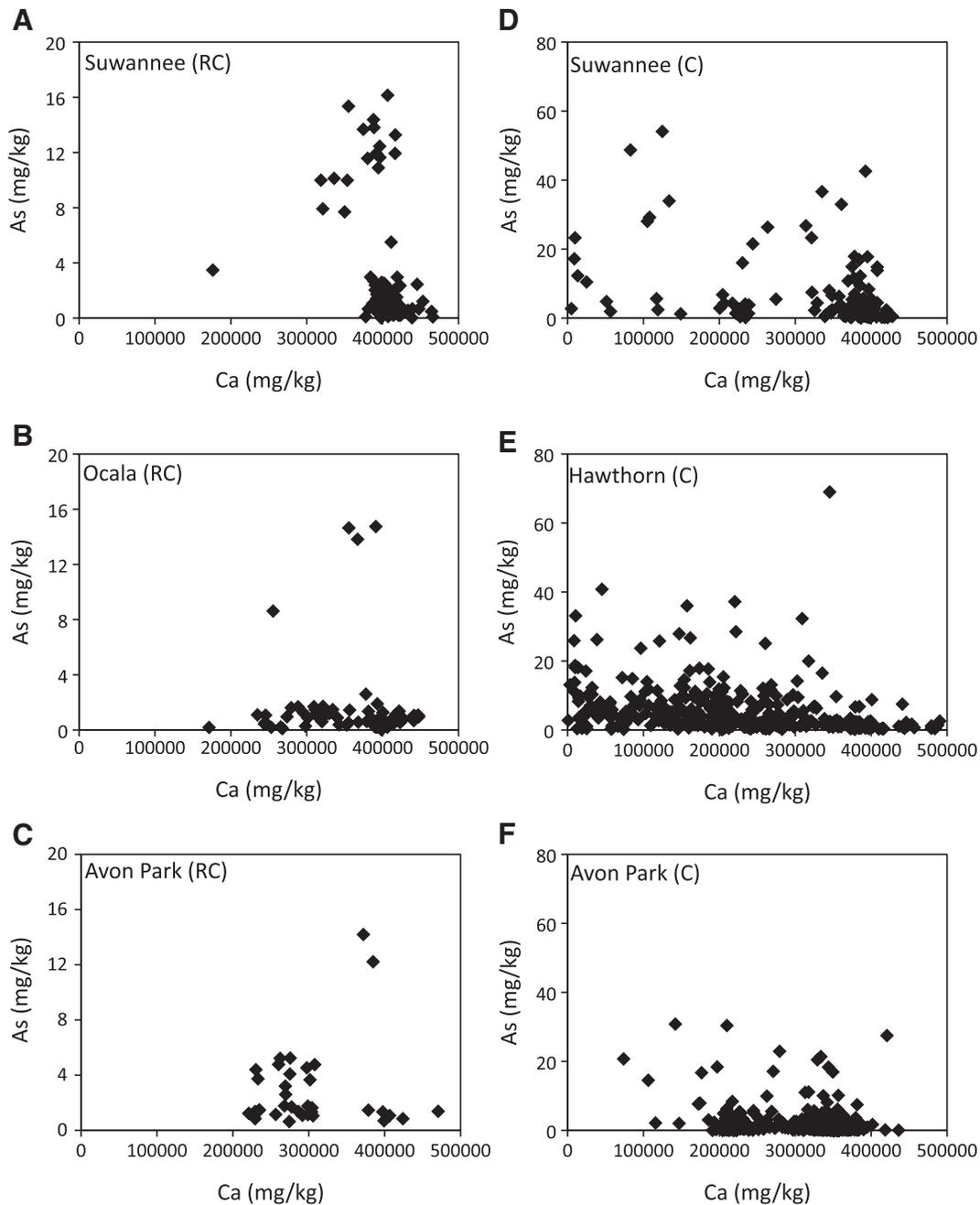
### 5.1. Spatial distribution of As in the study area

Since one of the objectives of our study was to aid implementation of ASR in the study area, an important question was whether or not there are regional As hotspots that should be avoided. Based on the average As concentrations in all samples from the ROMP wells and in all samples from rock cuttings, it became obvious that As cannot be avoided. Particularly, targeted core samples contained As in appreciable amounts at all depth intervals. There was no horizontal (geographic) trend, i.e., in the study area the average As concentrations for each stratigraphic unit was randomly distributed. There was however, a trend of decreasing average As concentrations with stratigraphic depth, i.e., the highest As values were in the Hawthorn Group and the lowest in the Ocala Limestone and Avon Park Formation (Fig. 5). The comparison of averages of As concentrations in samples from the ROMP cores shows that when in a core the As concentration is high in the Hawthorn Group it is most of the time high in the Suwannee Limestone (Fig. 5A). This relationship breaks down for cores DV-1, TR-4-1, TR-9-2 and TR-SA-1, where As concentrations are approximately the same for the Hawthorn Group and for the Suwannee Limestone (Fig. 5A). In these cores, mainly samples from the Arcadia Formation (including Tampa and Nocatee Members) were analyzed, which consist mainly of limestone and thus, are relatively similar to the Suwannee Limestone. This is also represented by the similar average As concentrations in those core samples from the Arcadia Formation and the complete Hawthorn Group (Table 1, numbers in brackets). The observation that As values were mostly highest in the upper siliciclastic sediments of the stratigraphy leads to the conclusion that the As present in the lower carbonaceous sediments could be the result of leaching As from the Peace River Formation during the downward percolation (recharge) of groundwater.

### 5.2. The role of pyrite

In a study like the present where more than 1000 samples are involved, time consuming petrographic techniques may not be a suitable methodology of investigation. However, it can be beneficial to combine bulk chemical data with analyses of individual minerals to obtain semi-quantitative information about the abundances of certain minerals and associated minor elements. That approach was successfully employed during the study of the Hawthorn Group, where phosphorus (P) was used as a proxy for apatite and francolite and, thus, the associated depositional environment (Lazareva and Pichler, 2007). Similarly, the presence of aluminum (Al) was successfully applied as a proxy for clay size mineral abundance and the relationship between As, Fe and S proved extremely useful for the determination of the pyrite abundance and As distribution (Lazareva and Pichler, 2007; Price and Pichler, 2006). Compared to pyrite, other trace minerals contained much less As and based on EMPA elemental maps the association between As, Fe and S could be clearly demonstrated (see Figs. 10 and 12 in Lazareva and Pichler, 2007, see Fig. 6 in Price and Pichler, 2006).

Assuming that Fe and S in bulk rock samples were exclusively derived from the breakdown of pyrite, one can calculate its abundance in the aquifer matrix. This approach was warranted by the strong linear correlation between Fe and S and its closeness to the slope of 0.875 (pyrite line) when plotted in X–Y diagrams (Figs. 7, 8 and 9), which



**Fig. 4.** Plots of As versus Ca concentrations measured in samples taken from rock cuttings (RC; left side) compared to plots of As versus Ca concentrations in samples obtained from ROMP cores (C; right side). Data in plot 4D are from Price and Pichler (2006) and data in plot 4E are from Lazareva and Pichler (2007).

indicates the relative concentrations of Fe and S in pyrite in mg/kg ( $\text{Fe} = 2\text{S}$  or  $56 \text{ mg Fe} = 64 \text{ mg S}$ ,  $s = 56/64 = 0.875$ ). This approach worked well for the Hawthorn Group and for samples of rock cuttings, but less for the ROMP core samples from the Suwannee Limestone and Avon Park Formation, which had a lower linear correlation between Fe and S (Table 3). In conjunction with petrographic observations, however, the correlation between Fe and S in samples from the Suwannee Limestone improved when samples high in organic matter were omitted (Price and Pichler, 2006). The Avon Park Formation samples contained appreciable amounts of gypsum ( $\text{CaSO}_4$ ) and celestite ( $\text{SrSO}_4$ ), and thus had too much S. By assigning all Fe and S to pyrite, its abundance in mg/kg can be calculated. As a next step, the calculated abundance of pyrite can be multiplied by the average As concentration in pyrite (as determined by EMPA). This provides an estimate of As concentration in a bulk rock sample, which can be compared to the actual concentration of As

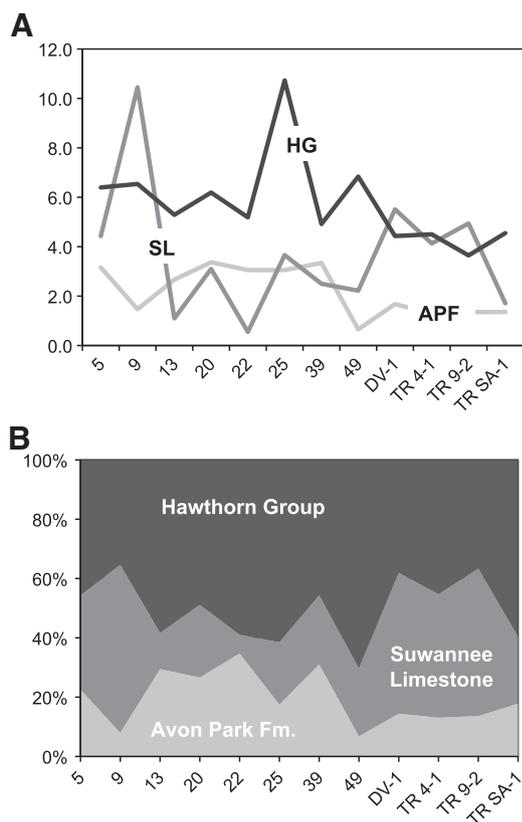
measured. In those bulk rock samples, with higher measured than calculated As concentrations, As measured cannot be explained by As in pyrite alone. On the other hand, in those bulk rock samples with a lower measured As concentration, As measured can be adequately explained by As in pyrite. Only a few bulk rock samples high in clay content had higher measured concentrations. This supports the observation that pyrite is the dominant As-bearing phase in the Hawthorn Group, Suwannee Limestone and Ocala Limestone with clay minerals being a distant second (Lazareva and Pichler, 2007; Price and Pichler, 2006). In the Avon Park Formation, clay minerals and organic matter played a much larger role for the occurrence of As concentrations (Dippold, 2009; Dippold and Pichler, 2008).

Indirect evidence for the role of pyrite is provided through the ASR process itself. The injected water and the groundwater in the Floridan aquifer are virtually As-free (Jones and Pichler, 2007), whereas the

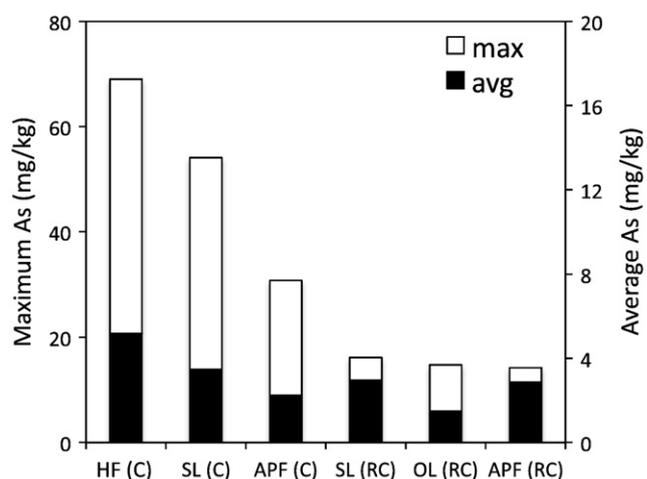
**Table 2**  
Statistical data for As concentrations (mg/kg) samples collected from rock cuttings (RC).

Geology		Interval	Target	All
Suwannee	Average	2.1	4.2	3.0
	Minimum	0.1	0.1	0.1
	Maximum	16.1	15.4	16.1
	$\sigma$	2.8	5.3	5.3
	n	60	44	104
Ocala	Average	0.9	2.3	1.5
	Minimum	0.3	0.1	0.1
	Maximum	1.9	14.7	14.7
	$\sigma$	0.5	4.4	4.4
	n	40	30	70
Avon Park	Average	2.2	3.8	2.9
	Minimum	0.6	0.7	0.7
	Maximum	5.2	14.2	14.2
	$\sigma$	1.5	4.1	4.1
	n	20	15	35

recovered water can contain up to 130  $\mu\text{g/L}$  As (Arthur et al., 2005). Knowing that the bulk of As in the 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  $0.1$  (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



**Fig. 5.** (A) Average As concentrations in ROMP cores for locations where the complete section, i.e., Hawthorn Group (HG), Suwannee Limestone (SL) and Avon Park Formation (APF), was measured. (B) Average As concentrations given as cumulative % of the total As concentration in each of the cores. Data for the complete Hawthorn Group are from Lazareva and Pichler (2007) and data for the Suwannee Limestone are from Price and Pichler (2006).



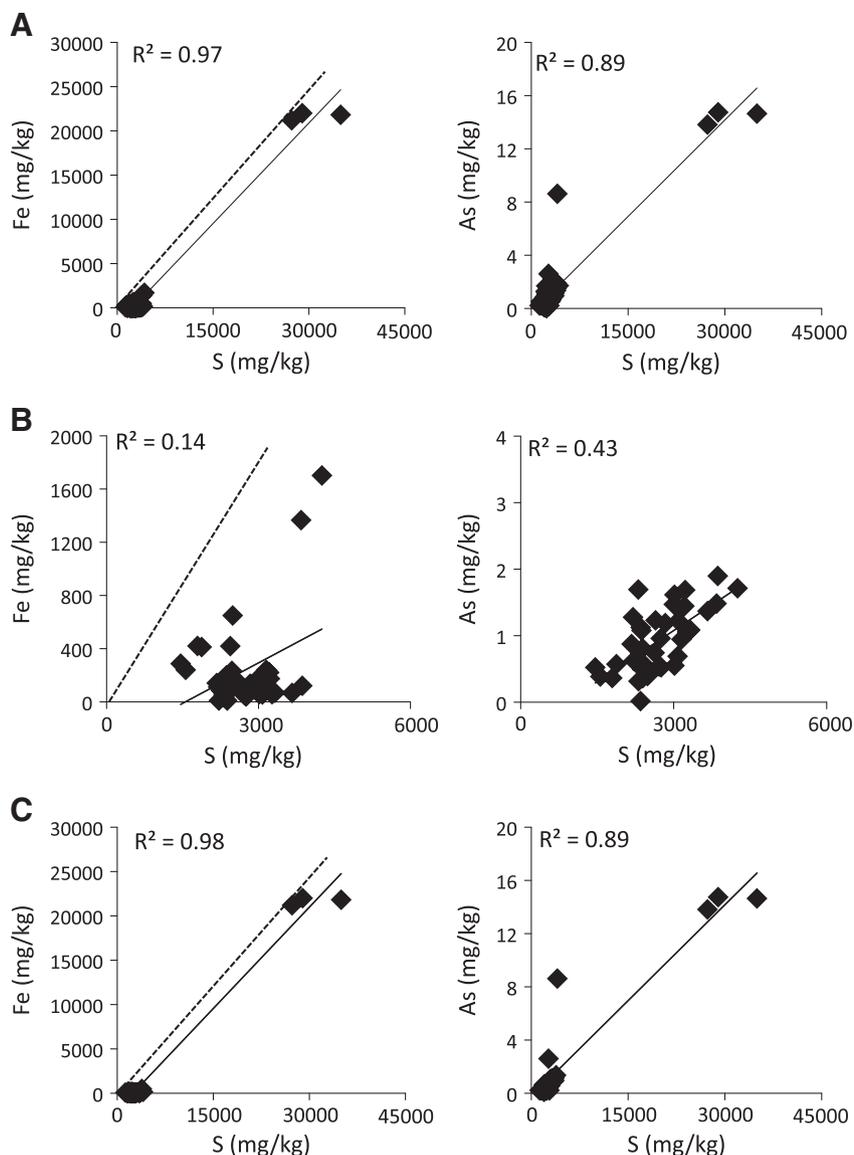
**Fig. 6.** Maximum and average As concentrations in ROMP cores and rock cuttings. AF = Arcadia Formation; SL = Suwannee Limestone; APF = Avon Park Formation, and OL = Ocala Limestone. Note: (C) = ROMP samples and (RC) rock cuttings. Data for SL are from Price and Pichler (2006) and data for HF are from Lazareva and Pichler (2007).

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. The injectate is generally treated surface water, which at the time of injection is approximately in equilibrium with atmospheric  $\text{O}_2$ , i.e., it contains more than 8 mg/L dissolved  $\text{O}_2$ . Additionally, the injectate can be treated with ozone ( $\text{O}_3$ ) for microbial control, bringing the concentration of dissolved  $\text{O}_2$  to more than 20 mg/L. A simplified chemical reaction for the uptake of oxygen is the breakdown of pyrite:  $\text{FeS}_2 + 3.5 \text{O}_2 = \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+$ . This reaction then releases iron ( $\text{Fe}^{2+}$ ), sulfate ( $\text{SO}_4^{2-}$ ) and As (in the case of As-rich pyrite) into the recharge water. An increase in As and Fe was observed in recovered water, along with a subsequent decrease in dissolved oxygen (Arthur et al., 2002). The decomposition of organic matter could be an alternative, but not likely oxygen-consuming reaction in the Suwannee Limestone, because in our study area organic material was observed in only a few samples.

### 5.3. Rock cuttings or solid core?

Compared to hollow core diamond drilling, rotary drilling is less expensive and faster. Thus the collection of rock samples as rock cuttings (the byproduct of rotary drilling) is also less expensive and faster than collecting samples as solid core. It seems, nevertheless, that average As concentrations in both types of samples were similar (Fig. 6), although maximum concentrations of As in the ROMP core samples were higher than the maximum concentrations in the rock cuttings (Fig. 6). This leads to the conclusion that it is easier to identify samples that contain clays, hydrous ferric oxides, pyrite and organic matter while sampling solid core. The reason for the similar average As concentrations in rock cutting and cores samples, however, could be that during sampling of the rock cuttings relatively more targeted samples were taken, i.e., at least two per interval and sometimes three. During sampling of the ROMP cores, only 20% to 25% targeted samples were collected. This demonstrates that sampling rock cuttings can be as efficient as sampling solid core. Unfortunately most structural information, such as fractures, is lost when sampling rock cuttings and it is impossible to relate the abundance of As to such features.

The As data of the rock cuttings showed that the average concentration of all interval samples from the Suwannee Limestone, Ocala Limestone and Avon Park Formation was lower than that of the targeted samples (Table 2, Fig. 6). Noteworthy, however, is that the



**Fig. 7.** Plots of As and Fe versus S in rock cutting samples from the Suwannee Limestone. The data are divided into A = all samples, B = interval samples and C = targeted samples. The coefficient of determination ( $R^2$ ) is an indicator of how well the linear regression line and data points correlate. A value of 1 for  $R^2$  indicates that the regression line perfectly fits the data. The dashed line represents the pyrite line ( $Fe = 2S$ ); see text for more explanation.

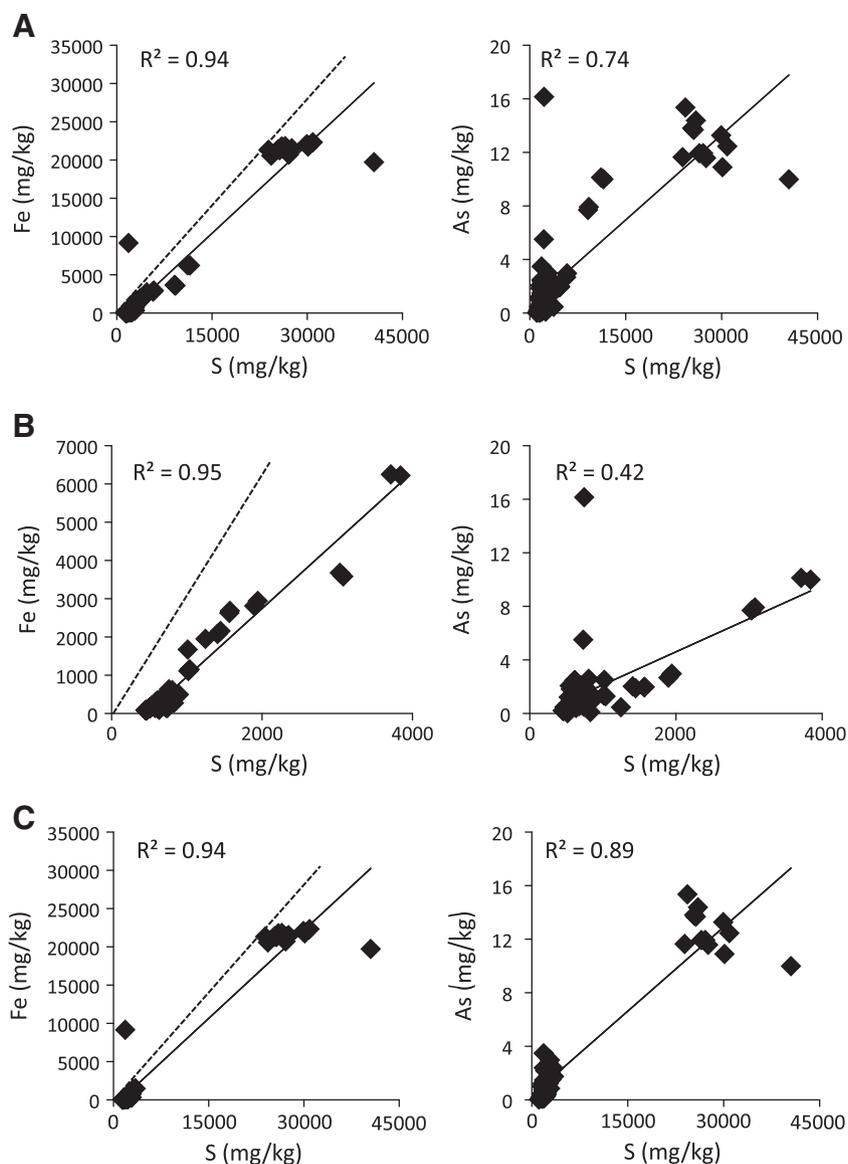
maximum As concentration in the Suwannee Limestone was measured in an interval sample (Fig. 3), whereas in the Ocala Limestone and Avon Park Formation the maximum As concentrations were (as expected) measured in the targeted samples (Fig. 3). The As in that sample was not associated with pyrite, as documented by the low Fe–As ratio (Fig. 8B). That sample contained visible discoloration and was likely selected as a targeted sample. This demonstrates that also during interval sampling, As-rich samples can be collected.

#### 5.4. Bulk rock considerations

The question “If the cleaner or purer a limestone, the less likely the presence of As?” arises. This question is logical because seawater does not contain high concentrations of As, which could be incorporated into calcite or aragonite during precipitation of these minerals in a marine environment. Even precipitation of calcium carbonate from an As-rich solution does not lead to its incorporation. For example, recent data for aragonite and calcite, which precipitated from a low temperature hydrothermal fluid in a coral reef, showed that As concentrations in the carbonates were less than 2 mg/kg (Pichler and

Veizer, 2004) despite very high As concentration in the fluid of more than 1 mg/L (Pichler et al., 1999; Price and Pichler, 2005). This suggests that As concentrations in excess of 2 mg/kg in limestone are not likely associated with the calcium carbonate phase, but rather with impurities, such as trace minerals and organic matter, which are common in limestone (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.

Considering that the As in our study was mainly associated with pyrite points toward its post-depositional origin. As mentioned above, As could have been leached from the overlying units and transported downward into the limestone by a diagenetic fluid, where under reducing conditions pyrite precipitated (Berner, 1984; Rickard, 1968). Due to its chalcophile nature, As was incorporated into the pyrite structure, hence the presence of As-rich pyrite. The observed microcrystals making up the pyrite framboids were colloid-sized, which indicates a post-depositional (diagenetic) formation 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 were also observed, possibly

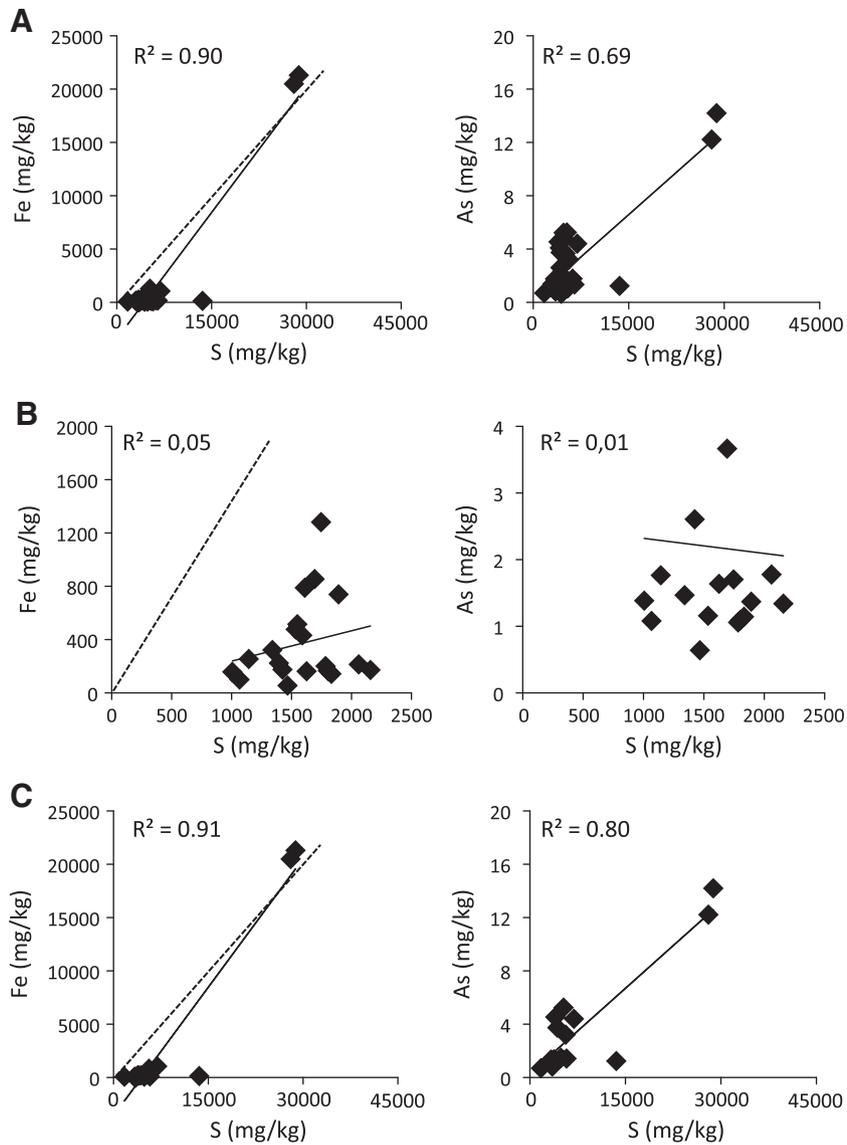


**Fig. 8.** Plots of As and Fe versus S in rock cutting samples from the Ocala Limestone. The data are divided into A = all samples, B = interval samples and C = targeted samples. The coefficient of determination ( $R^2$ ) is an indicator of how well the linear regression line and data points correlate. A value of 1 for  $R^2$  indicates that the regression line perfectly fits the data. The dashed line represents the pyrite line ( $Fe = 2S$ ); see text for more explanation.

suggesting two stages of crystallization (Lazareva and Pichler, 2007; Price and Pichler, 2006).

Thus, it seems that the cleanness or purity of a limestone may have no impact on its potential As concentration. In Fig. 4, As and Ca values were plotted for the rock cuttings and ROMP cores. The consistently high Ca values for the Suwannee Limestone rock cuttings indicate a pure limestone, although As values are elevated (Fig. 4A). The Ocala Limestone samples have Ca concentrations varying from about 250,000 mg/kg to more than 400,000 mg/kg, which indicates the presence of varying amounts of dolomite ( $CaMg(CO_3)_2$ ). Similar to the samples from the Suwannee Limestone, As concentrations in samples from the Ocala Limestone seem to be more directly related to higher Ca values (Fig. 4B). An even more pronounced bimodal distribution of Ca was observed in the samples of rock cuttings from the Avon Park Formation, clearly indicating the presence of dolomite (Fig. 4C). Nevertheless, elevated As concentrations in Avon Park Formation samples were again associated with high Ca values, indicating that high As concentrations are more likely found in association with calcite or aragonite than with dolomite.

The ROMP core samples showed a much larger variation in Ca and As concentrations than the rock cuttings (Fig. 4D, E and F). From these results, it seems that high As values can be found in samples containing only little Ca. The bimodal distribution for the Suwannee Limestone (Fig. 4D) indicates the presence of dolomite in those samples plotting around 200,000 mg/kg Ca and the presence of mostly calcite or aragonite in those samples plotting around 400,000 mg/kg Ca. This large variation in Ca (Fig. 4D) is likely an artifact of targeted sampling. As a result of targeted sampling, samples containing clay and organic matter are over-represented and, thus, Ca values should not reflect the true abundance of calcite and aragonite in the Suwannee Limestone. Elevated As concentrations in the Suwannee Limestone samples were associated either with low Ca or high Ca concentrations, indicating that dolostones contain less As. The Ca concentration in the Hawthorn Group samples varied across the whole range (Fig. 4E), indicating the variability and presence of siliciclastics in this formation. There seems to be a slight inverse relationship between As and Ca, indicating that in the Hawthorn Group the purer the limestone the less As is present. This observed trend of decreasing As concentrations with increasing Ca



**Fig. 9.** Plots of As and Fe versus S in rock cutting samples from the Avon Park Formation. The data are divided into A = all samples, B = interval samples and C = targeted samples. The coefficient of determination ( $R^2$ ) is an indicator of how well the linear regression line and data points correlate. A value of 1 for  $R^2$  indicates that the regression line perfectly fits the data. The dashed line represents the pyrite line ( $Fe = 2S$ ); see text for more explanation.

concentrations also followed the stratigraphy – the more siliciclastic units are in the upper section of the Hawthorn Group. The one exception of the highest As concentration was rather isolated. That sample was a pyrite concretion in a limestone matrix (Lazareva and Pichler, 2007). Similar to the rock cuttings, the Avon Park Formation samples taken

from the ROMP cores showed the same bimodal distribution (Fig. 4F), which points towards the presence of dolomite. There is less an indication of a pure calcite or aragonite, because only a few samples plot around 400,000 mg/kg. Elevated As values are distributed across the range of Ca concentrations, but are relative to the number of samples

**Table 3**  
Coefficients of determination ( $R^2$ ) among Fe, S and As data from core and rock cutting samples.

Geology	Type	Fe/S			As/S			As/Fe		
		A	I	T	A	I	T	A	I	T
Hawthorn Group	Core	0.87	0.69	0.95	0.40	0.26	0.17	0.35	0.32	0.13
Suwannee Limestone	Core	0.65	0.40	0.55	0.67	0.55	0.59	0.56	0.27	0.43
Avon Park Formation	Core	0.25	0.25	0.36	0.26	0.24	0.31	0.33	0.26	0.32
Suwannee Limestone	Rock Cutting	0.94	0.95	0.94	0.74	0.42	0.89	0.77	0.36	0.96
Ocala Limestone	Rock Cutting	0.97	0.14	0.98	0.89	0.43	0.89	0.87	0.06	0.88
Avon Park Formation	Rock Cutting	0.90	0.05	0.91	0.69	0.13	0.80	0.87	0.13	0.07

Note: A = all samples, I = interval samples, T = targeted samples. Data for the Suwannee Limestone are from Price and Pichler (2006) and data for the Hawthorn Group are from Lazareva and Pichler (2007).

lower in the range, which indicates the presence of dolomite (200,000 mg/kg to 400,000 mg/kg Ca). This supports the previous observations that dolostones generally have lower As concentration.

## 6. Conclusions

Modifications in sampling were made for the investigations of As in the lithologic formations comprising the Floridan Aquifer System to best suit their geologic characteristics. Targeted sampling could be improved based on the findings of the previous studies, since several sources of As were possible. If simply the average As concentration of a lithologic unit is the desired outcome of an investigation, targeted and interval sampling of rock cuttings seems to be sufficient, particularly when time and money are a factor. This approach should work well for any trace mineral. However, if structural sedimentary information is required, samples need to be collected in the form of solid cores obtained by hollow core diamond drilling, because this information is lost in rock cuttings. Simple statistical methods, such as linear regression can provide valuable information – but the data had to be examined on a case-by-case basis, to evaluate the occurrence and importance of outliers.

Despite analyzing more than 1200 samples from 20 cores, we could not find samples where bulk As was several orders of magnitude higher than the average. In a single sample, As was never higher than 70 mg/kg and average concentrations were around 3 mg/kg. It was crucial, however, to find the high concentrations of As in pyrite, because As could be easily released from pyrite via introduction of O<sub>2</sub> into the aquifer. There seems to be a decrease in As concentrations with stratigraphic depth, i.e., highest values in the Hawthorn Group and lowest in the Ocala and Avon Park. Dolostones had generally lower As concentrations than calcitic or aragonitic limestones. Concentrations of As, which was mainly present as an impurity in secondary pyrite, ranged from less than 100 mg/kg up to more than 11,000 mg/kg As. Pyrite was ubiquitous throughout the study area, but concentrated along fractures and zones with high moldic porosity. Compared to pyrite, other trace minerals contained much less As.

This study provided some insight into the question of whether a rock with an As concentration close to that of the global average for that rock type, can cause elevated As concentrations in groundwater. Obviously water–rock interaction in an aquifer whose matrix contains a few mg/kg of As, has the potential to cause high As concentrations in groundwater. In central Florida, all that is required to release As from the aquifer matrix is a change in redox, which affects pyrite stability (Jones and Pichler, 2007). Thus, the question arises if moving to stratigraphic units with lower As concentrations, such as the Ocala Limestone or Avon Park Formation could prevent the release of As during Aquifer Storage and Recovery.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.gexplo.2011.02.004.

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