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PhD Thesis

Investigations towards a better understanding of arsenic-sulfur speciation in aquatic environments

Elke Süß

Investigations towards a better understanding of arsenic-sulfur speciation in aquatic environments: Formation, stability, structural characterization, and conflicting analyses

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Elke Süß

Geoecologist (Dipl.-Geoökol./M.Sc.)
TU Bergakademie Freiberg
born March 23, 1980

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Examination Commitee:
Prof. Dr. Britta Planer-Friedrich (examiner)
Prof. Dr. Broder J. Merkel (co-examiner)
Prof. Dr. Stephan Clemens (chair dissertation committee)
Prof. Dr. Egbert Matzner (member dissertation committee)
Dr. Andreas Scheinost (external member dissertation committee)

Abstract

Arsenic is a widespread contaminant of global concerns due to its neurotoxicity and carcinogenicity. Particularly critical is the speciation of arsenic, influencing its mobility, toxicity and retention capability. Recently, it was analytically proven that arsenic-sulfur (As-S) species play a dominant role for arsenic cycling in sulfidic systems. The geochemistry of As-S species is not well investigated, yet, and especially the nature of these species, thioarsenites vs. thioarsenates, has been under intense debate. The major objective of the present PhD work was to improve the current knowledge about As-S species by structural characterization, investigations of their occurrence, formation and transformation, and evaluation of the analytical techniques, X-ray absorption spectroscopy (XAS) and ion chromatography coupled to ICP-MS (IC-ICP-MS).

By XAS it was shown that under strictly anoxic conditions thioarsenites form in arsenite-sulfide mixes with sulfide (SH^-) excess and as co-occurring intermediates during acidic transformation of thioarsenates. Thioarsenites can be specified as highly labile, converting rapidly to thioarsenates in the presence of traces of oxygen, e.g. during standard IC-ICP-MS analyses. Excess hydroxide (OH^-) either due to high pH or sample dilution in ultrapure water inhibits the formation of thioarsenites by SH^--OH^- competition. These facts make the current IC-ICP-MS method even under anoxic conditions unsuitable for thioarsenite analyses. However, thioarsenites were shown to be necessary intermediates for formation of thioarsenates. Thioarsenates determined in natural oxic systems are thus most likely the product of rapid in-situ thioarsenite oxidation. Direct thioarsenite determination is currently only possible by XAS with a limitation on > 5 mM-solutions for structural evaluations. The characteristic coordination and bond length ($R_{As\text{-}S}$ 2.23-2.28 Å) makes thioarsenites distinguishable from thioarsenates ($R_{As\text{-}O}$ 1.70 Å, $R_{As\text{-}S}$ 2.13-2.18 Å). The individual thioarsenates are distinct in their coordination and absorption edge energies, successively decreasing about 1 eV per sulfur atom. Generally, the absorption edge energies decrease in the order arsenate > thioarsenates > arsenite > thioarsenites. This primary XAS-dataset enables the evaluation of (thio)arsenites and (thio)arsenates in mixed solutions.

Despite the greater stability of thioarsenates vs. thioarsenites, they also have been shown to transform under certain conditions. Upon acidification they convert to thioarsenites (anoxic) or arsenite (oxic) with subsequent As-S precipitation. The presence of Fe^{II} in anoxic solutions or heating (80 °C) results in their decay to substantial amounts of arsenite. Thioarsenates are also easily oxidized by synthetic oxidants, air purging or naturally along hot spring drainage channels. For trithioarsenate, the major species of alkaline hot springs in Yellowstone National Park, two transformation processes have been identified: successive ligand exchange to arsenate, observed naturally and by using a strong oxidant, and the decay to arsenite (and trithioarsenate) in natural systems and under moderately reducing conditions. However, transformation under natural conditions was up to 500 times faster and is likely catalyzed by *Thermocrinis* spp..

Naturally important are also processes promoting mobilization or immobilization of arsenic from and at mineral surfaces. Arsenopyrite and orpiment belong to the most abundant (Fe-)As-S minerals with particular importance as host rocks for gold refractory. Oxidative leaching of both minerals yielded up to 50% thioarsenates. The release of thioarsenates from orpiment, at pH 7 and 12, is possibly caused by thioarsenite oxidation. Contrary, physisorption of OH^- is the proposed mechanism for arsenopyrite with thioarsenate formation only at highly alkaline pH. The immobilization of monothioarsenate by sorption on ironhydroxide was less effective and kinetically slower compared to arsenate and arsenite.

The presence of iron in As-S systems was hitherto considered to counteract thioarsenate occurrence. This was refuted by finding up to 17% thioarsenates in Czech spring waters. However, those Fe-As-S systems are a challenge for sample preservation. While acidification results in As-S precipitation and thioarsenate transformation, flash-freezing as preferred for thioarsenates induces ironhydroxide precipitation. An anoxic gas headspace, a strong matrix and an organic solvent supported the stability of pure thioarsenate solutions, whereas in the presence of iron a combination of EDTA-addition and cryo-preservation is required.

Overall, the present PhD thesis reveals the importance of thioarsenites and thioarsenates for arsenic cycling. The results significantly increase the present knowledge on As-S geochemistry and help to define potential for future studies.

Zusammenfassung

Arsen ist ein weitverbreitetes Umweltgift und stellt durch seine Neurotoxizität und Karzinogenität eine ernsthafte Bedrohung für Menschen und Organismen dar. Die Umweltwirkung, d.h. die Mobilität und Toxizität, von Arsen hängt dabei entscheidend von dessen Speziierung ab. Für sulfidische Systeme wurde in den letzten Jahren die Bedeutung von Arsen-Schwefel (As-S) Verbindungen für den Arsenkreislauf deutlich. Allerdings ist über die Geochemie dieser As-S Spezies noch relativ wenig bekannt und besonders die Natur dieser Spezies, Thioarsenate vs. Thioarsenite, wurde kontrovers diskutiert. Das Ziel dieser Promotionsarbeit war das aktuelle Wissen über As-S Spezies hinsichtlich ihrer Struktur, Vorkommen, Bildungs- und Transformationsmechanismen sowie die Nutzung von XAS (Röntgenabsorptionsspektroskopie) und IC (Ionenchromatographie) gekoppelt mit ICP-MS als Analysetechniken, zu erweitern.

Aus den XAS-Untersuchungen wurde deutlich, dass unter streng anoxischen Bedingungen Thioarsenite in Arsenit-Sulfid Mixen mit Sulfid-Überschuss (SH^-) gebildet werden sowie als intermediäre Spezies beim Ansäuern von Thioarsenat entstehen. Thioarsenite können als sehr labil gekennzeichnet werden, die bereits in Anwesenheit geringster Sauerstoffmengen, beispielsweise bei der Standardanalyse mittels IC-ICP-MS, sehr schnell zu Thioarsenaten konvertieren. Durch den Überschuss an Hydroxid (OH^-), entweder durch hohen pH-Wert oder Probenverdünnung in destilliertem Wasser, wird die Bildung von Thioarseniten durch SH^--OH^- Konkurrenz verhindert. Somit ist die OH^--Konzentration ist ein weiterer Faktor, der die Thioarsenite auch unter anoxischen Bedingungen nicht nachweisbar mit der derzeit etablierten IC-ICP-MS Methode macht. Es wurde gezeigt, dass Thioarsenite notwendige intermediäre Spezies für die Bildung von Thioarsenaten sind. In natürlichen oxischen Systemen bestimmte Thioarsenate sind deshalb höchstwahrscheinlich das Produkt der rapiden in-situ Oxidation von Thioarseniten. Die direkte Bestimmung von Thioarseniten ist derzeit nur mittels XAS möglich, wobei die strukturelle Charakterisierung auf Lösungen mit > 5 mM Arsen begrenzt ist. Aufgrund ihrer typischen Koordination und Bindungslänge ($R_{As\text{-}S}$ 2.23-2.28 Å) sind Thioarsenite sehr gut von Thioarsenaten ($R_{As\text{-}O}$ 1.70 Å, $R_{As\text{-}S}$ 2.13-2.18 Å) unterscheidbar. Die einzelnen Thioarsenat-Spezies unterscheiden sich ebenfalls in ihrer Koordination und der Absorptionsenergie, die sukzessive um 1 eV pro Schwefelatom sinkt. Generell verlaufen die Absorptionsenergien in folgender Reihenfolge: Arsenat > Thioarsenate > Arsenit > Thioarsenite. Dieser fundamentale XAS-Datensatz ermöglicht die Evaluierung von Mixen aus (Thio)arsenaten und (Thio)arseniten.

Trotz ihrer gegenüber Thioarseniten vergleichsweise größeren Stabilität wurde auch für die Thioarsenate gezeigt, dass sie unter bestimmten Bedingungen Umwandlungsprozessen unterliegen. Beim Ansäuern konvertieren sie zu Thioarseniten (anoxische Bedingungen) bzw. zu Arsenit (oxisch) und fallen schließlich als As-S Phasen aus. Die Anwesenheit von Fe^{II} sowie Erhitzen (80 °C) führen zur Bildung von überwiegend Arsenit. Aber auch durch Oxidationsmittel, Luftzufuhr oder natürlicherweise entlang der Drainagekanäle von Geothermalquellen werden Thioarsenate oxidiert. Für Trithioarsenat, die Hauptspezies in alkalischen Geothermalenquellen des Yellowstone National Park, wurden zwei Transformationswege erörtert: der sukzessive Liganden-Austausch zu Arsenat, beobachtet in Natura sowie bei der Verwendung eines starken Oxidationsmittels, sowie der Abbau zu Arsenit und Trithioarsenat, ebenfalls natürlicherweise oder unter mäßig reduzierenden Bedingungen im Labor beobachtet. Generell waren jedoch die Umwandlungsraten in den natürlichen

Quellen bis zu 500-Mal größer und vermutlich spielt dabei die Mitwirkung von *Thermocrinis* spp. eine maßgebliche Rolle.

Für die Arsenmobilität stellen aber auch Mobilisierungs- und Immobilisierungsprozesse an Mineraloberflächen eine wichtige Rolle dar. Arsenopyrit und Auripigment gehören zu den häufigsten und als Gold-haltige Erze zu den Bergbau-relevanten (Fe-)As-S-Mineralen. Beide sind bei der Lösung unter oxischen Bedingungen Arsenquellen mit bis zu 50% Thioarsenaten. Dabei wird die Freisetzung von Thioarsenaten bei der Auripigment-Lösung bei pH 7 und 12 vermutlich über Thioarsenit-Oxidation gesteuert. Dagegen wird für die Thioarsenatbildung beim Leaching von Arsenopyrit bei pH 12 die OH^--Physisorption als prozesssteuernd gesehen. Bezüglich der Immobilisierung zeigte Monothioarsenat eine geringere Effizienz und langsamere Kinetik an Eisenhydroxiden als Arsenit und Arsenat.

Bislang wurde angenommen, dass die Anwesenheit von Eisen in As-S Systemen die Bildung von Thioarsenaten unterbindet. Mit den für die Eisen-reichen Thermalquellen in Tschechien bestimmten Thioarsenatgehalten von bis zu 17% wird diese Annahme widerlegt. Aber solche Fe-As-S Systeme stellen eine große Herausforderung für die Probenstabilisierung dar. Während Ansäuern zur Ausfällung von As-S Phasen und Thioarsenat-Umwandlung führt, wird durch Schockfrieren, etabliert zur Stabilisierung von Thioarsenaten, die Ausfällung von Eisenhydroxiden erzwungen. Für pure Thioarsenatlösungen konnten ein anoxisches Gaspolster, eine starke Lösungsmatrix und organische Lösungsmittel die Stabilität verbessern. In Anwesenheit von Eisen kann eine Probenkonservierung aber nur durch die Kombination von EDTA-Zugabe und Kryo-Stabilisierung erreicht werden.

Insgesamt macht die Arbeit deutlich, dass Thioarsenate und Thioarsenite relevante Spezies im Arsenkreislauf sind. Die Ergebnisse aus den Forschungsarbeiten dieser Doktorarbeit tragen dazu bei, das bisherige Wissen zur Geochemie der As-S Verbindungen zu erweitern und zeigen Potential auf für zukünftige Forschungen.

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Nur wer sein Ziel kennt, findet den Weg.

(Laotse, 430 - 390 v. Chr., Chinesischer Philosoph)

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Abbreviations

As_2S_3	orpiment
σ [Å]	Debye-Waller factor ($\sigma^2 \pm 0.0005$ Å)
ΔE_0	phase shift (ΔE_0).
As-S species	arsenic-sulfur species
As^{III}-S species	trivalent As-S species (≙ thioarsenites), $H_3As^{III}O_xS_{3-x}$ (x = 0-2)
As^V-S species	pentavalent As-S species (≙ thioarsenates), $H_3As^VO_xS_{4-x}$ (x = 0-3)
CN	coordination number (CN±25%)
DCM	double crystal monochromator
DI (≙ $H_3As^VO_2S_2{}^{)}$	dithioarsenate
EDTA	ethylendiaminetetraacetic acid
ES-MS	electro-spray coupled to mass spectrometry
ESRF	European Synchrotron Radiation Facility
EXAFS	extended X-ray absorption fine-structure
$FeAsS_{HA/FG}$	arsenopyrite with origin Hartmannsdorf (HA)/Freiberg (FG)
FT	Fourier transform
HGAAS	hydride generation atomic absorption spectrometry
HIDS	hydroxyiminodisuccinic acid
HPLC	high-performance liquid chromatography
IC-ICP-MS	ion chromatography - inductively coupled plasma - mass spectrometry
ITFA	iterative transformation factor analysis
ITT	iterative target test
MONO (≙$H_3As^VO_3S$)	monothioarsenate
OH^-	hydroxyl group
PCA	principal component analysis (PCA)
Q-Q ES-MS-MS	quadrupole-quadrupole electro-spray tandem mass spectrometry
Q-TOF	quadrupole-time-of flight
R [Å]	radial distance (R±0.02 Å)
SH^-	thiol (sulfhydryl) group
SO^2	reduction factor
TETRA (≙ $H_3As^VS_4{}^3$)	tetrathioarsenate
TRI (≙ $H_3As^VOS_3$)	trithioarsenate
trithioAs^{III} (≙ $H_3As^{III}S_3{}^{)}$	trithioarsenite
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

I Extended Abstract

1 Introduction

Inorganic arsenic, an ubiquitous element which is historically regarded as the "king of poison"[1, 2], causes globally public attention due to its carcinogenicity and neurotoxicity[3-5]. Many studies have been conducted to provide arsenic-free drinking water, e.g. Bangladesh, Chile, India, Mexico, USA, and Vietnam [6-8], but even the current WHO drinking water standard of 10 µg/L poses a residual cancer risk of 1/500 [9]. Pollution, distribution, and contamination hotspots are widespread with both natural and anthropogenic origins [2, 6, 8]. Natural mobilization processes comprise weathering of arsenic containing minerals, especially arsenic sulfides, and desorption from mineral phases such as iron(hydr)oxides [6, 8]. The major anthropogenic source is the industrial leaching of arsenic-bearing sulfides [10-12] to extract elements of economic interest, such as Au, Ag, Pb, or Zn [8, 13, 14]. In general the geochemical behavior of arsenic as for other elements depends on its speciation and thus it is crucial to evaluate the environmental fate of this element in terms of mobility and toxicity.

In recent years, analytical methods have demonstrated that soluble As-S species constitute a major fraction of dissolved arsenic in sulfidic systems [15-17]. However, their general biogeochemical behavior is so far-largely unexplored and also the exact chemical nature of these compounds is still subject to controversial scientific debate, since X-ray absorption spectroscopy (XAS) data suggest the presence of (oxy)thioarsenites (≙ trivalent As-S species, $H_3As^{III}O_xS_{3-x}$, x = 0-2), while ion chromatographic (IC) and mass spectroscopic (MS) data indicate the presence of (oxy)thioarsenates (≙ pentavalent As-S species, $H_3As^{V}O_xS_{4-x}$, x = 0-3).

1.1 Arsenic-sulfur species: in historic view and as subject of late scientific discussions

As early as at the end of the 19th century As-S species were subject to chemical studies which reported the formation of thioarsenates from dissolution of arsenic-sulfides and interaction of sulfide and arsenic acid [18-24]. Thioarsenates, comprising mono- ($H_3As^{V}O_3S$), di- ($H_3As^{V}O_2S_2$), tri- ($H_3As^{V}OS_3$), and tetrathioarsenate ($H_3As^{V}S_4{}^{3}$), were proposed to form as a result of arsenite disproportionation to elemental arsenic and the binding of elemental sulfur to the free electron pair of arsenite. The existence of thioarsenites, comprising mono- ($H_3As^{III}O_2S$), di- ($H_3As^{III}OS_2$), and trithioarsenite ($H_3As^{III}S_3$), which would be expected based on geochemical expectations when reduced arsenic and sulfur species react, was excluded.

With the beginning of the late 1970`s sodium and potassium salts of trioxymono- [25-27], dioxydi- [28, 29], monooxytri- [30], and tetrathioarsenate [31-33] were synthesized, characterized and identified by radiocrystallographic structure and heat stabilization studies. Thilo and coworkers [34] focused on the aqueous thioarsenate complexes and determined their pK values (H_3AsO_3S: pK_{s1} 3.3, pK_{s2} 7.2, pK_{s3} 11.0; $H_3AsO_2S_2$: pK_{sl} 2.4, pK_{s2} 7.1, pK_{s3} 10.9; H_3AsOS_3, pK_{s3} 10.8; H_3AsS_4: pK_{s3} 5.2). They postulated that upon acidification, thioarsenates will be stable as long as AsOH-groups can form; once the formation of AsSH-groups is forced, the ions become instable. Thus tetrathioarsenate (H_3AsS_4) becomes immediately instable as pH decreases. The hydrolysis to trithioarsenate was suspected as a minor reaction, instead, the formation of polymeric trithioarsenites $(AsS_3)_n^{n-}$ was suggested.

However, modern analytical techniques, introduced for the measurement of As-S speciation in the late 1990s, yielded contradictory evidence on the formation of thioarsenites versus thioarsenates. Support for the identification of As-S species as thioarsenates in natural samples, arsenite-sulfide mixes and through thioarsenate acidification comes from studies using ion-chromatography (IC) and electro-spray coupled to mass-spectrometry (ES-MS) [15-17, 35-37]. By combining IC and ES-MS the previously labeled “thioarsenites” were later identified as thioarsenates [17, 38]. The line of evidence came from matching retention times of the unknown As-S-species with those of synthesized mono-, di-, tri-, and tetrathioarsenates, and ES-MS [17]. Because low-resolution mass spectrometry cannot distinguish between monothioarsenite/arsenate (m/z 141), dithioarsenite/monothioarsenate (m/z 157), and trithioarsenite/dithioarsenate (m/z 173), high-resolution quadrupole-time-of flight (Q-TOF) had to be used. It showed consistently better agreement between measured and theoretical exact *m*/*z* ratios postulating (oxy)thioarsenates rather than the corresponding (oxy)thioarsenites [17]. Furthermore, quadrupole-quadrupole (Q-Q) ES-MS-MS yielded a couple of characteristic fractionation patterns that excluded the presence of thioarsenites. For example, elimination of H_2O (m/z 18) from the molecule with m/z 173 confirmed its identification as thioarsenate $H_2AsO_2S_2^-$ because the respective trithioarsenite (H_3AsS_3) could not eliminate H_2O. Finally, molecular mass analysis by ES-MS of IC fractions with known As:S ratios confirmed their identification as thioarsenates.

Thioarsenites have so far never been positively identified by IC or ES-MS. A recent study [39] cautions that As^{III} and As^{V} differ greatly in their kinetic lability and therefore require different speciation approaches. While inertness of As^{V} species makes thioarsenates identifiable by chromatographic methods, thioarsenites could be much more labile and undergo speciation changes in the mobile phase. As potential reasons co-elution [40], oxidation [40], or hydrolysis [39-41] have been suggested. Co-elution of thioarsenites and thioarsenates can be excluded based on the different chromatographic behavior of As^{III} versus As^{V} species [39] as well as on the characterization of IC fractions by ES-MS [17] which reinforced thioarsenates vs. thioarsenites. Oxidation has been widely excluded by preparing samples under anoxic conditions and immediate analysis with oxygen-free eluents and thus was considered as unlikely regarding conversion of thioarsenites to thioarsenates [35]. Hydrolysis could be a factor, considering that chromatographic elution of thioarsenates requires highly alkaline eluents and excess OH^- may destabilize thioarsenites.

However, currently analytical evidence for the occurrence of thioarsenites in arsenite-sulfide mixes comes from X-ray absorption spectroscopy (XAS) and Raman spectroscopy experiments [40-43] with some support from earlier structural analysis by X-ray diffraction (XRD) for trithioarsenite salts [44-46]. Based on the arsenic oxidation state of +3 and characteristic As^{III}-S bond distances of 2.23-2.24 Å species in arsenite-sulfide model solutions were assigned as thioarsenites [40]. However, the XAS data suffer from a lack of thioarsenite reference material and the differentiation of individual thioarsenites. The use of methyl-thioarsenicals or copper-thioarsenates (e.g. used in Beak et al. [40]) is questionable since their spectroscopic and structural composition do not necessarily have to inevitably coincide with aqueous thioarsenite and thioarsenate complexes. Since the "thioarsenite" species mentioned above were deducted from undefined arsenite-sulfide mixes, separation or distinction from potentially co-occurring thioarsenates, postulated in quantum chemical *ab initio* calculations [39], fails also due to the lack of the respective reference spectra for thioarsenates. Thioarsenites were suggested to be unstable compared to thioarsenates but possibly also formed during their decay [34].

Structural and analytical evidence for stability of thioarsenates and thioarsenites, especially regarding beam-induced conversions and pH changes, did not exist. Thus, the challenge remained to collect a set of XAS reference spectra of solid, aqueous, and flash-frozen thioarsenicals, which can be used to distinguish between thioarsenites and thioarsenates, and as a basic dataset for evaluation of unknown mixes and their possible co-occurrence of species by statistical based methods. Furthermore, the alleged formation of thioarsenates in anoxic arsenite-sulfide mixes by IC and contrary, the structural proof of thioarsenites by XAS was questionable and required studies to evaluate the effect of certain parameters, such as redox-conditions, OH^- and SH^--concentrations, conversion kinetics, and a comparison of both techniques based on equimolar solutions.

1.2 Transformation processes of thioarsenates in natural systems

In natural environments thioarsenic species have been shown to play an important role for the chemistry and cycling of arsenic in sulfidic environments [15, 16, 35, 38]. However, there is still little information on their response to changing ambient conditions, e.g. of pH, temperature, or oxygen.

Upon acidification, synthesized thioarsenates have been shown to be unstable and precipitate as As-S phases at acidic pH [16, 34, 47, 48]. While mono- and dithioarsenate were reported to be stable over a wide pH-range of 1-13 and 4-13, respectively, tetrathioarsenate transforms, based on results from chromatographic separation quantitatively to trithioarsenate at pH 9 and to arsenite < pH 7 followed by substantial As-S precipitation at pH < 5 [48].

The behavior of thioarsenates under increasingly oxidizing conditions is largely unknown. One of the few published data reported the transformation of trithioarsenate ($H_3As^VOS_3$) from contaminated groundwater to arsenite ($H_3As^{III}O_3$) when bottles were stored with an air-filled headspace for 12 hours and to arsenate ($H_3As^VO_4$) after storage of 5-12 days [35]. The transformation of trithioarsenate can be seen as a consecutive ligand exchange (SH^- versus OH^-) from trithioarsenate via dithioarsenate ($H_3As^VO_2S_2$) and monothioarsenate ($H_3As^VO_3S$) to arsenate ($H_3As^VO_4$). However, neither the transformation mechanisms to arsenate are analytically proven nor can the formation of arsenite be explained by successive ligand exchange and thus this requires detailed investigations.

In geothermal waters of Yellowstone National Park thioarsenates occur in a variety of hot springs with pH between 2.1 and 9.3 beside arsenite and arsenate and are subject to transformation with the increasing presence of oxygen along the drainage channels [16]. Especially in alkaline springs trithioarsenate predominates and has been shown to convert to arsenite and arsenate at the study site Ojo Caljente, with a major transformation of trithioarsenate to arsenite within the first meters from the source, and successive ligand exchange only as a minor reaction [16]. However, the oxidation of arsenite to arsenate, previously described as the dominant transformation mechanism in geothermal springs [49-53] mediated by arsenite-oxidizing microbes, i.e. Archaea and Eubacteria [54], became only quantitatively important as thioarsenates have disappeared [16].

The importance of abiotic vs. microbially catalyzed thioarsenate transformation in sulfidic systems and the identity of involved microbes, e.g. the potential influence of sulfur metabolizing microorganism [55], are so far unknown. Also the effect of sulfide is unclear. Sulfide has been reported to cause inhibition of arsenite oxidation in acidic solutions [53], while recent laboratory studies suggested growth stimulation for sulfide and thiosulfate oxidizers by free sulfide or reduced arsenic-bound sulfur [36]. Thus conversion of thioarsenates needed further investigations to examine the role of biotic vs. abiotic processes, comprising redox-conditions, travel time, temperature and identification of microorganisms.

1.3 Mobilization and immobilization of arsenic-sulfur species by mineral dissolution and sorption

Overall, the formation of As-S complexes and their precipitation as amorphous As-S phases control arsenic cycling, i.e. arsenic solubility, mobility and toxicity in (natural) sulfidic systems [39, 56-62]. As formation of thioarsenic species can be the result of recombination reactions of arsenite and sulfide, the formation upon dissolution of arsenic and sulfur bearing minerals is only sparsely investigated but geochemically well feasible.

Although the leaching behavior of arsenic sulfides, such as arsenopyrite (FeAsS) and orpiment (As_2S_3) [13, 63], was investigated extensively due to the importance for ore recovery processes, the most studies focused mainly on dissolution rates and efficacy, which were shown to be positively influenced under oxic conditions and by the presence of redox-agents such as Fe^{III} and oxygen [63-71], pH-value [13, 63, 67, 70, 72], microorganisms [73-75], complex formation (arsenic-carbonate [76-80], iron-carbonate [81], As-S [62], gold-thiosulfate (FeAsS) or gold-sulfur (orpiment) complexes [12, 82, 83], temperature increase [56, 58, 61, 62, 83], and surface reactions induced by sulfide (FeAsS) [84].

Beside net arsenic release, determination of species formed at the mineral surface and in solution is of central importance to evaluate the impact and behavior of arsenic in sulfidic mineral systems. At the orpiment surface arsenite and disulfide are formed [63, 85] and complexes of S-As-S and

S-As-S-OH are assumed to detach from the surface by bond-polarization as a base (OH^-)-promoted reaction mechanism [64]. In sulfide-rich anoxic solutions the formation of trivalent thioarsenites was proposed [56, 58] and predicted by thermodynamic model calculations [39, 42], even though analytical evidence is still missing. In sulfide-deficient anoxic solutions arsenite was suggested as major species (70-90%) and analytically proven coupled with model calculations [56, 64]. Also oxidation of orpiment (pH 7-9) resulted in arsenite predominance (50-70%) beside the release of an unknown sulfur species (80-90%), suggested to be polythionate [57]. However, the authors used hydride generation techniques (HGAAS) for arsenic speciation analyses. For thioarsenates, this techniques showed As-S precipitation upon acidification prior to reduction or if pre-reduction was used that only monothioarsenate was co-determined with arsenate, while tetra-, tri-, and dithioarsenate react with the arsenite fraction [48]. Thus As-S species might have been overlooked in previous studies conducted by HG-techniques. For highly alkaline electrochemical oxidation experiments direct formation of thioarsenites by recombination of the released arsenide and sulfide was determined by cyclic voltametry [86]. However, based on the suggestions about redox-stability of thioarsenites [39] it is unlikely that these species are formed via electrochemical oxidation. Direct analytical evidence for thioarsenate formation came from IC-ICP-MS analyses of presumably anoxic sulfidic orpiment leachates at neutral pH, although thioarsenates occurred only as a minority beside arsenite [35]. As mentioned earlier the question about the nature of species formed under anoxic vs. oxic conditions remains unresolved. Detailed studies of kinetics-, pH-, and redox-depending species formation during orpiment leaching are missing.

Similarly for arsenopyrite extensive information exists about the formation of different surface species at acidic, neutral and alkaline conditions (metal-deficient sulfur-enriched surface, As:S > 1 [67, 87-90] vs. arsenic- and iron-oxide-surface coatings, Fe:As, Fe:S, As:S < 1 [67] vs. ironhydroxide formation , Fe:As < 1 [67, 87, 91]) in addition to some speciation studies in solution [69-71, 83, 92, 93]. In these studies arsenite was found to predominate over a broad pH-range from 2-12 in leaching studies of several hours up to one day [70, 71, 92, 93], while sulfate predominates at acidic to neutral conditions [67, 93] and thiosulfate at alkaline pH [83]. In long-term view arsenate will predominate even if abiotic oxidation is slow [94]. For the release of As-S species during arsenopyrite leaching, Rosskovsky [11] proposed the formation of thioarsenites at highly alkaline conditions. However, the only analytical evidence for As-S species as thioarsenates (monothioarsenate) was found by IC-ICP-MS analyses in an unpublished PhD-thesis [83] proposing hydroxide physisorption as release mechanism.

Overall the leaching of arsenopyrite is largely governed by surface structure and the formation of surface coatings, causing dissolution passivation at neutral pH resulting in a minimum net release and arsenic sorption on ironhydroxides at alkaline pH, which may reduce dissolution in the long-term view. However, sorption characteristics for thioarsenates are unknown and it is questionable if they follow the observed trends for pentavalent or trivalent arsenic or are completely different. From numerous sorption studies with arsenite and arsenate it is known, that arsenate has a higher sorption efficacy on goethite and ironhydroxides compared to arsenite at pH 5-6 (sorption maxima at pH 4), forming monodentate or/and bidentate-binuclear complexes at low/intermediate coverages, and bidentate-mononuclear complexing at high coverages [95]. Contrary arsenite sorbs preferentially at higher pH with sorption maxima between pH 8-9 [96, 97] appearing as bidentate-binuclear surface complexes [98], suggesting a stronger bonding at high pH for arsenite. Sorption kinetics is reported to be relatively fast for both arsenite and arsenate on ironhydroxides. At high concentration arsenite reaction is faster and at low concentrations arsenate reaction [97].

To what extent and under what conditions thioarsenate-formation plays a role during (oxidative) dissolution of orpiment and arsenopyrite and for re-sorption by mineral surfaces remained as an open, but for both natural and industrial leaching processes fundamental question.

1.4 Stability and sample stabilization of thioarsenates in iron-containing waters

Since As-S species play a key role in manifold systems from natural waters to industrial processes and laboratory investigations, samples preservation especially for the field studies is indispensable [99], to avoid speciation changes due to the redox-sensitivity of arsenic species.

Although abiotic redox-reactions are slow [100, 101] oxidation and reduction can be accelerated by pH and in low concentrated solutions [102], in the presence of redox-agents, e.g. Fe^{III}, H_2S [101, 103], or by photo-oxidation through radicals formed in the presence of acids (HNO_3, HCl) or Fe^{III} [104-106]. Microbially-catalyzed transformations are generally more important than abiotic reactions for arsenic species transformations in natural samples, but are widely excluded by the application of filtration (0.2 µm-pore-size), acidification (< pH 2), light exclusion, and cool storage (4-6 °C) [107]. In general HCl was reported as the most suitable acid, while HNO_3 is inappropriate because of its photo-oxidation potential, and H_2SO_4/H_3PO_4 due to formation of metal-sulfate or -phosphate precipitates [107]. However, in the presence of sulfide acidification results in precipitation of As_2S_3-phases [47, 108], as also reported for thioarsenate-containing waters [34, 48], predominant species in those systems [15-17, 109]. Due to their limited pH-stability, thioarsenates convert upon acidification and thus for their stabilization special preservation techniques are required. For preservation of total arsenic in sulfidic waters (> 0.4 mg/L) different methods were suggested, comprising a three-step preservation method with base addition, oxidation, and acidification [47] and on-site separation of As^V species with subsequent elution by NaOCl, a strong oxidant [108]. But these methods can only preserve total arsenic concentrations and fail due to oxidation and acidification for stabilizing individual thioarsenic species. More promising is cryo-stabilization, i.e. flash-freezing with storage in a freezer, already proposed for arsenate/arsenite stabilization by Crecelius and co-workers [110], and approved for thioarsenate-containing natural waters [15, 16].

In complex systems containing arsenic, sulfur, and iron, freezing (and thawing) is problematic because the technique is known to promote oxidation of iron and the co-precipitation of arsenic with the newly formed ironhydroxides [107, 111], resulting in a measurable loss of total arsenic. Also common methods for arsenic stabilization in iron-rich waters to prevent iron-induced (photo)oxidation [104, 106, 112] and ironhydroxide formation, comprising pH-buffering with HCl [113] or acetic acid [114, 115], iron-complexation by EDTA (ethylendiaminetetraacetic acid), and light-exclusion [105, 107, 111-113, 115-119] fail, due to the reported pH-sensitivity of As-S species and sulfidic solutions [16, 34, 47, 48, 108].

Although formation of iron sulfides is discussed as competing mechanism to formation of As-S species [38], arsenopyrite leaching studies support the potential for occurrence of thioarsenic species in iron-sulfide solutions [11, 83]. However, preservation strategies for those systems are challenging, since freezing, considered as the best preservation technique for arsenic-sulfide systems, and acidification, currently regarded as optimal for arsenic-iron systems, seem to be mutually exclusive and predestined to fail in more complex arsenic-sulfide-iron-systems.

Overall, As-S species were already in the focus of research studies as early as in the late 19th century. Their environmental relevance became more and more apparent over the last years. Although their existence in natural systems was analytically proven, only little information exists about the biogeochemistry and exact chemical nature of these As-S complexes. The analytical techniques give contradictory evidence for thioarsenates (IC-ICP-MS) vs. thioarsenites (XAS), suffer from the lack of available reference materials and spectra and remain an analytical challenge. However, for evaluation of natural sulfidic systems, industrial processes and prospective As-S sources/pools, extensive information on As-S species formation, (co-)occurrence of thioarsenites and thioarsenates, stability and stabilization, abiotic/biotic transformation mechanisms and toxicity are definitely necessary.

2 Objectives

The general aim of this PhD thesis was to contribute to a better understanding of the nature and geochemistry of aqueous arsenic-sulfide species. To reach this goal scenarios and experiments about formation mechanisms had to be examined as well as preservation techniques and analytical procedures developed and tested under laboratory and natural conditions. The following objectives can be summarized:

- Structural characterization of aqueous and solid thioarsenate species with the XAS, a non-destructive and redox-state preservative technique, using synthesized reference materials consolidating existing information of solid thioarsenate salts (XRD) and aqueous thioarsenate complexes (IC-ICP-MS and ES-MS) as basic dataset for further characterizations (Study 1).
- Structural investigations of the pH-dependent stability of (tetra)thioarsenate under controlled redox-conditions to get analytical proof for possible co-occurrence of thioarsenites and thioarsenates with comparison of existing transformation data [37, 48, 120] and modeling results (Study 1).
- Comparative investigations of thioarsenate and thioarsenite formation in arsenite-sulfide mixes using XAS and IC-ICP-MS by evaluation of redox-conditions, dilution, and pH on As-S species formation and stability (Study 2).
- Determination of abiotic and biotic thioarsenate transformation pathways in natural geothermal systems vs. laboratory oxidation studies (Study 3).
- Formation of thioarsenates during oxidative dissolution of arsenic-sulfide and arsenic-iron-sulfide minerals as further naturally and industrially relevant formation mechanism (Study 4).
- Sorption of monothioarsenate on ironhydroxide exemplary as a first information for the natural behavior of released aqueous thioarsenates and potential immobilization processes (Study 4).
- Examination of iron-containing natural spring waters for resolving the importance of thioarsenates in As-Fe-S systems (Study 5).
- Behaviour and stability of thioarsenates in the presence of iron (Study 5).
- Evaluation and development of preservation strategies of thioarsenates under the aspect of sampling and redox-influence, storage time, stabilizing amendments and presence of iron (Study 5).

3 Methodology

The key-experiments to resolve the geochemical behavior of thioarsenic species are based on structure and redox-state characterizations by X-ray absorption spectroscopy (XAS; see 3.1) and aqueous thioarsenate speciation by ion-chromatography coupled to inductively coupled plasma mass spectroscopy (IC-ICP-MS; see 3.2).

Currently, IC-ICP-MS with a high-alkaline eluent is the standard method to determine the speciation of aqueous inorganic arsenic species in sulfidic systems, i.e. arsenite, arsenate, and monomeric thioarsenates [16, 17], within detection ranges of approximately 0.5 µM to 0.1 mM, i.e. higher concentrated solutions require dissolution. Determination of thioarsenites is presently not possible by this technique. Structural and direct redox-state information of the complexes cannot be deduced from the results.

Structural characterization (local coordination, Extended X-ray absorption fine-structure, EXAFS) and redox-state determination (X-ray absorption near-edge structure, XANES) can be received by XAS, a non-destructive technique for analyses of solutions at room temperature and flash-frozen as well as for solid materials. Redox-state transformations can be prevented by using cryo-techniques (cryo-preservation = flash-freezing in dry-ice (-79 °C)/liquid N_2 (-196 °C) and storage in a freezer (-18 to -20 °C), cryostat), which enables the investigation of extremely redox-sensitive species. By resolution of characteristic local complex coordination combined with the prediction of the redox-state the distinction of several species is possible, even though "average" signals in mixtures require statistically based evaluation techniques, e.g. iterative transformation factor analysis (ITFA). In contrast to IC-ICP-MS detection limits of XAS are magnitudes of order higher and thus the analytical use is limited to high concentrated arsenic solutions, synthetic model and/or reference solutions.

In the following, brief information on the analytical techniques is given; detailed experiments can be looked up in the respective studies, in the Annex or briefly summarized in Table 2.

3.1 X-ray absorption spectroscopy

Structural characterization by XAS was done for synthesized reference materials of thioarsenates (Table 1), for the pH-dependent tetrathioarsenate transformation experiments under anoxic conditions, and the evaluation of As-S species in oxic and anoxic arsenite-sulfide mixes in comparison to anoxic and standard IC-ICP-MS speciation. Samples were handled under nitrogen atmosphere (exceptions were samples to evaluate the effect of oxidation) and either pressed as pellets (solids) or pipetted into slit-sample holders as aqueous solutions, caped with Kapton® tape, and finally stored under nitrogen atmosphere (thioarsenate reference solutions only, max. 1 hour) or flash-frozen, as redox-stability had to be guaranteed (thioarsenate reference solutions, solids, tetrathioarsenate titration, and As-S mixes, 1 hour to max. 8 days).

XANES and EXAFS spectra (arsenic K-edge, 11,867 eV) were collected at the Rossendorf Beamline (BM20) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France), using a Si(111) double crystal monochromator (DCM) and the settings described in more detailed in the respective publications [121, 122]. Fluorescence spectra were collected with a 13-element Ge-detector (Canberra). The measurements of aqueous reference samples were performed at room temperature (RT), while flash-frozen aqueous and solid samples were measured at 15 K in a closed-cycle He cryostat (CryoVac). By using the cryostat, sample stabilization could be guaranteed by exclusion of oxygen and photon-induced redox-processes during the measurements [123, 124] and the detection was improved by elimination of thermal vibrations [125]. Data processing of several fluorescence spectra was performed with the software packages *SixPack* and *WinXAS* 3.1 [126, 127]. To determine the local structure of the As-S complexes, shell fitting was performed on the Fourier transforms (FTs) using As-O and/or As-S paths with *FEFF* 7.02 and *WinXAS* 3.1. Fitting parameters included the passive electron reduction factor (SO^2), the coordination number (CN±25%), the radial distance (R±0.02 Å), the Debye-Waller factor ($\sigma^2 \pm 0.0005$ Å), and the phase shift (ΔE_0). The sample coordination, local structure, and edge positions were compared with those of defined references: arsenic pentoxide (As_2O_5, solid), orpiment (As_2S_3, solid), and sodium arsenite ($NaAsO_2$).

Table 1: Description of thioarsenate reference materials and standard handling procedure

Reference material (synthesis [122])	**pH-stability and handling**
monothioarsenate (MONO) $Na_3AsO_3S \cdot 12\ H_2O$	stability pH 1-13 [48], aqueous complex (AsO_3S^{3-}) by dissolution in ultrapure water (in specific experiments 0.1 M NaOH, 1% EtOH)
dithioarsenate (DI) $Na_3AsO_2S_2 \cdot 11\ H_2O$	stability pH 4-11[48], conversion to arsenite, aqueous complex ($AsO_2S_2^{3-}$) by dissolution in UPW, final solution contains 1% EtOH from synthesis [122, 128]
trithioarsenate (TRI) AsS_3O^{3-}	not available as solid, aqueous complex (AsS_3O^{3-}) by dissolution in UPW (pH 9-10) for standard IC-ICP-MS, synthesized aqueous reference for XAS, stability pH 7-10 [48], conversion to arsenite + precipitation
tetrathioarsenate (TETRA) $Na_3AsS_4 \cdot 8\ H_2O$	stability pH 11-13 [34, 48] resp. 13-9 [37, 122], aqueous complex (AsS_4^{3-}) by dissolution in 0.1 M NaOH

For species determination in mixed solutions, iterative transformation factor analysis (ITFA, [129, 130]), combining principal component analysis (PCA) with the factor analysis procedures varimax rotation and iterative target test (ITT), were performed with the EXAFS spectra of mixes and references. PCA was used to determine the number of components in the model solutions (minimum Malinowski factor, graphically on PCA FTs) and to identify the spectra corresponding to the components, which were then added to the ITFA series. Visually the series spectra are recombined by linear combination (LC) of the principle components displaying the goodness of the reproduction. To estimate the component distribution in the model solutions concentrations of the references were normalized to 100% for ITT calculations. For trithioarsenite a theoretical chi-function was built with FEFF 7.02 [131], based on the structure of trithioarsenite [122] ($CN_{As\text{-}S}$ = 3 and $R_{As\text{-}S}$ = 2.2536 Å) and fixed fitting parameters ($S_0^2 = 0.9$, $\sigma^2 = 0.003$ Å^2 , $\Delta E = 11.59$ eV). ITFA analyses and EXAFS shell fitting were used complementary to identify and ensure the speciation in mixes.

3.2 IC-ICP-MS

The samples from oxic and anoxic arsenite-sulfide mixes as described above were subjected to speciation analyses by IC-ICP-MS. Furthermore the solutions to determine thioarsenate stability in iron-containing systems, solutions from batch sorption experiments, oxic leachates of arsenopyrite and orpiment, and natural samples (Yellowstone National Park, Czech Republic) were analyzed by IC-ICP-MS (Annex and Table 2). If not stated otherwise, species determination was done with an instrument outside the glovebox (= standard IC-ICP-MS). Only for selected samples a gradient pump inside the glovebox was used (same setting as the standard IC-ICP-MS) to avoid any oxygen in the instrument, not at least to show that standard IC-ICP-MS even by using N_2 purged eluents is affected by oxygen traces.

Samples of redox-sensitive solutions (As-S mixes, flash-frozen natural, sorption and stability study solutions) were handled in the glovebox prior to standard IC-ICP-MS analyses, oxic leachates were filled outside, and selected sample solutions were handled and directly injected into the HPLC pump in the glovebox. In general, sample preparation comprised filtration and centrifugation (natural samples, sorption studies), dilution of high concentrated samples, and finally pipetting into IC sample vials with filter cap. After preparation samples were analyzed immediately, i.e. injected manually (HPLC inside the glovebox) or by autosampler (outside).

Arsenic speciation measurements were conducted by anion-exchange chromatography with an AG16/AS16 IonPac® column using an alkaline gradient (20-100 mM NaOH) at a flow rate of 1.2 mL/min [16, 109, 121, 128, 132]. Especially for analyzing the arsenic-sulfide mixes the eluents were nitrogen-purged and kept under constant nitrogen pressure during analysis. The standard setup was an ICS-3000 SP (Dionex) with an anionic self-regenerating suppressor (ASRS) outside the glovebox coupled to an ICP-MS (X-Series2, Thermo Scientific or Elan DRC II, PerkinElmer). Arsenic and sulfur were monitored as AsO^+ (m/z 91) and SO^+ (m/z 48) using 10% oxygen in 90% helium as reaction/collision gas. Thioarsenates were quantified based on calibration curves for commercial arsenite and arsenate standards. For selected experiments, an HPLC gradient pump (System 525, BioTek Instruments) was set up inside the glovebox coupled to the ICP-MS (outside the glovebox) to exclude any traces of oxygen during chromatographic separation. Sample injection and gradient changes were done manually.

Total analyzes of arsenic (and sulfur) were determined as AsO^+ (and SO^+) by ICP-MS as described above. Calibration, data correction, and quality-control can looked up in the respective publications. All samples for total determinations required dilution, performed by addition of UPW.

Table 2: Summary of studies, objectives, major experimental settings and results

Objective	Experimental setup/Sampling	Analyses	Results
Study 1: Discrimination of Thioarsenites and Thioarsenates by X-ray Absorption Spectroscopy			
► structural characterization (EXAFS) and arsenic redox-state determination (XANES) of aqueous and solid As^{V}-S complexes to provide a dataset for differentiation of the species in the homologue series and As^{III}-S species ► structural monitoring of TETRA pH-instability under anoxic conditions – differentiation of As^{V}-S and As^{III}-S in mixes	reference structures + evaluation of possible transformation via dissolution, cryo-preservation, and analyses ► sample handling under N_2-atmosphere ► pellets (8.9 mg As) of solid As^{V}-S reference salts (see below), 10 mM solutions (aqueous, flash-frozen in liquid N_2, anoxic/cryo-storage max. 1h) ► further references $NaAsO_2$(arsenite), As_2S_3, As_2O_5 (arsenate) pH-dependent behavior of TETRA ► 10 mM TETRA in 0.1 M NaOH (pH 12), in UPW (pH 9.5) → acidification (HCl) to pH 6.3, 5.8, and 2.8 ► cryo-preservation + anoxic handling PhreeqC-modeling of TETRA-acidification ► 10 mM As, 40 mM S^{-II}, pe -4	► XAS (As K-edge (E_0)11,867 eV, XANES E_0±50 eV, EXAFS E_0+50 to 12,600 eV) ► He-cryostat (15K) for solids, cryo-preserved solutions ► spectra evaluation *SixPack, WinXAS, Feff 7.02* ► ITFA (PCA, ITT) for mixed solutions (TETRA acidification)	As^{V}-S species characterization with EXAFS and XANES ► structural similarity of solid, aqueous (RT, flash-frozen) complexes = stability towards dissolution, flash-freezing → cryo- and redox-state preservation, use as references for liquid based analytics ► $R_{As\text{-}O}$ 1.67-1.69 Å, $R_{As\text{-}S}$ 2.14-2.15 Å, CN as expected ±25% (arsenates: $R_{As\text{-}O}$ 1.68-1.71 Å, arsenites: $R_{A\text{-}O}$ 1.80 Å, As^{III}-S $R_{A\text{-}S}$ 2.21-2.25 Å, As_2S_3 2.28Å) ► XANES edges differ by ≈1 eV, edge↓ with SH↑ (arsenate→MONO→ DI→TETRA), Δ TETRA and arsenite ≈1 eV → misidentification in mixes Differentiation of As^{V}-S and As^{III}-S species in mixes ► conversion of TETRA through acidification (edge shift -2eV, $R_{As\text{-}S}$↑ to 2.28 Å) ► evaluation with ITFA: TETRA-pH-series two aqueous species = end members pH 12 (= TETRA) and pH 2.8 (= trithioAs^{III} →EXAFS CN 3.8/ $R_{As\text{-}S}$ 2.28 Å) ► pH 6.3, 5.8 co-existence of TETRA and trithioAs^{III} Modeling ► support of TETRA-transformation to trithioAs^{III} (pH 5-7), TRI 0.1% at pH 7 (below XAS detection limit), underestimation of TETRA-stability at alkaline pH (arsenate prediction) CONCLUSION: ► detection limits XAS (≥ 0.5 mM XANES, ≥ 5 mM EXAFS, ITFA 5%) → limitation high conc. (synthetic) systems ► structure solids = aqueous complexes → use as IC-standards ► As^{V}-S /As^{III}-S structurally distinct ► TETRA-conversion by pH ↓(anoxic) → trithioAs^{III}, co-existence and triggered by polysulfides

Objective	Experimental setup/Sampling	Analyses	Results
Study 2: Arsenic Speciation in Sulfidic Waters: Reconciling Contradictory Spectroscopic and Chromatographic Evidence			
► comparative analyses of anoxic arsenite-sulfide (As^{III}-S^{-II}) mixes with IC-ICP-MS (undiluted) and XAS ► effect of oxygen elimination on As-S speciation in anoxic mixes during IC-ICP-MS analyses ► oxidation kinetics of As-S species in As^{III}-S^{-II} mixes (XAS/IC-ICP-MS) ► effect of dilution in mixes with SH^--excess (S:As 10) (IC-ICP-MS) ► effect of pH mix S:As 10 (0.1 mM As) with IC-ICP-MS	S:As mixes for XAS/IC-ICP-MS ► speciation in anoxic As^{III}-S^{-II} mixes: (10 mM As, S:As ratio of 0.1, 1, 2, 4, and 10, anoxic preparation, i.e. glovebox, pH 11.2 to 12.5, immediate analyzes/sampling ► mix S:As 10 after 3 days under N_2 ► oxidation: subsamples mix S:As 10 on air (1h/24 h) → cryo-preservation of XAS samples, standard IC-ICP-MS (undiluted!) Dilution effect (IC-ICP-MS) ► mixes with S:As 10 → dilution series 0.1, 0.5, 1, 5, and 10 mM As ► pH-influence (IC-ICP-MS) ► S:As 10, As 0.1 mM ► pH-values 3, 5, 6, 7, 9, 11, 12, 13 ► analyses immediately/after 7 days Oxidation kinetics of As^{III}-S species by anoxic determination with HPLC in glovebox ► mix S:As 10 (0.1 mM As) exposed to oxygen for 0.5-96 h in open/ 1-96h closed IC-vials (filter-cap) ► anoxic reference 3/24 h	► XAS of cryo-preserved mixes and evaluation by fitting, ITFA (cf. study 1) ► species/totals with standard IC-ICP-MS (eluents purged with N_2), sample handling in glovebox prior analyses ► selected experiments with HPLC gradient pump in glovebox (coupled to ICP-MS) for oxygen exclusion ► pH (HACH)	Comparison speciation with XAS and IC-ICP-MS ► analyses match at S:As 0.1 (SH^--deficient) = arsenite ► S:As > 0.1 → XAS predominance trithioAs^{III} ($CN_{As\text{-}S}$ ≈3, $R_{As\text{-}S}$ 2.21-2.24 Å), standard IC-ICP-MS DI/DI+TRI, loss 23-26% Oxidation of As^{III}-S to As^{V}-S species (HPLC gradient pump in glovebox) ► S:As 10: anoxic As^{V}-S < 1%, arsenite+peak-splitting, air-exposed: share of As^{V}-S ↑, half-life of arsenite 130”- 240”, loss 20% ► confirmation by XAS → air-exposure edge shift (As^{III}-S→As^{V}-S), bond-distances↓ ($R_{As\text{-}S/As\text{-}O}$ 2.16-2.17 / 1.70 Å, $CN_{As\text{-}S/As\text{-}O}$ 2.9/1.8 → suggestion TRI) ► As^{III} -S anoxic stability ≤ 24h, then decay into TRI/mix (XAS), arsenite (IC) ► As^{III} -S appear as arsenite and As^{V}-S in standard IC (outside glovebox!) → no co-elution of As^{III}-S and As^{V}-S Dilution 10 mM→0.5mM (S:As 10) ► 50% DI/TRI, loss 26% → 64% arsenite, 15% loss ► stability of As^{III} -S dependent on SH^-:OH^- ► analyses with IC (even anoxic) - requires dilution + NaOH-eluent → SH^-:OH^-↓ ► suggestions: thioAs^{III} conversion to arsenite at OH^--excess due to OH^-↔SH^- exchange ► no formation of As^{III}-S at OH^--excess (diluted As:S 10-mixes) → arsenite ► As^{III}-S = necessary intermediates for As^{V}-S formation CONCLUSION: ► As^{III}-S = formed in anoxic As:S mixes (SH^--excess), oxic conversion to As^{V}-S ► As^{III}-S = necessary intermediates for As^{V}-S formation in As^{III}-S^{-II} solutions ► As^{III}-S properties: labile, rapid conversion under oxic/anoxic conditions, OH^--excess, only detectable by XAS (actually) ► IC-analyses: As^{III}-S appear as arsenite (anoxic), As^{V}-S (oxic) ► natural waters: As^{V}-S “true” species, due to rapid trithioAs^{III} conversion on air

Objective	Experimental setup/Sampling	Analyses	Results
Study 3: Oxidative Transformation of Trithioarsenate Along Geothermal Drainages – Abiotic versus Microbially Mediated Processes			
► evaluation of transformation processes of As^{V}-S species upon exposure to oxygen in natural sulfidic systems and in laboratory based experiments	sampling along drainage channels ► on-site parameters, flow-time ► samples for As-S species analyses (filtered + cryo-preservation) ► microbial samples - retention on filters (0.22 µm, ca. 1-15 L natural water) + lysis buffer → cryo-preservation laboratory investigations ► oxidation (air-purging for 5”-36 h, addition of 2×10^{-13} – 4×10^{-2} M H_2O_2) ► temperature effect (20, 50, 80 °C) ► reference solutions: MONO/TRI	► species: standard IC-ICP-MS (anion-exchange AG16/AS16 IonPac®, eluent-gradient 20-100 mM NaOH, ICP-MS as AsO^+ and SO^+ (reaction with 10% O_2, 90% He), instruments outside the glovebox, sample handling prior to analysis in glovebox) ► totals: ICP-MS ► microbiology: incubation, DNA purification and concentration, PCR amplification + DGGE	abiotic oxidation/temperature experiments ► MONO stable towards air-purging/heating at 80 °C, oxidation with H_2O_2 conversion to arsenate ► TRI → air-purging, $H_2O_2 < 2\times10^{-6}$ M sequence: TRI+arsenite+thiosulfate (equilibrium), ► TRI → $H_2O_2 > 2\times10^{-6}$ M sequence (= successive ligand exchange): TRI → DI → MONO+arsenate → arsenate; sulfur: thiosulfate → sulfate ► 80 °C: TETRA → TRI + arsenite natural waters (12-33 µM As, 90-130 µM S^{-II}, 60-89% As^{V}-S ► transformation sequences: (1) Ojo Caliente: TRI→ arsenite (abiotic/microbial by unknown species) → arsenate (possibly by *Thermocrinis* spp.) = cf. abiotic air oxidation, but exclusively arsenite formation and later transformation to arsenate = transformation rate ×500 cf. abiotic oxidation (2) Gibbon Geyser Basin: successive ligand exchange TETRA/TRI to finally arsenate (+ arsenite increase) = cf. abiotic oxididation with strong oxidant, possibly parallel mechanisms observed stepwise in (1) CONCLUSION: ► naturally two conversion sequences (microbial mediated) ► 40-500 times faster as abiotic oxidation (catalyzes possibly by *Thermocrinis* spp.) ► direct conversion to arsenate only with strong oxidant, naturally by arsenite oxidation ► transformation processes naturally not inhibition by sulfide (28-91 µM)

Objective	Experimental setup/Sampling	Analyses	Results
Study 4: Thioarsenate formation, release and re-sorption during oxidative dissolution of arsenic-iron-sulfide minerals			
► As^V-S speciation in mineral solutions (As_2S_3, FeAsS) depending on pH and time ► influence of leaching solution composition on leaching behavior of FeAsS (ionic strength) ► effect of reactive sulfide species on As^V-S formation and dissolution intensity of FeAsS ► sorption of MONO on α-Goethite	open system As_2S_3 and FeAsS leaching ► ≈ 290 mg As/L, pH 2, 6, 12 (0.04 M $NaHCO_3$, 0.1 M NaOH), open flasks (50 rpm) → sampling species/totals 6-144 h FeAsS leaching with restricted O_2 (separate batches, overhead shaker 20 rpm) ► ≈ 290 mg As/L, FeAsS (Freiberg/Hartmannsdorf) ► pH-dependence: pH 2, 5, 7, 9, 12, 13 (0.04 M air-purged $NaHCO_3$/ 0.1 M NaOH) → leaching time 10”-6 weeks ► effects of ionic strength: 48 h, 0.004, 0.04, 0.4, 0.8 M, NaOH/$NaHCO_3$ ► influence of sulfur-anions (pH 7/12, 48 h): oxic 3/30 µM thiosulfate, anoxic 30/300 µM polysulfide, 17/167 µM sulfide ($Na_2S{\cdot}9H_2O$)) sorption of MONO, arsenite, arsenate on α-Goethite ► suspensions 33 g/L, 5 mM NaCl ► batch, anoxic handling ► sorption isotherms: 48 h, 0.07-5.3 mM kinetics: 0.053 mM As, 0.03-336 h	► species standard IC-ICP-MS → dilutions pH 2,9-13 (1.7-10) ► totals ICP-MS → dilutions (10-250) ► sampling mineral leaching: filtration (0.2 µm), pH-measurement, immediate analyzes (only (poly)sulfide samples handled under N_2) ► sampling sorption: centrifugation, filtration + pH, handling under N_2	FeAsS vs. As_2S_3 ► FeAsS min. dissolution at neutral pH, As_2S_3 min. pH 2 and linear increase ► speciation: As^V-S formation at pH 12 (FeAsS, As_2S_3), pH 7 (As_2S_3) ► As^V-S species: MONO (FeAsS), TRI, DI (As_2S_3) → misidentifications by HG ► dissolution mechanisms: FeAsS physisorption of OH^- = direct As^V-S release, As_2S_3 – formation/release of As^{III}-S → rapid oxidation to As^V-S detailed FeAsS-studies ► As-speciation of different FeAsS-types equals (TAs different) ► dissolution min. pH 6 (Fe-As-oxide coatings), increase to pH 2 and pH 12/13 (max. dissolution), S:As ≈2 (pH2) → < 0.5 (pH 5-9) → ≈1 (pH12-13) ► MONO-formation pH 2-9 < 3%, pH 12/13 13-25% (t=35 d) ► As-speciation: pH 2 arsenate + arsenite, pH 6-7 arsenite, pH > 9 As^V species (highly alkaline As^V-S) ► S-speciation: pH 2-7 sulfate, pH > 9 thiosulfate (+ sulfate, S-associated with As^V-S) ► ionic strength: leaching efficacy NaHCO3↑ to ≈ NaOH-levels → no effect on As^V-S formation ($NaHCO_3$ (4%), pH 13(40%)) → supports OH^--physisorption release ► anoxic conditions dissolution at pH7/12 decreased (factor 2/7) ► no effect of thiosulfate, (poly)sulfide increased anoxic dissolution at pH 7, no As^V-S ↑ (suppression at pH 12, competition SH^-↔OH^-, slight As^V-S increase) sorption on α-Goethite: ► efficacy and kinetics arsenite > arsenate > MONO CONCLUSION: ► As^V-S substantial species formed during (Fe)AsS-dissolution ► different leaching mechanisms (physisorption vs. recombination/As^{III}-S release) ► ionic strength, (poly)sulfide affect leaching efficacy, but less speciation

Objective	Experimental setup/Sampling	Analyses	Results
Study 5: Thioarsenate stabilization in iron-rich waters			
► evaluation of preservation techniques for natural iron-containing waters ► laboratory evaluation of thioarsenate preservation techniques in presence and absence of iron: addressing influence of gas-headspace, redox-conditions, effect of Fe^{II}, effect of EDTA, and preservation by flash-freezing+EDTA	natural waters ► mineral spring water (Frantiskovy Lazne, Cisarsky Spring, Czech Republic) ► in-situ: T, pH, conductivity, S, Fe-species ► preservation: cryo-preservation, 0.1% HCl, 0.65% HNO_3, 0.33 mM Na-EDTA+flash-freezing laboratory experiments influence of headspace, redox- and matrix ► As^V-S/As^{III}/As^V-reference solutions (approx. 13 µM As) ► MONO in 1% EtOH, 0.1 M NaOH ► preparation: PE-vials with small (17 cm^3)/large headspace (47 cm^3), oxic/anoxic ► cryo-preservation/analyses after 0, 1,7, 21 (45) days effect of Fe(II), EDTA on As^V-S and + preservation of Fe(II)- As^V-S-solutions ► reference solutions of MONO, DI, TRI+Fe^{II} (1.8 mM, $FeSO_4·7H_2O$)/ MONO, DI, TRI+0.01 M EDTA, and +Fe^{II}+EDTA(pH 7) ► cryo-preservation/analyses 0, 11d	► species with standard IC-ICP-MS (sample handling under N2, instrument outside the glovebox) ► totals (TAs) with ICP-MS	natural waters ► up to 17% As^V-S in Fe-rich waters (1.3-66 mg/L), stabilization techniques – high variability, TAs by 0.65% HNO3 → no optimal species preservation technique yet laboratory stability tests ► cryo-preservation stability: arsenite, arsenate (45 d), DI and TETRA (21 d) → headspace/redox-independent, variability < 3%, MONO/TRI anoxic, small headspace (21 d, <3%), oxic 10-20% ► matrix influence: MONO in EtOH, NaOH ➔ headspace, redox-independent (21 d, < 1%) effect of Fe^{II} ► TAs↓ (Fe-As-complexes?, sorption on Fe-colloids?), As^V-S conversion to arsenite, lowest affected MONO (3%, but TAs↓), no further variation by flash-freezing preservation of Fe^{II}-As^V-S solutions by EDTA+cryo-preservation ► As^V-S - EDTA cryo-stability (pH 7) guaranteed ► cryo-preservation TAs in Fe^{II}-EDTA-As^V-S systems possible (0, 11 d) ► cryo-preservation of Fe^{II}-DI and Fe^{II}-MONO solutions (0, 11 d) ► effect on lower SH$^-$-substituted As^V-S impurities and TRI ➔ reduction to arsenite (former excluded to occur) CONCLUSION: ► As recovery of natural Fe-rich samples HCL > EDTA+cryo-preservation ≫ cryo-preservation → TAs in 0.65% HNO_3, no species-preservative method yet ► pure As^V-S solution stabilization best by cryo-preservation anoxic, small gas headspace, organic solvents/high matrices increase stability ► EDTA+flash-freezing preserves TAs in Fe^{II}-As^V-S solutions and conservation of MONO and DI possible

4 Results and Discussion

4.1 Structural characterization and differentiation of thioarsenates and thioarsenites (study 1, study 2)

The EXAFS-coordination of thioarsenates showed typical properties with As-O bond length of 1.70±0.01 Å and As-S bond lengths of 2.16±0.02 Å matching pathways of previously reported XRD data of thioarsenates [25, 27, 31-33, 133] and XAS structures of other As^V-compounds such as scorodite ($FeAsO_4 \cdot 2H_2O$; 1.68 Å [131]) and As_2O_5 (1.71 Å) (cf. Table 2). With their shorter bond lengths the structure of thioarsenates and As^V-compounds differ distinctly from that of thioarsenites and As^{III}-compounds with the respective bond lengths of $R_{AsIII\text{-}O}$ of 1.80 Å (arsenite [134]), $R_{AsIII\text{-}O}$ 1.77-1.82 Å and $R_{AsIII\text{-}S}$ 2.21-2.25 Å (thioarsenites [40-42, 135, 136]), and 2.28 Å (orpiment [42]). The modeled coordination numbers for As^V-O/As^V-S pathways (Table 2) are in line with theoretical expectations.

The similarity of XAS spectra of aqueous thioarsenate complexes (measured either at room temperature or flash-frozen at 15 K) and solid salts reveal their molecular stability (provided pH conditions are appropriate, see below) towards dissolution, flash-freezing, and beam-induced reduction [137] and thus justify the use of cryo-preservation for thioarsenates in solution [16] and the use of the solutions for liquid-based analytical methods (e.g. liquid chromatography).

Based on the XANES edge energies the distinction of the individual thioarsenates was possible. Their edge positions fall in between those of arsenate ($As^V{}_2O_5$, 11872.3 eV) and arsenite ($As^{III}NaO_2$, 11868.2 eV) and decrease successively by ≈1 eV with increasing SH^--substitution due to the increasing covalent character of As-S vs. As-O [41] (mono- 11871.3 eV > di- 11870.3 eV > tri- and tetrathioarsenate 11869.3 - 11869.8 eV, Figure 1). Misidentifications with arsenite or arsenate are unlikely for the pure substances, since the two end members of the thioarsenate family are sufficiently far apart (≥ 1.0 eV) from both arsenic compounds, as well as distinctly different from thioarsenites, for which edge positions between arsenite and orpiment ($As^{III}{}_2S_3$) were reported [40, 41].

However, arsenic XANES studies in sulfidic environments may be problematic, because tetrathioarsenate has an edge position much closer to that of arsenite than to that of arsenate and thus thioarsenates may have been mistakenly identified as arsenite. Another disadvantage of using only the XANES edge position for identification of As species in sulfidic environments is that mixtures of thioarsenites and thioarsenates might yield an “average” edge position close to or below that of arsenite, and would consequently be misidentified.

In this case, principal component analysis could be used to separate the spectral components [138-145] and to determine their quantitative composition by iterative transformation factor analysis (ITFA) [145, 146] and least square fitting [141, 143, 145, 147]. Nevertheless, fundamental requirements are the sufficient variance in the spectral data of the contributions and the availability of XAS spectra of the individual components.

Table 3: Arsenic K-edge, XAS-derived absorption edge energies and fitted first-shell coordination numbers for thioarsenate and thioarsenite references, the tetrathioarsenate titration series, arsenite-sulfide mixes, and arsenic references

				As-O			As-S			
	pH	**Edge**	**Res**	**CN**	**R**	**σ²**	**CN**	**R**	**σ²**	**ΔE**
References										
Arsenite/arsenate										
$NaAsO_2$		11868.5	11.4	3.4	1.79	0.0047				10.2
As_2O_5		11872.3	14.2	4.6	1.69					7.8
Thioarsenates										
monothioarsenate ($H_xAsSO_3^{3-x}$)	11.7	11871.0	18.6	3.0	1.68	0.0015	0.9	2.12	0.0009	10.1
dithioarsenate ($H_xAsS_2O_2^{3-x}$)		11870.3	10.3	2.2	1.69	0.0023	1.8	2.15	0.0015	11.1
trithioarsenate ($H_xAsS_3O^{3-x}$)		11869.4	13.2	1.5	1.69	0.0013	2.5	2.16	0.0012	11.9
tetrathioarsenate ($H_xAsS_4^{3-x}$)	12.3	11869.3	9.1				4.0	2.17	0.0014	9.6
Thioarsenites										
trithioarsenite (Feff-model)							3.0	2.25	0.0030	13.9
orpiment		11866.8					3.5	2.28	0.0050	
realgar		11866.3								
Tetrathioarsenate titration										
$H_xAsS_4^{3-x}$	12.3	11869.3	9.1				4.0	2.17	0.0014	9.6
pH 9.5	9.5	11869.3	7.7				4.4	2.17	0.0019	12.0
pH 6.3	6.3	11867.3	6.4				4.1	2.20	0.0088	23.9
pH 5.8	5.8	11867.5	7.9				3.2	2.24	0.0054	19.3
pH 2.8[+] (≙ trithioarsenite, $H_xAsS_3^{3-x}$)	2.8	11867.0	8.6				3.8	2.28	0.0035	13.9
Mixes with variation of S^{-II}:As^{III} ratios at an As concentration of 10 mM – ratio series										
0.1	11.2	11868.5	13.9	3.1	1.78	0.0034				6.4
1	12.0	11867.5	8.9	2.8	1.77	0.0095	0.9	2.23	0.0028	8.0
2	12.1	11867.5	2.6	1.0	1.73	0.0009	2.4	2.23	0.0041	9.6
4	12.3	11867.5	5.3				3.2	2.24	0.0022	9.8
10	12.3	11867.0					2.8	2.23	0.0035	10.4
10 (2nd determination)	12.5	11866.9	8.5	0.7	1.70	0.0001*	3.3	2.22	0.0037	10.8
Mixes (ratio S^{-II}:As^{III} 10) time depending under various redox conditions										
10 (pH 14)	13.2	11866.9	5.9	0.9	1.70	0.0001*	3.0	2.21	0.0038	11.0
10 (anoxic, 3 days)		11869.4	10.7	1.2	1.69	0.0015	2.9	2.17	0.0026	9.1
10 (oxic, 1 h)		11869.4	16.1	1.7	1.70	0.0019	2.3	2.16	0.0001*	11.7
10 (oxic, 1 day)		11869.9	9.6	1.6	1.69	0.0017	2.6	2.16	0.0014	11.7

[a] CN: coordination number, error ±25% [b] *R*: radial distance, error ±0.01 Å[c] σ²: Debye–Waller factor, error ±0.0005 Å², [*]constrained from 0.001-0.05 As-As shell: CN 0.8, R 3.59, σ² 0.0057, [+]As-As shell: CN 0.8, R 3.59, σ² 0.0057

As suggested in earlier studies, tetrathioarsenate is instable towards pH changes [34, 48] and converts possibly into a mixture of arsenic species which requires the evaluation of the XAS spectra by ITFA. Principal component analysis (PCA) revealed the occurrence of two species in the solutions of the titration series, relatively purely represented as end members at pH 12.3/9.5 and pH 2.8. By resolving the EXAFS spectra, the species at pH 12.3 and 9.5 is unambiguously identified as tetrathioarsenate (Table 3). The species at pH 2.8 showed a significantly longer bond distance, a lower coordination number ($R_{As\text{-}S}$ 2.28 Å, $CN_{As\text{-}S}$ 3.8± 25%) and an edge position lower than that of arsenite, assigned in the following as monomeric trithioarsenite. Due to the absence of As-O or As-As shells formation of arsenite and/or polymeric As^{III}-S species [39, 41, 42, 148] could be excluded.

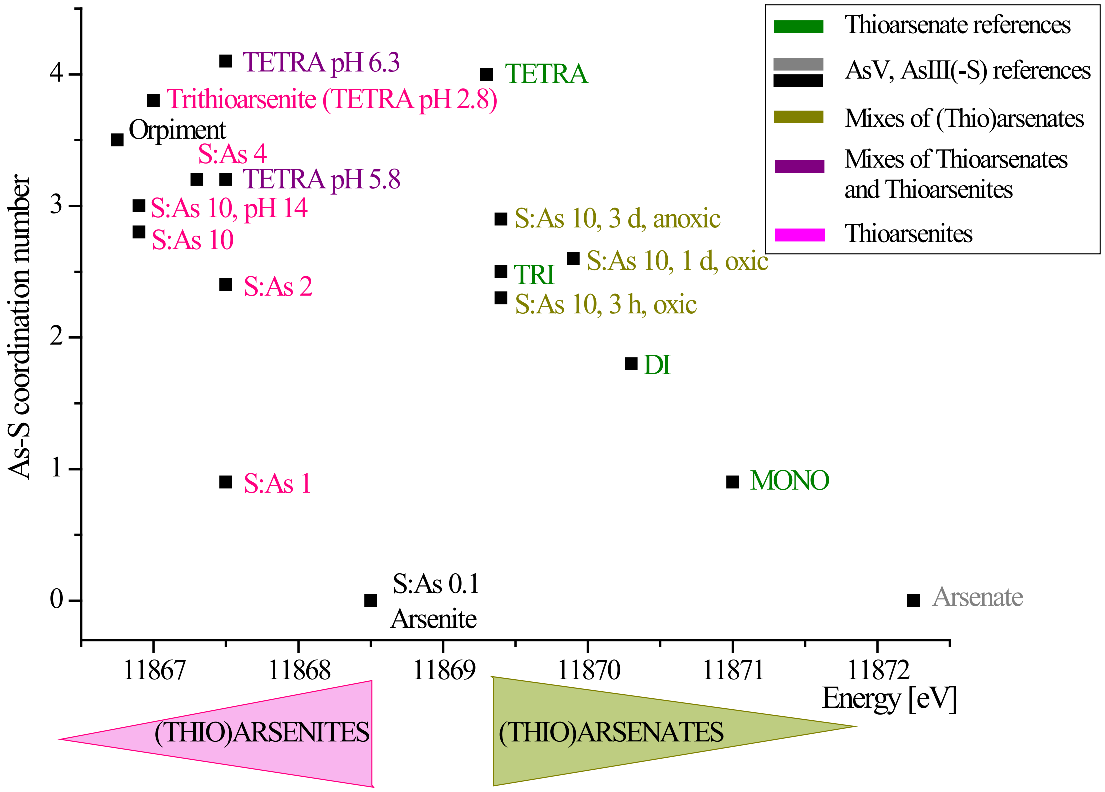

Figure 1: Arsenic K-edge XANES edge position vs. EXAFS-derived As-S coordination number (CN) of the 10 mM flash-frozen thioarsenate solutions, the tetrathioarsenate titrations, and arsenite-sulfide mixes beside the references As_2S_3, $AsNaO_2$, and As_2O_5

However, in the transition region (at pH 6.3 and pH 5.8), the PCA indicated the presence of a mixture between the two end members and thus gave the first evidence for co-occurrence of thioarsenates and thioarsenites as so far only postulated [39]. The positions of the XANES absorption edges for the pH between 2.8 and 6.3 are already in the range characteristic for As^{III}-S species (Figure 1), as is the As-S bond length (2.20-2.28 Å). Hence without paying attention to these indicators and without the help of the PCA, the "average" absorption edge position (or As-S bond length) for the mixture would easily be misinterpreted as complete conversion to (unspecified) thioarsenites.

Overall, it can be assumed that tetrathioarsenate converts to trithioarsenite under anoxic, acidic conditions, formally expressed as: $-$, in which arsenic is reduced and one of the four sulfur atoms is oxidized possibly by polysulfides, which are known donors and acceptors of elemental sulfur, but so far analytical not proven.

Hydrochemical modeling results based on thermodynamic constants derived partially from *ab initio* calculations [39] provide support for the observed transformation of tetrathioarsenate to trithioarsenite in the pH range between 7 (tetrathioarsenate) and 5, with conversation to trithioarsenite at pH 6.

Summarizing, thioarsenates can be distinguished from thioarsenites by their XANES edge positions, which also enables differentiation of individual thioarsenates as well, and their EXAFS coordination. Co-occurrence of thioarsenates and thioarsenites was analytically proven by evaluation of XAS spectra with ITFA-based methods combined by EXAFS evaluation of the respective end members of the series. Thioarsenites are intermediates during thioarsenate transformation, but both species can co-occur under certain conditions.

4.2 Thioarsenite formation in anoxic systems and their transformation to thioarsenates by oxygen traces (study 1, study 2)

4.2.1 Thioarsenite formation traced by XAS and standard IC-ICP-MS

Already the tetrathioarsenate titration showed differences between XAS results (indicating formation of thioarsenites) and IC-ICP-MS results (indicating formation of trithioarsenate and/or arsenite) [48]. The reason for this discrepancy was suggested to be due to lower As concentrations (10^{-2} M As in XAS study vs. $3.5 \cdot 10^{-4}$ M in the previous study [48]), an OH^- surplus during chromatographic separation with a high alkaline eluent (exchange of thioarsenite SH^- for OH^-) as well as oxidation during the IC analyses.

More extensive investigations comparing XAS and standard IC-ICP-MS analysis were performed with equimolar solutions of sulfide and arsenite in ratios of S:As 0.1 to 1, 2, 4, and 10. The analyses matched only for sulfide-deficient conditions and showed arsenite as predominant species (Figure 2). For solutions with excess sulfide, XAS displays the formation of trithioarsenite successively with increasing SH^-, contrary to IC-ICP-MS which proves the formation of dithioarsenate (Figure 2). With one exception (S:As 1), the species sum up to 100±5%, which is the typical error of this kind of analysis, suggesting the truth of the references (arsenite and thioarsenite) as real components of the mixtures and that no further components are present in amounts greater 5% (the limit within which speciation can be resolved by ITFA). The larger deviation of the sample with the ration S:As 1 may indicate the presence of an unidentified species (< 10%), but their elucidation fails due to the lack of a respective reference.

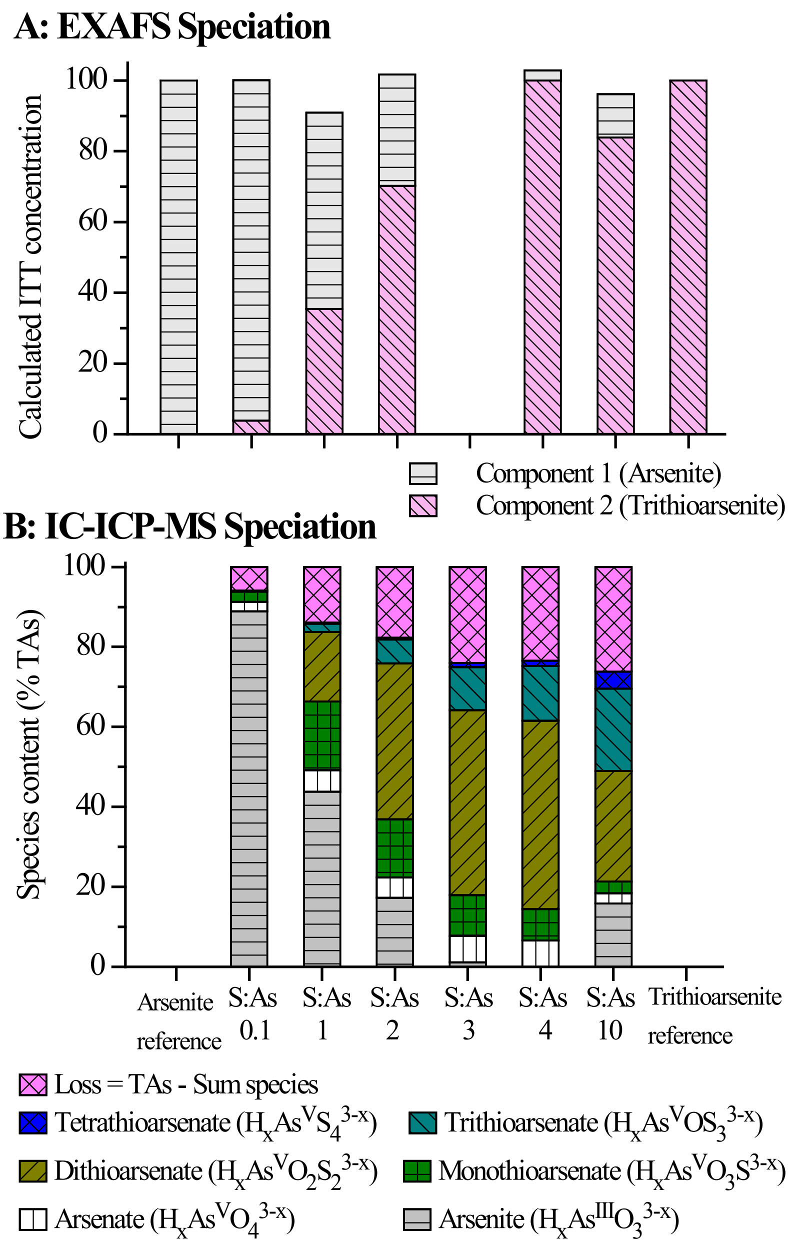

Figure 2: Comparison of a) the arsenic-sulfur species distribution derived from EXAFS spectra by ITT and b) determined by IC-ICP-MS analysis

For the ITT calculation of species concentrations, only the references (trithioarsenite and arsenite) were fixed to 100%. For the calculation of the mix concentrations the normalization to a species sum of 100% was not defined, which thus gives indications for the resolution potential of the species and possible unidentified species by the ITT calculation within the methodical limit of 5%.

XAS speciation determinations by ITFA were supported by structural evaluation of the end-member species arsenite and trithioarsenite, relatively pure in the mixes with S:As 0.1 ($R_{As\text{-}O}$ 1.78 Å, $CN_{As\text{-}O}$ 3.1, $CN_{As\text{-}S}$ 0) and S:As 4, 10 ($R_{As\text{-}S}$ 2.22-2.23 Å, $CN_{As\text{-}S}$ 2.8-3.3, $CN_{As\text{-}O}$ 0), respectively, and their justification with the respective references [40-42, 44, 122, 149]. There was no indication for thioarsenates neither as mixed components in ITFA-examinations nor by relation with thioarsenate reference structures [122] (see study 1, Table 3). However, observations from one previous study [41] on arsenite-sulfide mixes where significantly shorter bond lengths (2.14-2.18 Å) were interpreted as deprotonated As^{III}-S bondings, appear, based on our current results doubtful. Comparing these bond lengths with our results for thioarsenites and thioarsenates, the measured compounds were most likely thioarsenates (formed by oxidation in the arsenite-sulfide mixes), not thioarsenites.

The XANES edge of the model solutions shifted from a position analog arsenite for S:As 0.1 (11868.5 eV) successively towards that of previously determined trithioarsenite (11867.0 eV) for S:As 10 (Figure 1), supporting the mentioned occurrence of As^{III}-S species and indicate a mixed composition for the solutions with a S:As ratio of 1 and 2 as verified by ITFA (Figure 2). With increasing sulfur presence EXAFS fitting showed the consistent decrease in the As-O coordination and increasing importance of As^{III}-S bonds (2.22-2.23 Å, Table 3, Figure 1). Appearance of As-O and As-S coordination in the mixes S:As 1 and 2 could be an indication for monothioarsenite ($CN_{As\text{-}O}$ 2.8/ $CN_{As\text{-}S}$ of 0.9) and dithioarsenite ($CN_{As\text{-}O}$ 1.0/$CN_{As\text{-}S}$ 2.4), respectively, despite even lower bond distances compared to typical As^{III}-O bonds. However, for both species no reference spectra exist and it is uncertain if they could be discriminated as separate spectra in mixtures.

Overall the XAS findings for arsenite-sulfide mixes with arsenite predominance at low S:As ratios and formation of monomeric thioarsenite with increasing sulfur content are assumed to depict the "true" speciation in the mixes and generally agree with those of prior studies [40, 41]. By using cryo-techniques redox-transformations could in contrast to one previous study [41] be effectively prevented (the arsenic oxidation state is undeniably +3), which previously required an elaborately designed nitrogen-purged flow-cell for XAS [40].

In contrast to other studies comparing XAS and IC-ICP-MS and proposing co-elution of thioarsenites and thioarsenates [40], As-S speciation analyses here were performed on identical solutions. Comparably a predominance of arsenite at S:As ratios of 0.1 was found for both methods, but in contrast to the trithioarsenite predominance in XAS, the formation of dithioarsenate as predominant species besides monothioarsenate at S:As ratios of 1 and trithioarsenate at S:As ratios of 10 was found by ion chromatography (Figure 2). Thus co-elution can definitely be excluded and support prior studies [17, 39]. However, during chromatographic analyses some unusual findings have been made. First, a discrepancy between the sum of the arsenic species and the initial arsenite concentration ("loss") was found and increases with increasing sulfide concentrations from 6% (S:As of 0.1) to 26% (S:As of 10), either due to an unidentified species or formation of polymeric/colloidal species. Furthermore, a peak splitting for arsenite was observed, not only as a simple matrix effect due to the high concentrations used, but depending on total arsenite and sulfide concentrations, as well as on the S:As and the SH^-:OH^- ratios. Since the identity of the peaks is not clarified yet, both peaks were interpreted as arsenite.

The continuous decrease of arsenite in all solutions up to a S:As ratio of 4 and its re-appearance in the solution with the highest sulfide excess (S:As 10) does not seem to be an analytical artifact, since re-analyzes and ITT calculations show a similar pattern (Figure 2). For formation of trithioarsenite ratios exceeding the S:As stoichiometry of 3 are required, beyond that further reactions are supposed to occur either preventing complete reaction of arsenite with sulfide, or forming new arsenite. As potential mechanism formation of tetrathioarsenate is discussed, by complexation of trithioarsenite with elemental sulfur donated from long-chain polysulfides in sulfide rich systems [150, 151]. Due to the pH-dependency of tetrathioarsenate a partial conversion to trithioarsenate and arsenite can be expected for IC analyses [48]. However, ITT calculations and EXAFS spectra did not reveal any indications for the presence of tri- or tetrathioarsenate.

Overall, the XAS-determined "true" fraction of trithioarsenite seems to correspond to the sum of thioarsenates and the "lost" arsenic (with exception of S:As 1) in the IC-ICP-MS analyses. Assuming trithioarsenite was the original species in solution, oxidation to thioarsenates and a lack of retention capacity on or incomplete elution from the column seem to be handicaps when analyzing samples by IC-ICP-MS.

4.2.2 Thioarsenites as necessary intermediates for thioarsenate formation: A function of redox- and OH^--instability

The controversial observations of the determination of As^{III}-S species by XAS vs. As^{V}-S species by IC-ICP-MS emphasized the extreme liability of thioarsenites towards changing ambient conditions. By analyzing the respective solutions with an HPLC pump inside the glovebox and thus eliminating any oxidation potential, arsenite was determined as predominant species, while the share of thioarsenates was less than 1% (Figure 3). The disappearance of thioarsenates proves that even though it was considered unlikely [35] traces of oxygen can quantitatively oxidize initially formed thioarsenites during standard ion chromatography even when using oxygen-free eluents. Exposing the sample vials to ambient air before analyzing under N_2, the arsenite concentration decreased exponentially by a first-order rate ($k = 0.32\ h^{-1}$ open vials, $0.17\ h^{-1}$ IC-caped vials), while di-, tri- and monothioarsenate concentrations increased. Even kept inside the oxygen-free glovebox, thioarsenites were only stable up to 24 hours then converting in a similar way by oxidation as shown. The rapid transformation of thioarsenites to thioarsenates under oxic and anoxic conditions was also confirmed by XAS analysis, showing a XANES edge shift towards As^{V}-S species (≈ 2.5 eV, Figure 1) accompanied by decreasing bond distances typical for thioarsenates (Table 3). Based on the coordination ($CN_{As\text{-}S}$ 2.8-2.9, $CN_{As\text{-}O}$ 1.7-1.8) formation of trithioarsenate can be suggested or a mixture of several thioarsenate species.

As previously mentioned differences between XAS and IC beside oxygen exposure are sample dilution and the highly alkaline eluent, causing a decrease of the $SH^-:OH^-$ ratio in the samples for chromatography. Due to OH^- excess thioarsenites are assumed to become instable and transform to arsenite by competitive OH^- versus SH^- exchange and dissociation [39].

In experiments with diluted samples (S:As 10) with arsenic concentrations of 10 mM ($SH^-:OH^-$ 5) to 100 µM ($SH^-:OH^-$ 0.2) at a stable (alkaline) pH, arsenite increased from 16 to 80%, while di- and trithioarsenate - predominant at high concentrations - decreased to less than 1% of total arsenic accompanied by a decrease in the loss from 26 to 18%, respectively. Due to the analytical artifact that thioarsenites rapidly transform to thioarsenates upon air exposure, but not arsenite, speciation results obtained by IC-ICP-MS allow conclusions regarding thioarsenite stability. Thus, the lower the total arsenic and sulfide concentrations are (at the same pH) the less arsenite reacts with sulfide (competitive dissociation) to form thioarsenites, appearing as decreasing shares of thioarsenates in the IC chromatograms. Following it can be concluded that a) thioarsenites cannot form or are at least not stable in the presence of excess of OH^-, b) thioarsenates cannot form as the necessary intermediates (thioarsenites) are missing, and c) arsenite remains the only species detectable in solution.

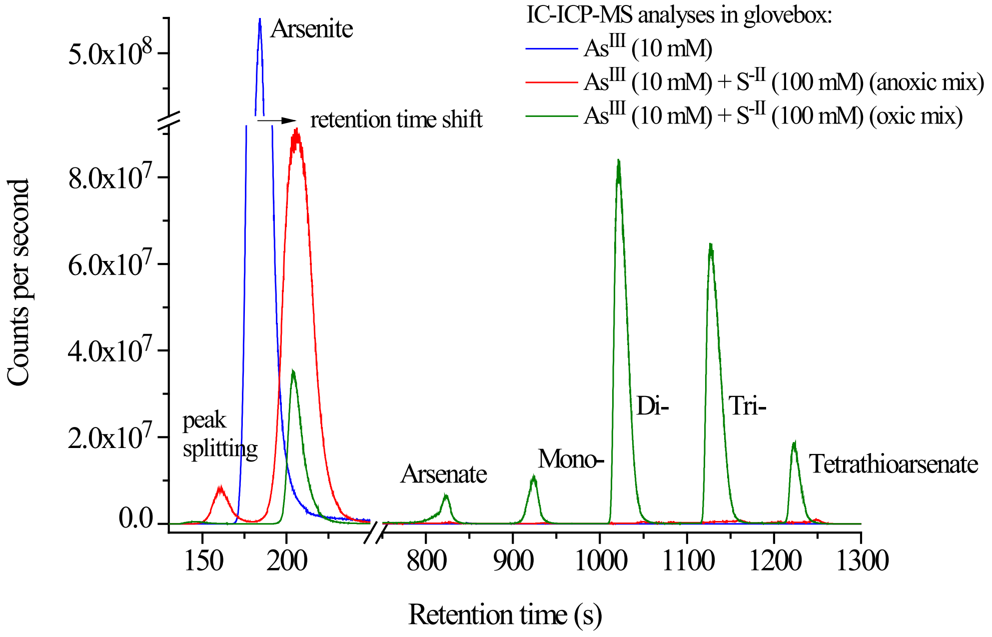

Figure 3: Chromatogram of 10 mM arsenite (As^{III}) and 100 mM sulfide (S^{-II}) solution prepared inside the glovebox and analyzed with an IC outside the glovebox using nitrogen-purged eluents yielding thioarsenates by oxidation (green line) in comparison to an identical sample prepared and analyzed inside the glovebox where thioarsenites are transformed to arsenite (red line). Comparison to a 10 mM pure arsenite solution shows a retention time shift for arsenite (blue line).

Variation of the pH-value also changes the SH^-:OH^- ratio (S:As 10) and showed comparative results with mainly thioarsenate formation between pH 6 and 11 (as a product of thioarsenite intermediates oxidation). At alkaline conditions and acidic conditions thioarsenite formation is prevented by competitive dissociation and thioarsenite transformation prior precipitation as As-S phase (study 1), respectively. Thus only arsenite (or a loss in total arsenic) is observed during IC-ICP-MS. Within 1 week under anoxic conditions speciation in the samples changed towards increasing (tri)thioarsenate formation. Especially for pH 11 (SH^-:OH^- 0.8) the time-depending thioarsenate formation was shown, which was initially hampered due the slow reaction of arsenite and sulfide through electrostatic repulsion at alkaline pH but forced with time due to deprotonation reactions.

Summarizing, it could be stated, that in anoxic arsenite solutions with excess sulfide thioarsenites (trithioarsenite) are formed as the predominant species (Table 4) as also observed for conversion of tetrathioarsenate at acidic conditions (study 1). The trivalent As-S species are fairly unstable even under anaerobic conditions and extremely sensitive towards oxidation. Contact with ambient air e.g. through open or even cap-sealed IC vials, during injection into the sixport valve or contact with non-purged eluents leads to quantitative transformation to thioarsenates within minutes. This artifact can be exploited to make thioarsenites detectable by ion chromatography. However, contrary to thioarsenates [48, 122] thioarsenites are sensitive towards the ratio SH^-:OH^-, usually caused by sample dilution, pH-buffering, and elution with highly alkaline eluents. Thus formation of thioarsenites is hampered under alkaline conditions and consequently no thioarsenates formed through oxidation. Under acidic conditions thioarsenite transformation and As-S precipitation opposes to thioarsenite presence, determined by IC as a loss and arsenite.

Table 4: Original arsenic species formed under anaerobic conditions from arsenite-sulfide solutions and the analysis of artifacts (marked in red) due to the influence of excess OH^- or oxygen under anaerobic or aerobic conditions dependent on the SH^-:OH^- ratio

SH^-:OH^- ratio	Species formed under anoxic conditions	Species analyzed by chromatography under anoxic conditions	Species analyzed by chromatography under oxic conditions
$SH^- > OH^-$	thioarsenites	arsenite (artifact: transformation of thioarsenites to arsenite due to excess of OH^- by elution at pH 13)	thioarsenates (artifact: oxidation of thioarsenites before alkaline transformation to arsenite; thioarsenates are stable at excess OH^-)
$SH^- = OH^-$	initially arsenite, after some days thioarsenites	arsenite (initially true speciation, later artifact)	initially arsenite (true speciation) then thioarsenates (artifact)
$SH^- < OH^-$	arsenite (thioarsenites are instable due to excess of OH^-)	arsenite	arsenite (true speciation, even though there is oxygen, there is no formation of thioarsenates without initial formation of thioarsenites)

The reasons for not being able to detect thioarsenites by IC-ICP-MS even under anoxic conditions are thus yielded their instability or prevented formation by the highly alkaline eluent and/or sample dilution. Overall, since oxidation of thioarsenites is extremely fast, thioarsenates determined in natural spring and geothermal waters [16] by standard IC-ICP-MS represent most likely the true natural composition. Contrary for anoxic systems there is an urgent need to develop methods capable for detecting thioarsenites.

4.3 Natural occurrence and transformation patterns of trithioarsenate (study 3)

Thioarsenates have previously been shown to be important species in the geothermal waters of Yellowstone National Park [16]. If assuming that arsenite and sulfide are released from host rocks in the inner of the hot springs based on the current findings (study 2) [121] possibly thioarsenites are formed as initial species under exclusively anoxic conditions. By rising of these waters and due to the great turbulence where contact with oxygen is unavoidable thioarsenites oxidize quickly to thioarsenates. Consequently thioarsenites are only ephemeral intermediates restricted to the anoxic regimes in the source. Thioarsenates determined in these geothermal waters (as not the anoxic innermost parts were sampled) are thus assumed to be the true natural species - a product of in-situ thioarsenite-oxidation rather than induced by IC-ICP-MS analyses. However, study 3 focuses on alkaline hot springs, as there trithioarsenate, the analytically most challenging species [48], is predominant among the thioarsenates [16].

The monitored, alkaline (pH 7.7 to 9.6) geothermal features from Gibbon and Lower Geyser Basin with source temperatures of more than 90 °C contained total arsenic in concentrations from 11.5 to 33.3 µM and sulfide at the source in a range of 90.6 to 128 µM. Thioarsenates were the predominant arsenic species in the sources (60 to 89%) except for Ojo Caliente with only 43-44% thioarsenates beside arsenite. However, trithioarsenate was the dominant As-S species within the thioarsenates.

In the drainage channels the species undergo conversion by abiotic and biotic processes, e.g. mediated by temperature (temperature drop to 25-64 °C) and increasing redox-potential/oxygen saturation, which can reach up to 64-100%. For trithioarsenate conversion two seemingly different transformation patterns were observed at the sampled drainage channels:

1. Conversion of trithioarsenate to arsenite without substantial changes in the concentrations of arsenate and mono- or dithioarsenate and a further oxidation of arsenite to arsenate, only as thioarsenate concentrations dropped below 10% of total arsenic (Ojo Caliente, Flat Cone, unnamed geyser LG09).

2. Conversion of tetra- and trithioarsenate via mono- and dithioarsenate to arsenate and arsenite (unnamed geysers LG03 and LG04, Mound Spring, hot spring in Gibbon Geyser Basin).

The first transformation pattern resembles the laboratory findings of trithioarsenate purging with air. In these experiments trithioarsenate conversion to arsenite followed a first-order rate with $k \approx 0.004\ \text{min}^{-1}$ with conversion of sulfide to thiosulfate and finally reaching a steady state between trithioarsenate, arsenite, and thiosulfate after 3 hours. A further oxidation of thiosulfate to sulfate or arsenite to arsenate was not observed.

In contrast to the laboratory experiments, naturally trithioarsenate is completely converted to arsenite in the drainage channel and the rate constant $1.9\ \text{min}^{-1}$ is about 500 times higher than in the laboratory ($k = 0.004\ \text{min}^{-1}$). This could indicate microbial catalysis, as it is comparable to rate constants reported for microbially mediated arsenite oxidation (1.2 min^{-1} [53], 4-5 min^{-1} [49]). But also temperature can mediate trithioarsenate conversion (still 84 °C at 22 m), as observed in the laboratory experiments where trithioarsenate converted by 50% to arsenite within 2 hours at 80 °C, without formation of lower SH-substituted thioarsenates. However, no steady state is reached in the natural system, but a conversion of arsenite to arsenate as trithioarsenate reached < 10%.

In the second transformation pattern, successive ligand exchange is the predominant transformation mechanism with finally simultaneous increases for arsenate and arsenite. Under laboratory conditions this pattern was abiotically only reproducible by using a strong oxidant ($H_2O_2 > 2 \times 10^{-6}$ M), while lower H_2O_2-concentrations yielded conversions respective to air purging. Abiotically trithioarsenate dissociated to di- and subsequently to monothioarsenate and arsenate, while the reduced sulfur from thioarsenate dissociation oxidized to thiosulfate and further to sulfate.

However, to explain the arsenite oxidation following thioarsenate disappearance (pattern 1) and the characteristic contemporaneous increase of arsenate and arsenite (pattern 2) as well as the rapid transformation rate microbial catalyzed processes have to be considered. Following phylogenetic analyses *Thermocrinis* spp. (≥ 97% sequence identity *Thermocrinis ruber*) were identified as major species in the investigated springs with an upper temperature limit of approx. 84 °C. The predominance of *Thermocrinis* spp. in the channels Ojo Caliente and unnamed geyser (LG03) coincides with the onset of significant arsenate production and seems to be a key factor in understanding the two different trithioarsenate transformation patterns in the springs.

At Ojo Caliente (pattern 1) hot spring the relatively low temperature gradient preserves temperatures > 84 °C for the first 25 m downstream of the source, and the dominant mechanism is transformation of trithioarsenate to arsenite. *Thermocrinis* spp. filaments become visible approx. 22 m from the source, where di- and trithioarsenate concentrations have already decreased to 2 µM or 14% of total arsenic and arsenite is predominant arsenic species. We thus observe two separate, consecutive reactions: First, trithioarsenate transformation to arsenite - abiotic or potentially triggered by an unknown microorganism - and second, arsenite oxidation to arsenate, which coincides with the occurrence of *Thermocrinis* spp..

The pattern observed at the geyser (LG03, pattern 2) is more complex. Its outflow cools quickly after discharge from the source with a temperature drop < 84 °C after 5 m from the source. *Thermocrinis*-like organisms are again observed coincident with the significant arsenate production, observed at approx. 7 m from the source. Di-, tri-, and tetrathioarsenates constitute the predominant arsenic species (55% of total arsenic, 13.8 µM) at this point. Thus, the two reactions (trithioarsenate transformation to arsenite and arsenite oxidation to arsenate) that occur consecutively at Ojo Caliente, happen contemporaneously at the geyser LG03. The fact that arsenite concentrations continue to increase downstream confirm that direct transformation of thioarsenates to arsenate is a minor reaction, if at all. Most of the thioarsenates are still transformed to arsenite prior to further oxidation to arsenate. The role of mono- and dithioarsenate is unclear at the moment.

In contrast to previous observations at an acidic hot spring [152] microbial arsenite oxidation was not inhibited by high sulfide concentrations (28-91 µM). Support was given to our observations by a prior lab study where sulfide and potentially also thioarsenate-bound sulfur triggered the growth of sulfur-oxidizers which catalyzed the transformation of arsenite and thioarsenates to arsenate in alkaline waters [36] and might also be considered for these geothermal waters.

In summary, trithioarsenate conversion to arsenite under mildly reducing conditions in geothermal drainages can be compared to abiotic reactions as observed in the laboratory. However, in the natural environment the reaction proceeds until all trithioarsenate is converted and rate constants are about 500 times higher than under abiotic conditions, either due to higher temperatures or microbial catalysis. A direct conversion of thioarsenates to arsenate, abiotically catalyzed by strong oxidants, was not found under natural condition. On the contrary arsenate seemed to form exclusively from arsenite oxidized by microorganisms. Since prior studies focused on arsenite and arsenate transformation extensive investigations are necessary to evaluate type and metabolism of microorganisms potentially transforming thioarsenates to arsenite (or arsenate). However, it could be shown that thioarsenates and their microbially mediated transformation to arsenite or arsenate must be considered when investigating arsenic redox processes in sulfidic environments.

4.4 Thioarsenate formation during oxidative dissolution of arsenopyrite and orpiment (study 4)

The previous study (study 3) confirmed the importance of thioarsenates in certain natural systems as previously reported [15-17, 36], but their formation and release into natural systems is not entirely understood. Based on the latest results (study 2) it could be shown, that thioarsenites are necessary intermediates for formation of thioarsenates from arsenide-sulfide solutions in the presence of oxygen [121]. Under natural conditions an important mobilization mechanism for arsenic is mineral dissolution, which comprise to a large extent arsenic-sulfides [6]. Since only little information exists on the role and conditions of thioarsenate formation upon As-S mineral leaching, batch experiments with the most abundant As-S minerals, orpiment and arsenopyrite, were performed under varying conditions with regard to pH and kinetics, focusing on matrix solution, redox-potential and the effect of reactive sulfur for leaching in Fe-As-S systems.

In line with prior knowledge arsenopyrite showed a higher leaching at acidic and alkaline pH compared to the low leaching at near neutral conditions (Figure 4). In contrast orpiment dissolution increased with increasing pH, yielding the 10-100 fold arsenic release at pH > 7 compared to arsenopyrite [13, 63]. No thioarsenate formation was observed for leaching of both sulfides at acidic conditions, in accordance with the known instability of As-S species at low pH [48, 121, 122]. However, at highly alkaline conditions thioarsenates contributed up to 43% to total arsenic speciation (Figure 4).

Especially the occurrence of dissolved thioarsenates in arsenic-sulfur-iron systems is not trivial as strong competition exists between the formation of aqueous As-S species or arsenic-iron complexes and the formation of iron-sulfides or ironhydroxides which could precipitate and sorb arsenic [87, 153-155]. However, speciation analyses showed that orpiment dissolved into approximately equal shares of mono-, di-, and trithioarsenate, while only monothioarsenate was formed upon arsenopyrite leaching (Figure 4). For orpiment already at neutral conditions thioarsenates were formed (50%) with a predominance of the higher SH^--substituted trithioarsenate (31%).

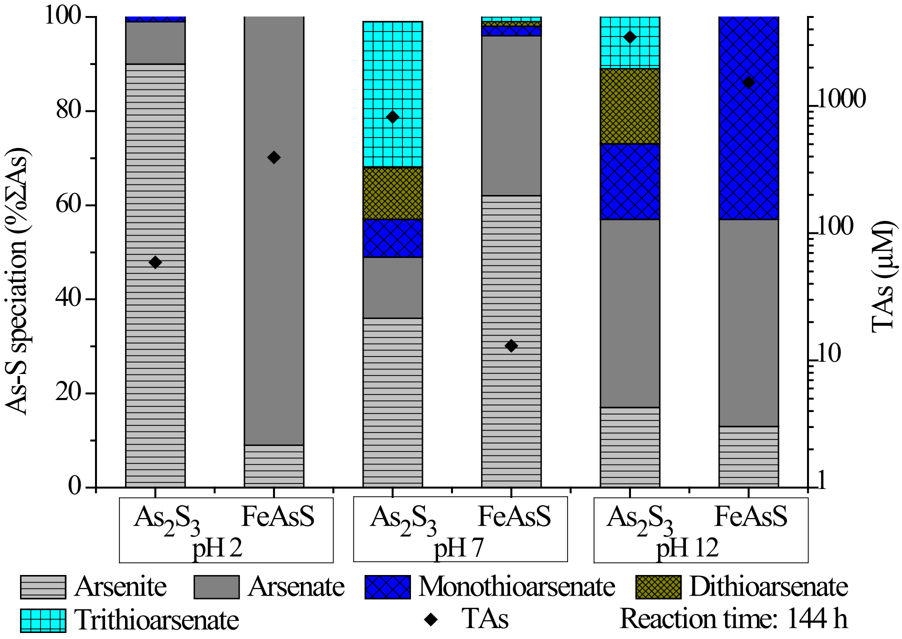

Figure 4: Speciation and total arsenic concentrations for 144 h-open system leaching of arsenopyrite ($FeAsS_{HA}$) and orpiment (As_2S_3)

While at acidic conditions precipitation of arsenic-sulfides, instability of thioarsenic complexes, and/or release of oxidized sulfur and arsenic prevent thioarsenate formation, different leaching mechanisms cause the observed speciation differences between arsenopyrite and orpiment at neutral and alkaline conditions. Thioarsenate formation by orpiment leaching occurs via recombination of sulfide and arsenite to and/or direct release of thioarsenites [39, 42, 56, 58, 64], transforming to thioarsenates under oxic conditions (study 3, [121]). The As-S speciation pattern is quite comparable with that of sulfide-arsenite mixes in study 2 (Appendix B), were thioarsenate distribution was shown to be highly dependent on the S:As and SH^-:OH^- ratio with greatest (tri)thioarsenate formation under SH^- excess and neutral pH and the conversion to arsenite, arsenate, and lower SH-substituted thioarsenates by increasing pH (lowering SH^-:OH^-). This supports to the initial release/formation of thioarsenites from orpiment and their rapid oxidation within leaching process. In case of arsenopyrite physisorption of OH^- is suggested as formation mechanism for thioarsenates. Formation via thioarsenite oxidation is excluded, by the fact that OH^--excess compared to sulfur at pH 13 (OH^- 100 mM vs. 2.4 mM total sulfur) would result in transformation of thioarsenites or even prevent their formation as discussed in study 3 [121]. Physisorption [83] comprises sorption and transposition of OH^- to either iron or arsenic sites accompanied by electron transfer, followed by the detachment of As-OH-S complexes and FeOOH from the surface. The As-OH-S complexes further form thioarsenates, arsenate by thioarsenate decomposition, and oxidized sulfur species. At neutral conditions possibly iron-arsenic oxide complexation is kinetically favored [67], which become unstable with increasing pH [156, 157], where the physisorption mechanism prevails and forms thioarsenates, thiosulfate, and ironhydroxide. Iron(hydr)oxides, appearing as orange precipitates at pH 12-13 in the current work as reported previously [11, 83, 87, 155], provide potential sorption sites for arsenic and were supposed to minimize dissolution in the long-term view [67]. The specific sorption behavior of monothioarsenate the major species under conditions when iron(hydr)oxides as possible re-sorption sites are formed, will be discussed briefly in the next chapter compared to the arsenite and arsenate.

Conducting detailed investigations of arsenopyrite dissolution it could be confirmed that the leaching is strongly decreased at anoxic conditions dissolution [67, 68, 94], especially at anoxic highly alkaline conditions (decrease by a factor of 2 (pH 7) and 7 (pH 12); Figure 5). The substantial decrease corresponds to previous observations that oxygen is the main oxidation agent at high pH, while it is ferric iron at low pH [70]. The share of thioarsenates increased under anoxic conditions at pH 12, possibly due to the instability of thioarsenate under oxic conditions [16] or an indication for additional formation by arsenite-sulfide recombination in solution due to greater release of reduced sulfur species [121]. However, by addition of (poly)sulfides leaching could be increased at least for neutral conditions by approximately a factor of 4 at the highest applied concentrations of 167(300) µM (poly)sulfide, with formation of minor shares of monothioarsenates. Sulfide addition did not show an obvious effect for leaching at pH 12, only a slightly greater share of thioarsenates but less total dissolution. Also the addition of thiosulfate, a industrial lixiviate for gold leaching, did not change speciation or total arsenic release for neutral and alkaline oxic leaching.

The evaluation of a possible acceleration of thioarsenate formation by increasing the ionic strength of the leaching solution did only show a positive effect on total arsenic release, which increased by a factor of ≈ 200 as $NaHCO_3$ concentration was increased from 4 to 800 mM (pH 8-9), rather than for speciation changes. Thereby the total arsenic release at > 400 mM $NaHCO_3$ was comparable to NaOH addition of 40-800 mM at pH 12-13, which showed substantial thioarsenate formation increasing from 13 to 40% with finally excusive As^V species (arsenate + thioarsenate) presence. Thus thioarsenate formation is more the result of pH or OH^--presence than the product of ionic strength variation. However, the increased dissolution for the carbonate solution can likely be due to arsenic-carbonate or iron-carbonate complexation [76-79, 81, 158].

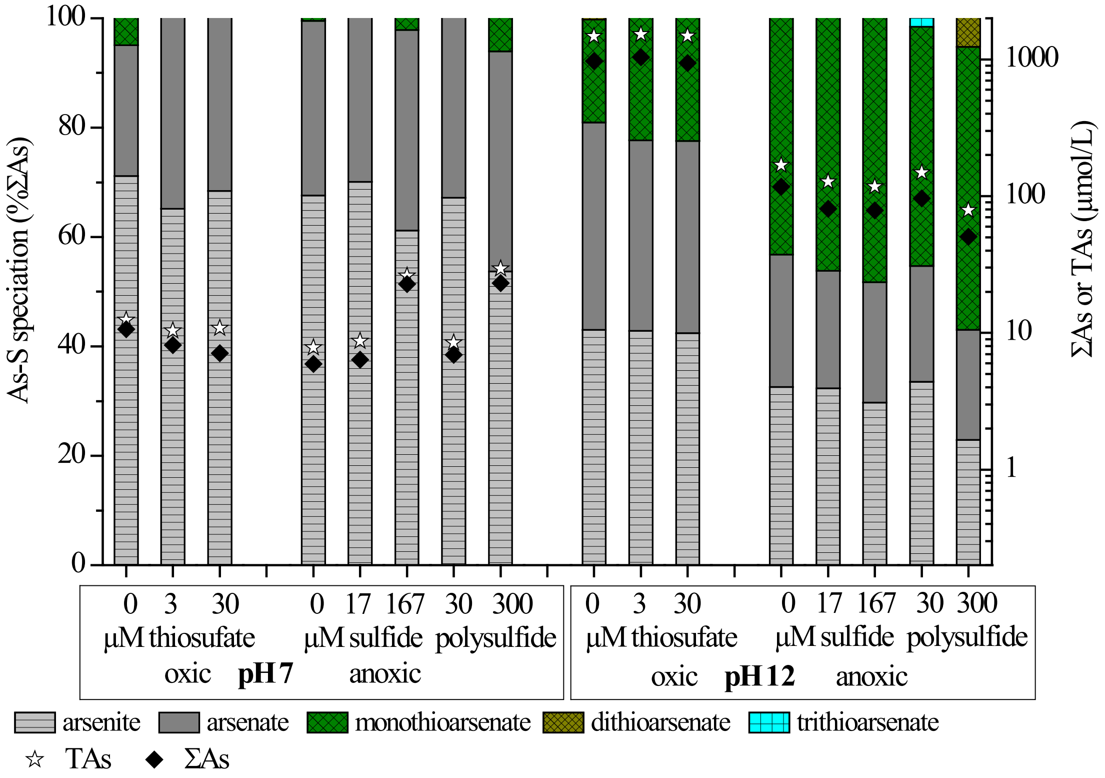

Figure 5: Arsenic speciation in arsenopyrite leachates ($FeAsS_{HA}$) depending on redox-state and solution composition

Summarizing, it could be shown that thioarsenates, even the higher sulfur-substituted trithioarsenate, are potential species released through dissolution of arsenopyrite and orpiment at (highly) alkaline and neutral pH for orpiment, conditions existent in calcite-treated tailings or industrial highly alkaline leaching. Regarding the toxicity of the released species, at acidic and alkaline conditions As^V species predominate the arsenopyrite leachates with a lower toxicity (arsenite > arsenate > thioarsenate [59]), while for pH 7 and acidic conditions for As_2S_3 the more toxic arsenite prevails in the leachates. Since the formation of ironhydroxides is especially incisive at basic to high alkaline conditions in Fe-As-S systems, the exposition of FeAsS to acidic conditions, e.g. acid mine drainage or acid-based ore recovery, provides the greater risk for environmental health, while at higher pH's sorption on ironhydroxides and formation of surface coatings will slow down arsenic release in long term view. However, while for arsenopyrite calcite-treating of tailings and neutralization can reduce arsenic release, for orpiment this would act counterproductively as the release of arsenic at pH > 7 is increased by several magnitudes and arsenic mobility only restricted at acidic conditions.

4.5 Immobilization of thioarsenates by sorption on ironhydroxides (study 4)

Ironhydroxides were observed to form during high alkaline arsenopyrite leaching, but are especially naturally important as trace metal immobilization sites [159]. Generally, it was reported that arsenate sorbs preferentially at pH 5-6 (sorption maxima at pH 4) on goethite and arsenite at higher pH with sorption maxima between pH 8-9 [96, 97]. Thioarsenate sorption was not investigated so far and thus preliminary results are presented in this PhD thesis.

The batch experiments with goethite showed that sorption efficacy (Figure 6) and kinetics are lower for monothioarsenate than for arsenate and arsenite. The initial arsenite sorption reached equilibrium conditions already after 1 hour as observed previously [97, 160]. Arsenate and monothioarsenate on the other hand showed slower kinetics with equilibration after 1 and 3 days, respectively. Maximal sorption capacities were determined with 11, 23, and 26 µmol As/g goethite for monothioarsenate (pH 12), arsenate (pH 9), and arsenite (pH 10) respectively.

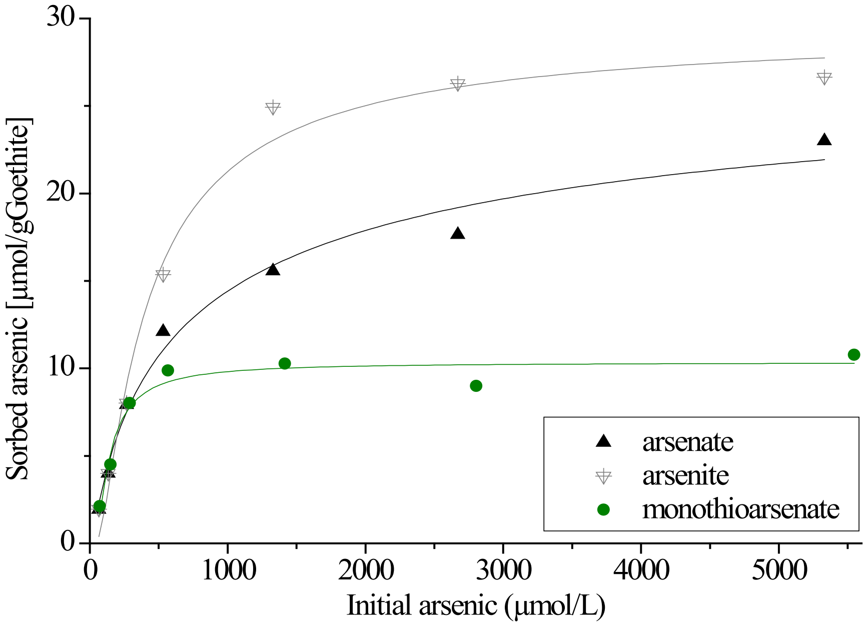

Figure 6: Sorption isotherms of arsenate, arsenite, and monothioarsenate on α-Goethite

The reason for the lower sorption efficacy and kinetics of monothioarsenate compared to arsenate might be due to the larger size of SH^--group compared to OH^- which hamper the formation of surface complexes. For the higher sulfur-substituted thioarsenates (di-, tri- and tetrathioarsenate) thus an even lower efficacy would be assumed.

Overall, monothioarsenate sorption was only half of that of arsenite and arsenate and thus for the thioarsenates a higher mobility and lower retention by ironhydroxides can be proposed. However, to what extent sorption characteristics are comparable with arsenate, what influence the SH^--groups have on sorption, and if desorption follows the same trend, has to be clarified under consideration of structural studies and investigating the complete series of thioarsenates.

Regarding arsenic-sulfur-iron systems the release of thioarsenates additionally provides to the present knowledge a higher environmental risk compared to arsenite and arsenate not through toxicity, which is lower, but due to a higher mobility and lower sorption efficacy.

4.6 Importance of thioarsenates in iron-rich natural waters and possible sample preservation strategies (study 5)

Although it was disputed for a long time that thioarsenates can occur in iron-rich systems [38] since interaction of sulfide and iron was thought to yield Fe-S complexes or precipitates, it could be shown that thioarsenates can occur in iron-rich systems (1.3 to 66 mg/L) with up to 17% mono- and dithioarsenate determined in mineral springs (pH 5.5 to 6.1) of Czech Republic as a first field study site (Table 5). Samples preservation with HNO_3 emerged as the best way for receiving total arsenic concentrations unaffected by precipitation of either iron(hydr)oxides or arsenic-sulfides, while the relative arsenic recovery decreased between the other tested approaches in the general order HCl > EDTA+flash-freezing ≫ flash-freezing. Although this is in sharp contrast to the excellent results obtained previously in hot springs in Yellowstone National Park [16], it has to be noted that those waters did not contain significant iron concentrations (median 0.06 mg/L). Thioarsenates were detected in samples preserved by EDTA combined with cryo-preservation (= flash-freezing in dry ice and storage at -18 °C) or HCl, but the results showed such a high variability that the "true" speciation cannot be determined. Thus arsenic stabilization methods have to be improved for systems containing both iron and sulfide, which was investigated with synthetic thioarsenate solutions.

Table 5: Summary of chemical parameters for thioarsenate and iron containing mineral springs

Springs	**Frantisek**			**Novy**			**Natalie**			**Stepanka**			**Solni**		
temp [°C]	14.1			10.4			10.0			8.0			10.8		
conductivity [mS/cm]	12.03			2.96			2.19			2.39			4.15		
pH	5.92			5.84			5.61			5.55			6.05		
S^{-II} [mg/L]	0.07			0.30			0.43			0.53			0.11		
Fe(tot) [mg/L]	1.32			4.8			13.8			20.8			7		
Fe^{II}/Fe(tot)	56			23			90			64			74		
	As species preservation*														
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
arsenite [%]	59	76	82	84	68	91	93	52	88	90	66	88	82	70	95
arsenate [%]	35	20	13	14	23			31			24		16	24	1
monothioarsenate [%]	2	2	5	2	1	9		2	12		3	12	2	1	4
dithioarsenate [%]	3	3			8		7	15		10	7			4	

[*] Preservation strategies: A flash-freezing, B EDTA, C HCl

In contrast to arsenite and arsenate which can be effectively stabilized by filtering and acidification against redox-transformations [107], thioarsenates require flash-freezing, since these species are highly pH-sensitive and will precipitate as As_2S_3 [16, 48, 122]. Cryo-preservation, i.e. flash-freezing and cryo-storage, has been shown to preserve thioarsenate speciation in iron-free solutions for 21 days, best by avoiding oxygen influence with an anoxic or even small gas headspace in the sample vials. Also for arsenite and arsenate this technique provided their stability for at least 45 days independent from the redox conditions. Freezing is thus an alternative to acidification (H_3PO_4, H_2SO_4) which can yield in metal precipitation or photo-oxidation (HNO_3) [107]. Interestingly, high ionic strengths (0.1 M NaOH) or organic solvents (1% EtOH) helped to preserve the thioarsenate speciation such that complete stability could be guaranteed independent from the redox-condition. Thereby the higher ionic strength and/or pH might reduce the activity of thioarsenate ions towards their transformation reactions and ethanol acts weakly reducing towards oxygen, thus preventing its interaction with and oxidation of sulfur-groups as previously observed for methylated arsenic species [161]. However, at low ionic strengths or in the presence of excess redox-sensitive species (such as sulfide) a small headspace and anoxic conditions are required to minimize losses and species conversion during sample cryo-storage.

In the presence of iron, thioarsenates transform quickly, typically into arsenite accompanied by a loss of arsenic between 30% and 75% (Figure 7). Although oxidation of iron and the precipitation of ironhydroxides upon thawing, with co-precipitation and sorption of arsenic was previously described to lead to losses of TAs [111], macroscopic precipitation was not observed during the experiments. As formation of colloids cannot be excluded, the observed decreases in the sum of arsenic could be explained either by colloidal co-adsorption or even iron-arsenic complexation in solution, which remained undetected during IC-ICP-MS analyses.

Sample acidification to keep iron in solution and complexation of iron by EDTA and acidification, to yield maximum sorption efficacy at low pH [116], is not an option for thioarsenate-containing systems, as it leads to precipitation of amorphous arsenic-sulfide phases [16, 34, 37, 48, 122]. As alternative complexation with neutralized EDTA (EDTA at pH 4.5 induced speciation changes by decreasing the pH), in combination with flash-freezing, minimizing the sample gas headspace, and excluding oxygen, has been proven to be the most effective preservation technique available for thioarsenate solutions containing iron, with initial recoveries of 94% of originally 93% mono-, 68% of originally 67% di- and 45% of originally 70% trithioarsenate, and variations in the sum of species of < 10% for mono- and dithioarsenate and approximately 20% for trithioarsenate for an 11-day cryo-storage.

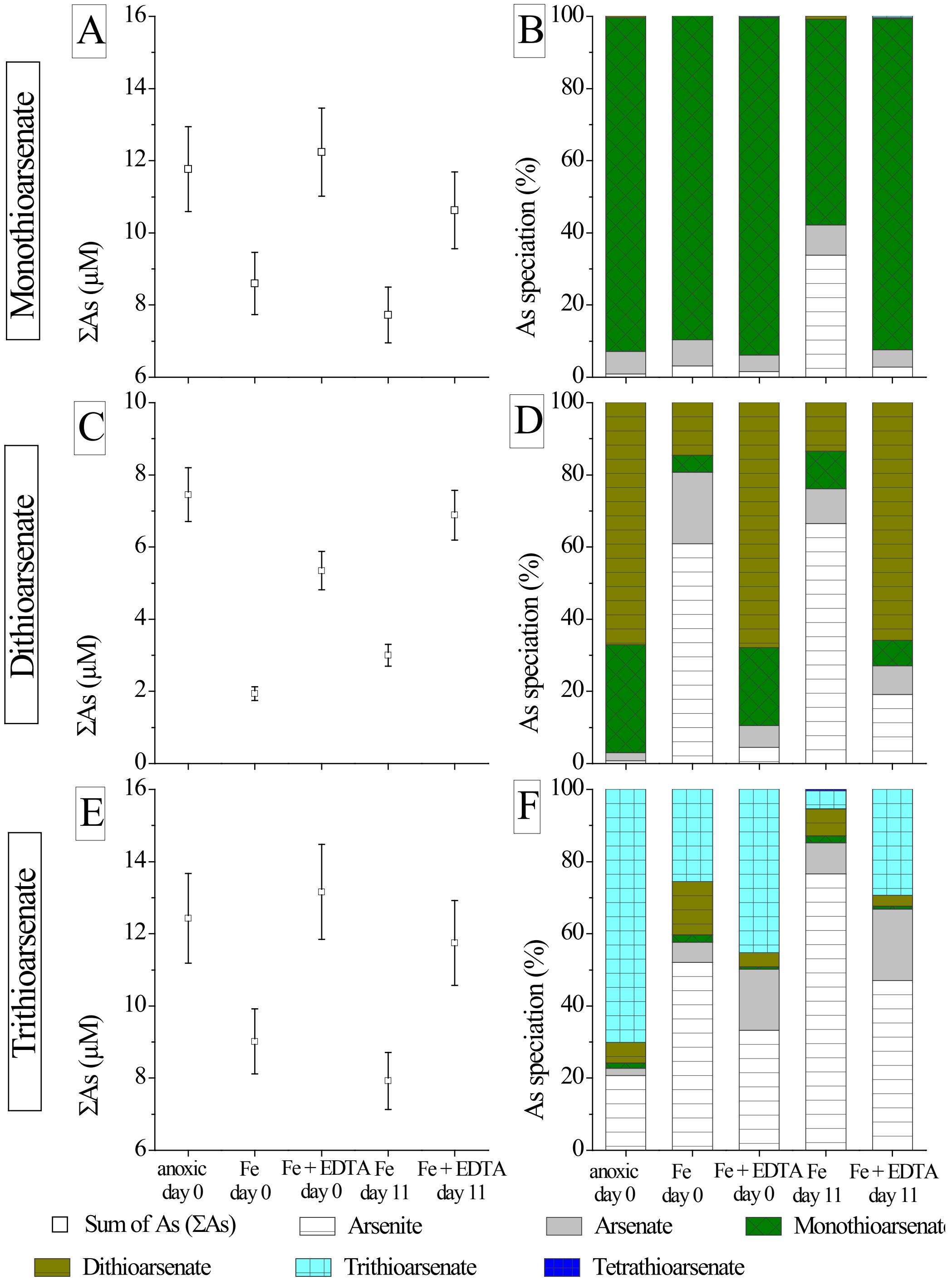

Figure 7: Effect of iron on thioarsenate solutions and their preservation with neutralized EDTA

Summarizing, the study shows the importance of suitable preservation of thioarsenates in iron-rich natural solutions. Both thioarsenates and iron complicate preservation strategies, by instability towards acidification and precipitation upon oxidation due to flash-freezing or neutral pH, respectively. Combination of EDTA-application and flash-freezing is a promising strategy for thioarsenate preservation in iron-rich waters, but requires further development.

5 Conclusion and future perspectives

The environmental relevance of As-S species, comprising the trivalent thioarsenites and the series of pentavalent thioarsenates (mono-, di-, tri., and tretrathioarsenate), has become apparent over the last couple of years [15-17, 38, 42, 59, 109, 122]. Their geochemical nature and behavior under different environmental as well as under different sample storage conditions is still a subject of debate. The general aim of the present PhD thesis was to increase the knowledge about structure and analytical determination, natural occurrence, formation, transformation and stability of As-S species.

Overall, thioarsenites and thioarsenates were both found to occur under certain conditions. Thioarsenites are extremely labile, instable in presence of oxygen and excess OH^- versus SH^-, degrade over time, only occur under anoxic conditions and are necessary intermediates for the formation of thioarsenates. Thioarsenates are more stable and the only species found under (natural) oxic conditions, either from spontaneous thioarsenite oxidation or by release from arsenopyrite by physisorption. Currently, the direct analytical determination of the unstable thioarsenites requires in-situ XAS, able to distinguish them from arsenite, (thio)arsenate, and As^{III}-S phases via oxidation state (XANES) and complex coordination (EXAFS). However, XAS lacks on the requirement of high concentrations (> 5 mM As), sufficiently precise species quantification, and availability of beam time. The greater stability of thioarsenates makes them detectable by IC-ICP-MS. Although they can be determined and distinguished from each other by XAS, under consideration of the mentioned deficiencies, IC-ICP-MS could be assured as routine technique by verification of the aqueous complexes from synthesized thioarsenates. IC-ICP-MS can be used for thioarsenate speciation analyses in the concentration range 0.5 µM to 0.1 mM, magnitudes lower compared to XAS, but also for a indirect thioarsenite determination by using a comparative measurement of their “thioarsenate”-artefacts under oxic and arsenite under anoxic conditions, eventually with adaption to moderate pH. However, also thioarsenate-stability is controlled by ambient temperature, pH-, and redox-conditions in abiotic systems and possibly also mediated by microorganisms in natural systems. Two major processes play a role: successive ligand exchange (in presence of an oxidant or under natural conditions) or direct partial or complete conversion to arsenite (in presence of a strong oxidant or air, or under natural conditions) High temperature, acidification, and Fe^{II} resulted in thioarsenate transformation to substantial amounts of arsenite and precipitates at acidic conditions. Despite the interaction of thioarsenates with iron in synthetic solutions, both species have been shown to co-occur as equilibrium was reached in the synthetic solutions and as proofed for natural spring waters (Czechs Republic) with 17% thioarsenates. However, sample preservation is indispensable to preserve the speciation against redox-transformation and adsorption on precipitated ironhydroxides, even as sorption efficacy has shown to be lower compared to arsenite and arsenate. Cryo-preservation can be recommended for thioarsenates and thioarsenites, although only under strong restriction to oxygen in case of the trivalent As-S species. In the presence of iron the combination of neutralized EDTA with cryo-preservation can be recommended, even though this technique needs further improvement. The main results from the present PhD thesis are summarized in Table 2 and refer to the following key-points:

(I) Thioarsenites vs. thioarsenates in XAS

- differentiation of thioarsenates from one each other, arsenite, and arsenate, and from thioarsenites by XAS (XANES absorption edge position, EXAFS-coordination, by ITFA in mixes of thioarsenates and thioarsenites)
- analytical proof of pH-depending thioarsenate and thioarsenite co-occurrence in anoxic tetrathioarsenate solutions (pH 5-7)
- compilation of thioarsenate, arsenite, arsenate, and trithioarsenite spectra as basic reference dataset for evaluation of mixes and species verification

(II) XAS vs. IC-ICP-MS

- XAS for structural evaluation of thioarsenates/ thioarsenites as solids, solutions (flash-frozen), and mixes → restrictions/unsuitability as routine technique due to availability of beam time, required high concentration (5 mM EXAFS, 0.5 mM XANES), and species quantification
- suitability of IC-ICP-MS as routine analyses for aqueous thioarsenates → restrictions by species transformation due to sample dilution, alkaline eluent, oxidation (analyses outside the glovebox)
- “thioarsenite artefact” = rapid oxidation to thioarsenates, while arsenite remains unmodified → indirect evidence for thioarsenites by comparative analyses under oxic and anoxic conditions

(III) (Trans)formation of thioarsenites

- in anoxic arsenite-sulfide mixes with SH^--surplus, via acidification of thioarsenates (anoxic)
- no formation under excess of OH^-
- necessary intermediates for thioarsenate formation
- transformation: → to thioarsenates over time (anoxic, >24 h), in the presence of oxygen (traces), → to arsenite by OH^- surplus (high alkalinity, dilution), → to As-S precipitates (acidification)

(IV) (Trans)formation and occurrence of thioarsenates

- formation necessarily via oxidation of thioarsenites in arsenite-sulfide solutions (As < SH^-) and upon oxic orpiment dissolution (pH 7 (50%), 12 (43%), tri- > di-, monothioarsente), or directly by physisorption of OH^- upon alkaline arsenopyrite leaching (pH 12, 43% monothioarsenate)
- natural occurrence: as predominant species in geothermal waters (trithioarsenate alkaline hot springs), and up to 17% in iron-rich thermal springs (mono- and dithioarsenate, Czech Republic)
- oxidative transformation of higher substituted thioarsenates: → successive ligand exchange to finally arsenate (oxidants, naturally), → to arsenite by air purging, strong oxidants, heating, oxic acidification (with precipitation and ligand exchange)
- anoxic systems: → transformation to arsenite in the presence of Fe^{II} (anoxic) , → to thioarsenites and precipitation via acidification
- oxic transformation processes observed in natu~~re~~presumably microbial mediated due to higher transformation rates and final arsenite/arsenate formation

(V) Mobility of thioarsenates

- thioarsenates more mobile compared to arsenite and arsenate→ sorption kinetics and efficacy on Goethite in the order arsenite > arsenate > monothioarsenate

(VI) Stabilization of thioarsenates and thioarsenites

- anoxic cryo-preservation for labile thioarsenites
- cryo-preservation with minimizing oxygen influence for thioarsenates

(VII) Dissolution of (Fe)AsS minerals

- orpiment linear dissolution increase, arsenite at acidic conditions, thioarsenate (trithioarsenate) formation at pH 7 and pH 12
- arsenopyrite minimum dissolution at neutral pH, maximum at acidic/alkaline pH, speciation: arsenate and arsenite (pH 2), arsenite (pH 5-7) and arsenate + (mono)thioarsenate pH 9-13
- arsenopyrite leaching restricted under anoxic conditions
- increase of leaching efficacy by (poly)sulfides (neutral, anoxic), ionic strength ($NaHCO_3$), pH (NaOH – limit reached at 400 mM, exclusively As^V-species)
- evaluation for natural systems: orpiment leaching more critical since release of more mobile thioarsenates and higher amounts of total arsenic, alkalinisation of tailing material increases mobility of arsenic for both minerals, acidic conditions only relevant for FeAsS release of arsenate and arsenite, long-term view arsenate due to oxidation

Although the work makes major contributions to understand the geochemistry of As-S species, both for characterization and also to understand their natural cycling more studies and information are necessary. From the present knowledge the following missing facts and recommendations for future investigations can be stated:

A) Thioarsenite/thioarsenate geochemistry

- for evaluation of mixes and verification of certain thioarsenite species→ references for thioarsenites, XAS characteristics and determination of their behavior in (standard) IC-ICP-MS
- further need for thioarsenite references arises for the development of suitable routine techniques to analyze thioarsenites and in environmental relevant concentrations as well as for studies to determine their environmental behavior, i.e. mobility and mobilization, toxicity and stability
- instability of thioarsenates to evaluate role of polysulfides within the transformation process (comparison of anoxic, (hyp)oxic conditions and structural evidence)
- characterization of species released upon anoxic mineral leaching (orpiment, arsenopyrite, enargite → arsenic, sulfur, iron/copper species, redox-, pH-monitoring, cf. mineral dissolution)
- role of trithioarsenate/dithioarsenate upon trithioarsenite oxidation and pH-dependent tetrathioarsenate dissolution with respect to reaction kinetics and oxygen concentration

B) Thioarsenate/thioarsenite stability (in iron-containing systems)

- stability tests of thioarsenates (concentration dependent, as mixes, as As:S solutions) in solutions with strong matrix (NaCl), organic solvents (EtOH, MeOH), injected in N_2-filled septum vials and tests of cool storage vs. flash-freezing
- laboratory studies of thioarsenates (pure/mixes) in the presence of iron (other trace metals, e.g. manganese, copper), with different species (Fe^{II}/Fe^{III}) and concentrations under oxygen exclusion, monitoring of redox-conditions and speciation – tests for stabilization by addition of EDTA (concentration dependent), other iron-chelators (e.g. siderophores or HIDS (Hydroxyiminodisuccinic acid)) → promising methods for tests in the field

- laboratory experiments with iron for As:S mixes – use of comparative oxic/anoxic IC-ICP-MS to determine role of thioarsenites
- investigations of the effect of reactive iron on species of As:S mixes and thioarsenates under oxic, hypoxic, and anoxic conditions
- effect of UV-radiation - laboratory studies with UV chamber and check of possible transformation of thioarsenates to thioarsenite, test of natural waters containing thioarsenates (+ iron, time dependence), exposure to natural light at different altitude (Chile, Yellowstone, time dependence to verify stability during sample handling and packing) → check of toxicity for those UV-applied As-S waters (c.f. *Daphnia* spp. studies)

C) Thioarsenate formation upon sulfidic dissolution of arsenite and thioarsenate retention

- sorption and desorption studies with thioarsenates, As:S mixes under anoxic/oxic conditions with respect to pH, solid:solution ratio, time on synthetic goethite, fresh precipitated FeOOH, iron-sulfide minerals, and mica
- structural characterization of thioarsenate-mineral surface complexes by XAS
- desorption of arsenite on mineral phases (FeOOH, iron-sulfides) with sulfidic solutions – characterization of ambient conditions (pH, redox-potential) and thioarsenic and sulfur species
- investigations to determine the role of microorganisms on desorption of (thio)arsenate and arsenate in sulfidic systems (iron-sulfides) or sulfate solutions (FeOOH)
- sorption studies with natural soils and sediments, e.g. as column experiments

D) Mineral dissolution and As-S complex formation

- verification of thioarsenic species formation mechanism upon mineral dissolution (release of thioarsenites + oxidation for orpiment vs. thioarsenate release by physisorption for arsenopyrite), by structural (XAS) characterization with respect to pH, redox-conditions, and matrix solution ($NaHCO_3$, possibility of carbonate complexes)
- structural determinations of solutions from arsenopyrite leachates and thioarsenate-Fe^{II} solutions to proof the possibility of thioarsenate-iron complexation
- investigation of mineral dissolution of other arsenic-sulfides regarding thioarsenate (oxic)/ thioarsenite (anoxic) formation, e.g. enargite (copper-thioarsenate complexes?)
- formation of As-S complexes in arsenate and sulfate containing solutions (catalyzes by *Desulfotoculum auripigmentum*) or arsenic present in mineral phases
- role of microorganisms on thioarsenate formation during mineral dissolution
- monitoring of (poly)sulfide and trace-metal species (iron, copper), total concentrations, and redox-potential should be emphasized for the experiments beside determination of As-S species

Overall, the topic thioarsenic species and their behavior under natural and laboratory conditions, interactions with mineral phases equally to organisms and other elements, their redox-cycles and toxicity is a wide spread and greatly exciting topic with a broad need of scientific research. I'm proud, that I could contribute to this topic with some basic statements and characterizations of thioarsenates and thioarsenites and hope that some of the stated and recommended problems can be solved in future studies.

II Cumulative publications and manuscripts - Contributions

Study 1: Discrimination of Thioarsenites and Thioarsenates by X-ray Absorption Spectroscopy (published in Analytical Chemistry)

Elke Suess, Andreas C. Scheinost, Benjamin C. Bostick, Broder J. Merkel, Dirk Wallschlaeger, and Britta Planer-Friedrich

E. Suess	40 %	Concept and laboratory work: titration experiments, sample preparation and analyses - X-ray Absorption Spectroscopy (XAS) and IC-ICP-MS (As-S Speciation); Data analyses and spectra fitting/evaluation; Paper work: concept, manuscript editing
A.C. Scheinost	15 %	Laboratory and data evaluation XAS; Paper work: discussion (XAS) and proof-reading
B.C. Bostick, B.J. Merkel	5 %	Paper work: proof-reading
D. Wallschlaeger	10 %	Paper work: discussion (As-S speciation) and proof-reading
B. Planer-Friedrich	30 %	Concept and laboratory work: IC-ICP-MS; Paper work: concept, discussion, and proof-reading

Abstract: Soluble arsenic-sulfur compounds play important roles in the biogeochemistry of arsenic in sulfidic waters but conflicting analytical evidence identifies them as either thioarsenates (= As^{V}-S species) or thioarsenites (= As^{III}-S species). Here, we present the first characterization of thioarsenates (mono-, di-, and tetrathioarsenate) by X-ray absorption spectroscopy and demonstrate that their spectra are distinctly different from those of As^{III}-S species, as well as from arsenite and arsenate. The absorption near edge energy decreases in the order arsenate > thioarsenates > arsenite > As^{III}-S species, and individual thioarsenates differ by 1 eV per sulfur atom. Fitted As^{V}-S and As^{V}-O bond distances in thioarsenates (2.13-2.18 Å and 1.70 Å, respectively) are significantly shorter than the corresponding As^{III}-S and As^{III}-O bond distances in As^{III}-S species (2.24-2.34 Å and 1.78 Å, respectively). Finally, we demonstrate that thioarsenates can be identified by principal component analysis in mixtures containing As^{III}-S species. This capability is used to study the spontaneous reduction of tetrathioarsenate to As^{III}-S species (possibly trithioarsenite) upon acidification from pH 9.5 to 2.8.

Study 2: Arsenic Speciation in Sulfidic Waters: Reconciling Contradictory Spectroscopic and Chromatographic Evidence (published in Analytical Chemistry)

Britta Planer-Friedrich, Elke Suess, Andreas C. Scheinost, Dirk Wallschlaeger

B. Planer-Friedrich	55 %	Concept and laboratory work: Mixes and IC-ICP-MS analyses; Data analyses (IC-ICP-MS); Paper work: concept and manuscript editing
E. Suess	40 %	Laboratory work: Mixes and XAS-analyses; Data analyses and evaluation (IC-ICP-MS / XAS); Paper work: manuscript editing
A.C. Scheinost, D. Wallschlaeger	5 %	Paper work: discussion and proof-reading

Abstract: In recent years, analytical methods have been developed that have demonstrated that soluble As-S species constitute a major fraction of dissolved arsenic in sulfidic waters. However, an intense debate is going on about the exact chemical nature of these compounds, since X-ray absorption spectroscopy (XAS) data generated at higher (mM) concentrations suggest the presence of (oxy)thioarsenites in such waters, while ion chromatographic (IC) and mass spectroscopic data at lower (μM to nM) concentrations indicate the presence of (oxy)-thioarsenates. In this contribution, we connect and explain these two apparently different types of results. We show by XAS that thioarsenites are the primary reaction products of arsenite and sulfide in geochemical model experiments in the complete absence of oxygen. However, thioarsenites are extremely unstable toward oxidation, and convert rapidly into thioarsenates when exposed to atmospheric oxygen, e.g., while waiting for analysis on the chromatographic autosampler. This problem can only be eliminated when the entire chromatographic process is conducted inside a glovebox. We also show that thioarsenites are unstable toward sample dilution, which is commonly employed prior to chromatographic analysis when ultrasensitive detectors like ICP-MS are used. This instability has two main reasons: if pH changes during dilution, then equilibria between individual As-S species rearrange rapidly due to their different stability regions within the pH range, and if pH is kept constant during dilution, then this changes the ratio between OH^- and SH^- in solution, which in turn shifts the underlying speciation equilibria. This problem is avoided by analyzing samples undiluted. Our studies show that thioarsenites appear as thioarsenates in IC analyses if oxygen is not excluded completely and as arsenite if samples are diluted in alkaline anoxic medium. This also points out that thioarsenites are necessary intermediates in the formation of thioarsenates.

Study 3: Oxidative Transformation of Trithioarsenate Along Alkaline Geothermal Drainages – Abiotic versus Microbially Mediated Processes *(published in Geomicrobiology Journal)*

Britta Planer-Friedrich, Jenny C. Fisher, James T. Hollibaugh, Elke Suess, Dirk Wallschlaeger

B. Planer-Friedrich	55 %	Field work and organization: field sampling and on-site parameters; Laboratory work: arsenic-sulfur speciation and total analysis; Data analysis; Paper work: concept, manuscript editing
Jenny C. Fisher	15 %	Laboratory work: microbiology; Paper work: microbiology parts and manuscript proof-reading
E. Suess	15 %	Field sampling and on-site parameters; Laboratory work: arsenic-sulfur speciation; Paper work: Manuscript proof-reading
James T. Hollibaugh, Dirk Wallschlaeger	15 %	Paper work: Discussion and manuscript proof-reading

Abstract: Trithioarsenate is the predominant arsenic species at the source of alkaline, sulfidic geothermal springs in Yellowstone National Park. Kinetic studies along seven drainage channels showed that upon discharge the major initial reaction is rapid transformation to arsenite. When aerating a trithioarsenate solution in the laboratory, 10 to 20% of trithioarsenate dissociates abiotically before reaching a steady state with arsenite and thiosulfate. In the geothermal springs, trithioarsenate is completely converted to arsenite and rate constants of 0.2 to 1.9 min^{-1} are 40 to 500 times higher than in the laboratory, indicating microbial catalysis. Abiotic transformation of trithioarsenate to arsenate requires the presence of a strong oxidizing agent in the laboratory and no evidence was found for direct transformation of thioarsenates to arsenate in the geothermal drainage channels. The simultaneous increase of arsenite and arsenate observed upon trithioarsenate dissociation in some hot springs confirms that the main reaction is thioarsenate transformation to arsenite before microbially catalyzed oxidation to arsenate. In contrast to previous investigations in acidic hot springs, microbially catalyzed arsenate production in near-neutral to alkaline hot springs is not inhibited by the presence of sulfide. Phylogenetic analysis showed that arsenate production coincides with the temperature-dependent occurrence of organisms closely related to *Thermocrinis ruber*, a sulfur-oxidizing bacterium.

Study 4: Thioarsenate formation, release and re-sorption during oxidative dissolution of arsenic-iron-sulfide minerals (in review, Geochimica et Cosmochimica Acta)

Elke Suess and Britta Planer-Friedrich

E. Suess	60 %	Concept (oxidation As_2S_3, FeAsS, sorption) and laboratory work: batch and open system experiments, pH, total and speciation analyses; Data analysis; Paper work: concept and manuscript editing
B. Planer-Friedrich	40 %	Concept (oxidation FeAsS); Laboratory work: total and speciation analyses; Paper work: concept, discussion, and proof-reading

Abstract: Natural weathering and industrial leaching release arsenic and sulfur from the naturally abundant minerals orpiment (As_2S_3) and arsenopyrite (FeAsS). However, at highly alkaline conditions, where both minerals show their highest solubility, also binary As-S-species form which have so far largely been neglected in speciation studies. These thioarsenates ($AsO_{4-x}S_x^{3-}$) account for more than 40% of total arsenic with mono-, di-, and trithioarsenate being formed upon orpiment dissolution and only monothioarsenate upon arsenopyrite dissolution. At neutral pH, orpiment leaching yields 50% thioarsenates, predominantly as trithioarsenate. For arsenopyrite, the net arsenic release is approximately two orders of magnitude lower and arsenite is the predominant species; thioarsenates are negligible. At acidic conditions, thioarsenates are unstable; arsenite and arsenate predominates orpiment and arsenopyrite leaching solutions, respectively.

Different release mechanisms explain the variations in occurrence of thioarsenates upon dissolution of a pure arsenic-sulfide and an iron-arsenic-sulfide mineral. Oxidative orpiment dissolution initially yields thioarsenites ($AsO_{3-x}S_x^{3-}$), which are either directly released or formed by recombination of arsenite and sulfide and quickly oxidize to thioarsenates. During arsenopyrite dissolution under neutral conditions sulfur is released as sulfate which does not react with arsenite to yield thioarsenates. At alkaline conditions, physisorption of hydroxyl anions and transposition to As or Fe sites finally lead to formation of As-OH-S complexes and the release of monothioarsenate. The concentration of hydroxyl anions was found to be the main variable for thioarsenate release from arsenopyrite; neither total net arsenic release nor thio-anion concentrations affected aqueous monothioarsenate concentrations. Increasing ionic strength at near-neutral pH led to comparable total arsenic releases as at highly alkaline conditions, but the share of thioarsenates remained low. Addition of sulfides or polysulfides stabilized slightly more monothioarsenate in alkaline solutions, but did not significantly increase total arsenic release. Addition of thiosulfate, an industrial leaching lixiviate, neither influenced net release nor speciation. Re-sorption of monothioarsenate on secondary iron hydroxides formed during oxidative arsenopyrite dissolution was shown to be significantly lower than that of arsenite and arsenate, thus supporting long-term stability of elevated thioarsenate concentrations in solution.

The present study shows that thioarsenate species are far more important than has hitherto been considered, especially for iron-sulfide environments, which in many places are associated with very substantial human health risks.

Study 5: Stabilization of thioarsenates in iron-rich waters (published in Chemosphere)

Elke Suess, Dirk Wallschlaeger, and Britta Planer-Friedrich

E. Suess	50%	Concept; Laboratory work: stabilization experiments, IC-ICP-MS analyses; Data analyses and evaluation; Paper work: Concept, manuscript editing
D. Wallschaeger	10 %	Paper work: proof-reading
B. Planer-Friedrich	40%	Concept; Laboratory work and field sampling: IC-ICP-MS and on-site parameters/sampling; Paper work: Discussion and proof-reading

Abstract: In recent years, thioarsenates have been shown to be important arsenic species in sulfidic, low-iron waters. Here, we show for the first time that thioarsenates also occur in iron-rich ground waters, and that all methods previously used to preserve arsenic speciation (acidification, flash-freezing, or EDTA addition) fail to preserve thioarsenates in such matrices. Laboratory studies were conducted to identify the best approach for stabilizing thioarsenates by combination and modification of the previously-applied methods. Since acidification was shown to induce conversions between thioarsenates and precipitation of arsenic-sulfide minerals, we first conducted a detailed study of thioarsenate preservation by flash-freezing. In pure water, thioarsenates were stable for 21 days when the samples were flash-frozen and cryo-stored with a minimal and anoxic headspace. Increasing headspace volume and oxygen presence in the headspace were detrimental to thioarsenate stability during cryo-storage. Addition of NaOH (0.1 M) or EtOH (1% V/V) counteracted these effects and stabilized thioarsenates during cryo-storage. Addition of Fe(II) to thioarsenate solutions caused immediate changes in arsenic speciation and a loss of total arsenic from solution during cryo-storage. Both effects were largely eliminated by addition of a neutral EDTA-solution, and thioarsenates were significantly stabilized during cryo-storage by this procedure. Neutralization of EDTA was required to prevent alteration of thioarsenate speciation through pH change. With the modified method (anoxic cryo-preservation by flash-freezing with minimal headspace after addition of neutralized EDTA-solution), the fractions of mono- and dithioarsenate, the two thioarsenates observed in the iron-rich ground waters, remained stable over a cryo-storage period of 11 days. Further modifications are needed for the higher SH-substituted thioarsenates (tri- and tetrathioarsenate), which were not encountered in the studied iron-rich ground waters.

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IV Appendix – Submitted manuscript, links to publications, and enrollment form

Appendix A - Discrimination of Thioarsenites and Thioarsenates by X-ray Absorption Spectroscopy (weblink to Analytical Chemistry)

Appendix B - Arsenic Speciation in Sulfidic Waters: Reconciling Contradictory Spectroscopic and Chromatographic Evidence (weblink to Analytical Chemistry)

Appendix C - Oxidative Transformation of Trithioarsenate Along Alkaline Geothermal Drainages – Abiotic versus Microbially Mediated Processes (weblink to Geomicrobiology Journal)

Appendix D - Thioarsenate formation, release and re-sorption during oxidative dissolution of arsenic-iron-sulfide minerals

Appendix E - Stabilization of thioarsenates in iron-rich waters (weblink to Chemosphere)

Appendix F - Enrollment Form

Appendix 2

Appendix A - Discrimination of Thioarsenites and Thioarsenates by X-ray Absorption Spectroscopy

Elke Suess, Andreas C. Scheinost, Benjamin C. Bostick, Broder J. Merkel, Dirk Wallschlaeger, and Britta Planer-Friedrich

Analytical Chemistry 81(2009) pp. 8318-8326

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Appendix 4

Appendix B - Arsenic Speciation in Sulfidic Waters: Reconciling Contradictory Spectroscopic and Chromatographic Evidence

Britta Planer-Friedrich, Elke Suess, Andreas C. Scheinost, Dirk Wallschlaeger

Analytical Chemistry 82(2010) pp. 10228-10235

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Appendix 6

Appendix C - Oxidative transformation of trithioarsenate along alkaline geothermal drainages – abiotic versus microbially mediated processes

Britta Planer-Friedrich, Jenny C. Fisher, James T. Hollibaugh, Elke Suess,
Dirk Wallschlaeger

Geomicrobiology Journal 26(2009) pp. 330-350

http://dx.doi.org/10.1080/01490450902755364

Appendix D - Thioarsenate formation, release and re-sorption during oxidative dissolution of arsenic-iron-sulfide minerals

Elke Suess and Britta Planer-Friedrich

Geochimca et Cosmochimica Acta (under review)

Appendix 10

ELSEVIER

Under Review

Geochimica et Cosmochimica Acta

Geochimica et Cosmochimica Acta

Thioarsenate formation during oxidative dissolution of orpiment and arsenopyrite

Elke Suess [a,*] and Britta Planer-Friedrich[a]

[a] *University of Bayreuth, Environmental Geochemistry, Universitaetsstrasse 30, 95440 Bayreuth, Germany*

** Corresponding author. E-mail: elke.suess@uni-bayreuth.de. Phone: +4 99 21 55 36 43*

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Natural weathering and industrial leaching release arsenic and sulfur from the naturally abundant minerals orpiment (As_2S_3) and arsenopyrite (FeAsS). However, at highly alkaline conditions, where both minerals show their highest solubility, also binary As-S-species form which have so far largely been neglected in speciation studies. These thioarsenates ($AsO_{4-x}S_x^{3-}$) account for more than 40% of total arsenic with mono-, di-, and trithioarsenate being formed upon orpiment dissolution and only monothioarsenate upon arsenopyrite dissolution. At neutral pH, orpiment leaching yields 50% thioarsenates, predominantly as trithioarsenate. For arsenopyrite, the net arsenic release is approximately two orders of magnitude lower and arsenite is the predominant species; thioarsenates are negligible. At acidic conditions, thioarsenates are unstable; arsenite and arsenate predominates orpiment and arsenopyrite leaching solutions, respectively.

Different release mechanisms explain the variations in occurrence of thioarsenates upon dissolution of a pure arsenic-sulfide and an iron-arsenic-sulfide mineral. Oxidative orpiment dissolution initially yields thioarsenites ($AsO_{3-x}S_x^{3-}$), which are either directly released or formed by recombination of arsenite and sulfide and quickly oxidize to thioarsenates. During arsenopyrite dissolution under neutral conditions sulfur is released as sulfate which does not react with arsenite to yield thioarsenates. At alkaline conditions, physisorption of hydroxyl anions and transposition to As or Fe sites finally lead to formation of As-OH-S complexes and the release of monothioarsenate. The concentration of hydroxyl anions was found to be the main variable for thioarsenate release from arsenopyrite; neither total net arsenic release nor thio-anion concentrations affected aqueous monothioarsenate concentrations. Increasing ionic strength at near-neutral pH led to comparable total arsenic releases as at highly alkaline conditions, but the share of thioarsenates remained low. Addition of sulfides or polysulfides stabilized slightly more monothioarsenate in alkaline solutions, but did not significantly increase total arsenic release. Addition of thiosulfate, an industrial leaching lixiviate, neither influenced net release nor speciation. Re-sorption of monothioarsenate on secondary iron hydroxides formed during oxidative arsenopyrite dissolution was shown to be significantly lower than that of arsenite and arsenate, thus supporting long-term stability of elevated thioarsenate concentrations in solution.

The present study shows that thioarsenate species are far more important than has hitherto been considered, especially for iron-sulfide environments, which in many places are associated with very substantial human health risks.

Keywords: As-S species, arsenic-sulfides, mineral leaching, FeAsS, As_2S_3

1. Introduction

Worldwide, arsenic is an element of concern due to its carcinogenicity and neurotoxicity [1-3]. It is released into the environment through natural mobilization processes by weathering of arsenic containing minerals, especially arsenic sulfides, by desorption from mineral phases such as iron(hydr)oxides [4, 5] or industrial leaching of arsenic-bearing sulfides at acidic or alkaline conditions [6-8] to extract elements of economic interest, such as Au, Ag, Pb, or Zn [5, 9, 10].

Many studies have been performed to understand the leaching behavior of arsenic sulfides and two recent reviews give extensive information about the oxidation and dissolution of two of the most important arsenic-sulfides, orpiment, As_2S_3, [11] and arsenopyrite, FeAsS, [9]. While under abiotic, anoxic conditions sulfides are fairly stable [11-13], oxidation rates increase pH-dependent [9, 11, 14-16], in the presence of redox-agents as Fe(III) at low pH and O_2 at high pH [11, 14, 15, 17-20], and by microorganism [21-23]. Mineral leaching can further be increased by formation of arsenic-carbonate [24-28] and/or iron-carbonate complexes [29], in the presence of sulfide by arsenide-sulfide exchange at the mineral surface [30], As-S complex formation [31], or in the presence of thiosulfate by formation of gold-thiosulfate complexes [8, 32] or in the presence of orpiment by gold-sulfur or gold-thioarsenate-complexation [33]. Temperature increases can positively affect the leaching efficacy or cause precipitation by temperature decreases, observed for As_2S_3-precipitates in hot-springs [31, 33-36] or used for removal of arsenic from ore leaching solutions [37].

The general dissolution behavior and the leaching products of amorphous As_2S_3 and orpiment are comparable and differ only in terms of pH-dependency, reaction kinetics, and efficacy with generally lower activation energies for the amorphous phase [16, 34, 38]. Orpiment dissolution increases linear from acidic to alkaline conditions with activation energies decreasing from 60 kJ/mol at pH 2 to 28 kJ/mol at pH 14 [11, 38, 39]. Comparatively, arsenopyrite shows a minimum dissolution in the near-neutral pH-range [20, 40] and increases towards acidic and to a greater extent towards alkaline conditions [41]. Activation energies increase from 16-18 kJ/mol at pH 2 to 57 kJ/mol at pH 6-8 [14, 15]. Only under acidic conditions arsenopyrite dissolution efficacies exceed that of orpiment [11, 15, 38]. Since activation energies are < 20 kJ/mol, mass transfer, O_2-diffusion controlled reactions have to be considered for arsenopyrite dissolution at low pH conditions [14, 33]. With increasing pH chemical or electrochemical surface reactions prevail since activation energies are > 40 kJ/mol for both orpiment and arsenopyrite [11, 33] and thus with increasing reactant an increase in the leaching efficacy can be achieved.

To evaluate mobility and toxicity of arsenic released upon sulfide dissolution information not only about net total arsenic release but about the species formed at the surface and in solution is of central importance. While arsenite and arsenate are routinely determined as inorganic species, little attention has yet been paid to the relevance of arsenic-sulfur species. We have recently shown that thioarsenites are the primary reaction products of arsenite and sulfide in solution in the complete absence of oxygen. They transform quantitatively to thioarsenates if oxygen is not excluded completely and to arsenite at highly alkaline conditions due to competitive OH^- versus SH^- exchange [42]. At acidic conditions both thioarsenates and thioarsenites transform to arsenite before precipitation as amorphous arsenic-sulfide minerals [42-44]. What is known about the species-specific leaching of arsenic and sulfur for orpiment and arsenopyrite is summarized in the following paragraphs.

Under anoxic conditions, X-ray photoelectron spectroscopy (XPS) showed the occurrence of arsenite and disulfide surface species at freshly fractured orpiment surfaces [11, 45]. The orpiment dissolution is base-promoted, i.e. the release mechanism is a result of hydroxide adsorption at the mineral surface, and weakening of the bondings in the crystal lattice by bond-polarization favoring the release of arsenic and sulfur [12, 46]. For the layered crystalline mineral phase (S-As-S-As-S) hydroxide absorption depends on the interaction between sulfur and hydrogen atoms of the hydroxyl groups, while in case of the amorphous phase the hydroxide can directly (chemically) interact with arsenic. Thereby S-As-S and S·As-S-OH are assumed to detach from the surface [12]. In sulfide-rich solution the formation of trivalent thioarsenic species was proposed [34, 36] and predicted by thermodynamic model calculations [47, 48]. In sulfide-deficient solutions arsenite is the major species (70-90%) as determined in laboratory studies coupled with model calculations [12, 34]. Under oxic conditions, arsenite was determined as predominant species (50-70%) in carbonate-containing solutions with pH 7-9 by HGAAS. Interestingly, among the sulfur species an unknown, intermediate species, comprising presumably polythionates, accounted for 80-90% of total sulfur [38]. However, it has been shown that depending on the HG conditions, thioarsenates either precipitate upon acidification prior to reduction or if pre-reduction is used only monothioarsenate is co-determined with arsenate, while tetra-, tri-, and dithioarsenate react with the arsenite fraction [43] and thus arsenic-sulfur species might have been overlooked in previous studies conducted by HG-techniques. In highly alkaline electrochemical oxidation experiments direct formation of arsenite and sulfide after hydroxide adsorption was determined by cyclic voltametry [49]. Free sulfide-ions were then supposed to further react with the mineral surface to form and release thioarsenites which are based on our current knowledge unstable under oxic conditions and would oxidize to thioarsenates [42]. The only direct analytical evidence for thioarsenate occurrence upon orpiment dissolution comes from presumably anoxic sulfidic orpiment-leachates at neutral pH determined by IC-ICP-MS, although thioarsenates occurred as a minority beside arsenite [50]. However, we know today that thioarsenates only form in the presence of oxygen, so either the experiments were not anoxic or thioarsenates formed as oxidized artifacts during analysis by IC-ICP-MS [42]. Overall, no investigations regarding kinetics, pH-, and redox-dependence of thioarsenites or thioarsenates during orpiment leaching exist.

Although arsenopyrite was subject to numerous studies, only few focus on arsenic speciation. Dissolution rates and kinetics are largely governed by the surface structure of the arsenopyrite and the formation of surface coatings. At acidic conditions, a metal-deficient sulfur-enriched layer forms which consists of polysulfides and sulfate [14, 51-54]. Arsenic and iron are preferentially released compared to sulfur ($As/S > 1$) [14]. At near-neutral conditions, arsenic and iron oxide surface coatings form leading to Fe/As and Fe/S ratios < 1, and $As/S < 1$ [14]. At alkaline conditions, no sulfur oxidation products were determined at the surface and more arsenic than iron was released [51]. Arsenic oxides showed a high solubility at alkaline conditions [55, 56] but iron hydroxides form rapidly at $pH > 6$ [14, 57]. The formation of surface coatings, ironhydroxides, and (re-)sorption of arsenic [58, 59] may reduce the release of iron and arsenic over time to finally yield a passivation of the surface at neutral to basic conditions [14].

Additionally to the determinations of surface complexes also arsenic and sulfur speciation in solution was investigated [15, 19, 20, 33, 60, 61]. Arsenite was found to predominate over a broad pH-range from 2-12 in leaching studies of several hours up to one day [15, 20, 60, 61], with a considerable amount of arsenate at pH 7 (40%) as determined by Walker et al. [19]. Although abiotic arsenite oxidation is slow, arsenate will predominate on the long-term as found under natural leaching conditions of an alkaline mineral processing plant (Macreas) [40]. Thio-arsenite formation was proposed in one study at highly alkaline conditions [7]. Thioarsenate formation (monothioarsenate) has so far only be described in a PhD-thesis by Zhang [33] proposing hydroxide physisorption as release mechanism. Released sulfur forms sulfate, elemental sulfur, and S(x)-species [61] under acidic conditions and predominates as sulfate at neutral conditions [14]. Thiosulfate is unstable at acidic conditions and decomposes to elemental sulfur, sulfite, and/or polythionates in the presence of As(III) [62]. At highly alkaline conditions thiosulfate is the predominant sulfur species [33]. Upon leaching iron is proposed to be initially released as Fe(II), then predominate in solutions with $pH < 4$, but will be oxidized to Fe(III) rapidly with increasing pH ($pH > 5-6$) [14, 15]. Due to the formation of iron-arsenic oxide surface coatings and ironhydroxides the amount of iron in solution is depleted, especially at alkaline pH [14, 19, 33].

Overall, thioarsenite and thioarsenate formation has been suggested in several previous reports, however, systematic analytical evidence is rare. In the present study we compare thioarsenate time- and pH-dependent formation through orpiment and arsenopyrite leaching under fully oxidizing conditions. Arsenopyrite leaching mechanisms are investigated in more detail with restricted oxygen headspace and under anoxic conditions, as function of total net arsenic release, arsenic-sulfur speciation and ionic strength and in the presence of different reduced sulfur species.

Table 1: Overview over experimental set-up of batch and open system mineral leaching experiments

Mineral powder	Leaching solution	Redox-conditions	pH/amendments	Reaction time	Comments
Open system leaching experiments with arsenopyrite ($FeAsS_{HA}$) and orpiment (As_2S_3)					
$FeAsS_{HA}$, As_2S_3	$NaHCO_3$ (0.04 M) NaOH (0.1 M)	oxic conditions simulated for open systems	2, 6 12	6, 24, 48, 72, 144	pH adjustment with 50% NaOH/HNO3
190 mg FeAsS / 140 mg As_2S_3 in 300 mL leaching solution, horizontal shaker 50 rpm					
Batch leaching experiments with arsenopyrite from Harmannsdorf (HA, $FeAsS_{HA}$) and Freiberg (FG, $FeAsS_{FG}$)					
pH depending leaching kinetics					
HA, HA and FG*	$NaHCO_3$ (0.04 M) NaOH (0.1 M)	oxic conditions with air-purged leaching solutions	2*, 5, 7*, 9, 12* 13*	10”, 1 h, 2 h, 6 h,12 h, 24 h, 3 d, 5 d, 7 d, 3 and 6 weeks	pH adjustment with 50% NaOH/HNO_3
Leaching efficiency under (an)oxic conditions in presence of sulfur species					
HA	$NaHCO_3$ (0.04 M)	oxic conditions with air-purged leaching solutions	7, 12, thiosulfate	48 h	pH adjustment with 50% NaOH/HNO_3
		anoxic conditions with N_2-purged leaching solutions	7, 12, sulfide, polysulfide		
Leaching efficiency in subject to the strength of leaching solution					
HA	$NaHCO_3$ (0.004, 0.04, 0.4, 0.8 M) NaOH (0.004, 0.04, 0.4, 0.8 M)	oxic conditions with air-purged leaching solutions	pH 8.8, 8.6, 8.3, 8.1 pH 11, 12, 13, 13	48 h	no pH adjustment
25 mg FeAsS in 40 mL leaching solution, over-head shaker 20 rpm					

2. Materials and Methods

Laboratory experiments were conducted to examine the long-term leaching behavior of a commercial orpiment and arsenopyrite under fully oxidizing conditions as well as for two different types of arsenopyrite under a range of conditions representative for natural environments, industrial sulfide leaching or post-mining situations. With a focus on arsenic-sulfur speciation time-dependent dissolution was studied in relation to changes in pH, ionic strength, anoxic/oxic conditions, and the effect of different sulfur species (Table 1). Re-sorption of arsenic on iron(hydr)oxides was also investigated.

2.1. Orpiment and Arsenopyrite minerals

Orpiment was obtained from Alfa Aesar, Germany (As_2S_3) as fine powder and used without further preparation. Arsenopyrite minerals from two sites in Saxony, Germany (Hartmannsdorf $FeAsS_{HA}$, Freiberg $FeAsS_{FG}$) were provided by the Mineral Collection of the Technical University of Freiberg. For the preparation of the arsenopyrite powder the mineral blocks were crushed with a jaw crusher to a size of 2 mm and fine-grind in a disc mill with a CaC_2 head. The fraction with a grain size < 45 µm was separated by sieving. With a micro classifier (Alpine Multi-Plex Labor-ZZ-Sichter A 100MZR) the particles < 15 µm were separated using centrifugal and gravitation force. The particle size of the arsenopyrite powder (on average 5.7 µm (85% ≤ 15 µm) for $FeAsS_{HA}$ and 3.0 µm (99% ≤ 15 µm) for $FeAsS_{FG}$) was determined with a lasergranulometer (HELOS VECTRA, Sympactec) using a RODOS dry powder disperser (HELOS H0735, RODOS R3).

2.2. Dissolution experiments

2.2.1. Open system dissolution experiments on orpiment and arsenopyrite

To determine dissolution under fully oxidizing conditions, open vessel experiments were conducted. Arsenopyrite ($FeAsS_{HA}$, 0.19 g) and commercially available orpiment (As_2S_3, Alfa Aesar, Germany, 0.14 g) were suspended in 300 mL leaching solution (0.1 M NaOH for pH 12, 0.04 M $NaHCO_3$ for pH 2 and 6, adjusted with NaOH and HNO_3; Table 1) in open 1000 mL Erlenmeyer flasks. The flasks were constantly shaken at room temperature (20°C) on a horizontal shaker (50 rpm). After 6, 24, 48, and 144 h approximately 5 mL aliquot were sampled for total arsenic analyses and pH-measurement. Arsenic-sulfur speciation was checked for the 6 and 144 h samples.

2.2.2. Arsenopyrite dissolution experiments with restricted oxygen headspace

For the batch experiments 25 mg arsenopyrite powder ($FeAsS_{HA}$, Freiberg $FeAsS_{FG}$, < 15 µm) were dispersed in 40 mL leaching solution using 50 mL PE-vials (Sarstedt). If not stated otherwise, ultrapure water (Ultrapure Ionex Cartridge, Millipore) was used for solution preparation and dilutions. Depending on the respective experiment, the composition of the leaching solution and the leaching time were varied (Table 1). To guarantee proper mixing of the leaching samples, samples were rotated at 20 rpm on an over-head shaker (GFL 3040) according to their respective reaction time. For the pH-dependent kinetic experiments dissolution was performed in 0.04 M air-purged $NaHCO_3$ (sodium hydrogen carbonate, Caledon Laboratories LTD, ON, Canada) with initial nominal pH-values of pH 2, 5, 7, 9, 12 and 13. For each reaction time (10 min to 6 weeks) separate replicates were prepared. The pH-adjustment was performed by addition of HNO_3 (conc.) or 50% NaOH (sodium hydroxide solution, Fisher Scientific). Further experiments were carried out to test the effect of the ionic strength (0.004, 0.04, 0.4, and 0.8 M, NaOH or $NaHCO_3$) on the leaching efficacy ($FeAsS_{HA}$) and arsenic-sulfur species formation with a reaction time of 48 hours. Additionally, the influence of thiosulfate addition on arsenopyrite leaching ($FeAsS_{HA}$) was investigated at pH 7 and pH 12. A 100 mg S/L stock solution (sodium thiosulfate pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$, 99+%, Alfa Aesar, Lancaster) was added to obtain final concentrations of 3 and 30 µM in the suspensions. Reaction time for all sulfur species experiments was 48 h.

2.2.3. Arsenopyrite dissolution experiments in presence of reactive sulfide species under anoxic conditions

Experiments to test the influence of sulfide and polysulfides on arsenopyrite leaching ($FeAsS_{HA}$) at pH 7 and pH 12 had to be conducted in a glovebox (COY, 5% H_2, 95% N_2) due to the redox-sensitivity of these samples. A polysulfide stock solution (3.5 mgS/L, potassium(poly)sulfide, K_2S, Riedel de Haen, > 42%) was diluted to final concentrations of 30 and 300 µM sulfur. A sulfide stock solution (4000 mgS/L, $Na_2S \cdot 9H_2O$, Sigma-Aldrich, trace metal grade) was diluted to final concentrations of 17 and 167 µM sulfur. As dissolution under reductive conditions differs from that of oxidative conditions comparative experiments were conducted in the glovebox without addition of any sulfur species.

2.2.4. Sampling

After the respective reaction times, samples were filtered immediately (outside or for (poly)sulfide experiments inside the glovebox) using syringe filters with changeable filter paper (0.2 µm cellulose acetate, Sartorius, Germany). Approximately 1.5 mL of the filtrate was stored in the refrigerator (Pyrogene 1.5 mL microtubes, Ultident Scientific, Canada) for total arsenic analyses (ICP-MS). These samples had to be diluted with ultrapure water (dilution factor 10 for pH 5 and 7; 20 for pH 9; 100 for pH 2; and 250 for pH 12 and 13). Arsenic-sulfur speciation was analyzed immediately. Dilutions were required for the samples at pH 2, 9, 12, and 13. The dilution factors were 1.7 for $FeAsS_{FG}$ and 10 for the $FeAsS_{HA}$. The pH-values were determined in the suspensions after sampling (I.Q. 140 pH meter, USA, calibrated with buffers at pH 4, 7, and 10).

2.3. Sorption experiments

Sorption isotherms were determined in washed (Table EA 1) and pre-hydrated (24 hours, 5 mM NaCl, p.a. Merck) α-Goethite (Table EA 2) suspensions (33 g/L) with arsenic concentrations of 0.065 , 0.13 , 0.27 , 0.53 , 1.3 , 2.67, and 5.33 mM for arsenate ($AsHNa_2O_4 \cdot 7H_2O$, Fluka, p.a., ≥99%), arsenite ($NaAsO_2$, Fluka, p.a., ≥99%), and monothioarsenate (synthesized sodium-monothioarsenate, ≥96%, [44]) for 48 hours. Thereby the preparation of the solutions (including pre-hydration) was performed under anoxic conditions in the glovebox. Additionally, kinetic experiments were performed with sorption solutions in the medium concentration range (0.53 mM arsenic) and reaction times of 0.03, 0.5, 1, 5, 8, 14, 24, 72, 168, and 336 h, for arsenate, arsenite, and monothioarsenate.

After preparation of the suspensions, the PE-vials (30 mL, Sarstedt) were sealed and stored in N_2-filled containers for shaking outside the glovebox (20 rpm). Sampling was done after the respective reaction times, including centrifugation (6000 rpm, Centrifuge Hettich Universal) and separation of solids from the aqueous phase by filtration (0.2 µm, Membrex 25 CA, Membra Pure) in the glovebox. In the filtrates solution pH was determined. Samples for total arsenic analyses were stored in the refrigerator until analyses by ICP-MS. Speciation was checked by IC-ICP-MS in cryo-preserved samples [63].

2.4. (IC-)ICP-MS analyses

The simultaneous speciation of arsenic and sulfur was measured with ion chromatography (AEC; DIONEX, IC GP50), coupled to an ICP-MS (inductively coupled plasma-mass spectrometry) from PerkinElmer (Elan DRC II). Species were separated using an anion column (IonPac®, AG16/AS 16, 4 mm, Dionex) with a highly alkaline eluent with gradient flow (0.02-0.1 M NaOH, 1.2 mL/min) as described elsewhere [64]. The dynamic reaction cell technology with oxygen as reaction gas (10% O_2, 90% He) was used to remove interferences of $^{75}As^+$ and $^{32}S^+$ with $^{40}Ar^{35}Cl^+$ and $^{16}O_2^+$ and detect arsenic and sulfur as $^{75}As^{16}O^+$ (m/z 91) and $^{32}S^{16}O^+$ (m/z 48). The surplus of Na^+ was removed by H^+ exchange through an anionic self-regenerating suppressor (ASRS, 13 psi). Arsenic and sulfur of the thioarsenates were quantified using the calibration curves for sulfate and arsenate. They were determined from a mixed-standard calibration with arsenite ($NaAsO_2$, Fluka, purum p.a.), arsenate ($AsHNa_2O_4 \cdot 7H_2O$, Fluka, puriss. p.a.), and sulfate ($(NH_4)_2SO_4$, Fluka Sigma-Aldrich) in a range of 0.1-5 mgS/L and 0.01-1 mg As/L. Sulfide was calibrated separately due its reactivity with arsenite (0.1-1 mgS/L $Na_2S \cdot 9H_2O$, Sigma-Aldrich, trace metal grade).

Total arsenic and sulfur concentrations determined by ICP-MS as described above were corrected with iridium and rhodium for the instrument-based internal drift and a calibration check every 12 samples for external drift. For quality control, TM-DWS (Environment Canada, National Water Research Institute) was used as an external reference material.

3. Results and Discussion

3.1. Thioarsenate formation during oxidative dissolution of arsenopyrite and orpiment

To compare arsenic speciation during oxidative leaching of arsenopyrite and orpiment, parallel open system experiments were performed. We found in accordance with previous studies that in contrast to arsenopyrite which shows a dissolution minimum at near neutral pH, the solubility of orpiment increases linear (Fig. 1) and exceeds that of arsenopyrite for pH > 7 about 10 to 100fold. At acidic conditions, minimum orpiment leaching was observed with 40 to 50 µM total arsenic release for 6 and 144 h leaching, which was about 2-times to one order of magnitude lower than that of arsenopyrite (80 to 470 µM). At neutral (pH 7) and alkaline conditions (pH 12) orpiment leaching increased significantly by factors of ~ 20 and ~80, respectively, relative to pH 2. Compared to arsenopyrite the dissolution of orpiment is 10 to 100 fold greater at neutral conditions. At highly alkaline conditions, orpiment leaching is very fast and maximum solubility is already reached after 6 hours. Arsenic concentrations did not further increase between 6 h and 144 h.

Although arsenopyrite leaching is also increased at alkaline conditions, even after 144 h the release does not even reach half of that of orpiment (1940 µM vs. 4460 µM). This is in line with the predictions from model calculations as well as compared to published leaching rates for orpiment, As_2S_3 (am), and (arseno)pyrite [9, 11, 15, 65]. In these studies an increase in the dissolution rates for orpiment from $10^{-10.4}$ $mol \cdot m^{-2} \cdot s^{-1}$ at pH 2 to $10^{-9.57}$ at pH 7.5 and $10^{-3.25}$ $mol \cdot m^{-2} \cdot s^{-1}$ at pH 13 [11, 38, 39, 46] was determined, which are higher at alkaline conditions compared to arsenopyrite with $10^{-8.1}$ to $10^{-8.6}$ $mol \cdot m^{-2} \cdot s^{-1}$ between pH 2 and 12 (Fig. EA 1, [15]).

Speciation analyses show that the amounts of thioarsenates formed under acidic conditions were negligible (<1%) for both minerals which is in accordance with our previous observations that both thioarsenates and thioarsenites transform to arsenite before precipitation as amorphous arsenic-sulfide minerals [42-44]. At highly alkaline conditions, thioarsenates were formed during leaching of both minerals (Fig. 1). Pentavalent arsenic species are the predominant leaching products (> 70%) with thioarsenates accounting for approximately 55% and 30% from orpiment and arsenopyrite dissolution, respectively, after 6 hours. With time, thioarsenate concentrations decreased to 43% for orpiment and increased to 43% for arsenopyrite after 144 hours (Table 2). In contrast to arsenopyrite where only monothioarsenate was detected, also di- and trithioarsenate formed upon dissolution of orpiment. Thioarsenates have previously been suggested to form upon presumably anoxic orpiment dissolution, but only to a minor extent [50]. The authors observed peaks for di-, tri-, and monothioarsenate, but lower than those for arsenate and the predominant arsenite. They proposed that the observed arsenite concentrations were already a result of thioarsenate conversion. We assume that higher thioarsenate rates in our experiments are due to an overall higher dissolution rate at fully oxidizing conditions. In contrast to arsenopyrite, thioarsenates are already important leaching products at neutral pH during orpiment dissolution. Thioarsenates accounted for up to 50% and besides 8% of monothioarsenate also 11% of dithioarsenate and 31% of trithioarsenate were observed. Other studies determined arsenite as predominant leaching product in the pH-range of 6.8-9.4 [16, 38]. However, they used HGAAS to determine their arsenic speciation and as shown before di- and trithioarsenate are reduced to arsenite upon pre-reduction and acidification, thus are not determined correctly within the As(V) fraction but as As(III) fraction [43]. Like at alkaline conditions, the only thioarsenate species observed at pH 7 from arsenopyrite leaching was monothioarsenate contributing a very low percentage to total arsenic (5%). Potential reasons will be discussed in the following sections.

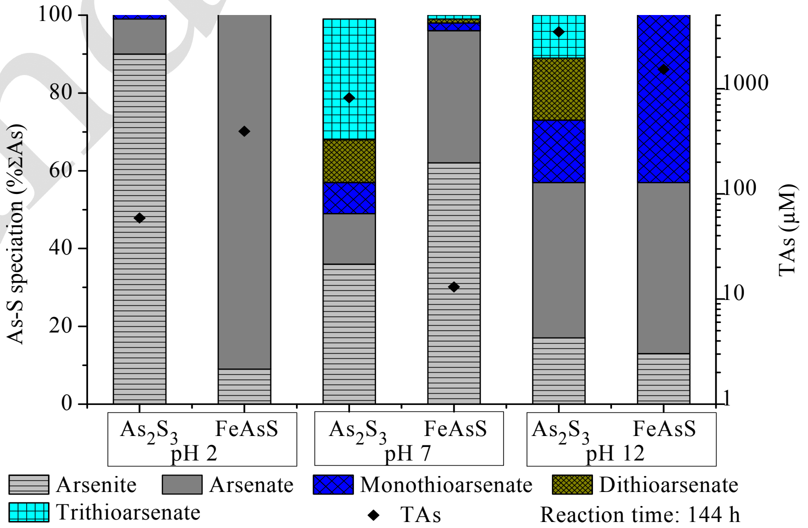


Figure 1: Speciation and total arsenic concentrations for 144h-open system leaching of arsenopyrite ($FeAsS_{HA}$) and orpiment (As_2S_3)

Table 2: Summary arsenopyrite (FeAsS$_{HA}$) studies in relation to orpiment (As_2S_3) leaching

	time (h)	ΣAs (µM)	Arsenite	Arsenate	Mono-	Di- (%ΣAs)	Trithio-arsenate	ΣThioarsenates (%ΣAs)
				acidic conditions (pH 2)				
As_2S_3	144	59	**90**	9	1			1
FeAsS	144	394	9	**91**				0
				neutral conditions (pH 7)				
As_2S_3	144	819	36	**13**	8	11	31	**50**
FeAsS	144	13	**62**	34	2	1	1	4
				alkaline conditions (pH 12)				
As_2S_3	6	3111	26	**20**	21	22	12	**55**
	144	3468	17	**40**	16	16	11	**43**
FeAsS	6	342	29	**44**	28			**28**
	144	1525	13	**44**	43			**43**

Overall, these initial studies proved that thioarsenate-formation is lower in iron-rich arsenic-sulfur systems compared to arsenic-sulfur systems, especially at neutral pH, but not at all negligible. We thus focused with more detailed studies on the dissolution of two types of arsenopyrite. To better mimic natural conditions we conducted all further experiments in closed vials with a restricted oxic or anoxic headspace instead of the open system approaches chosen for initial comparison of maximum orpiment and arsenopyrite dissolution.

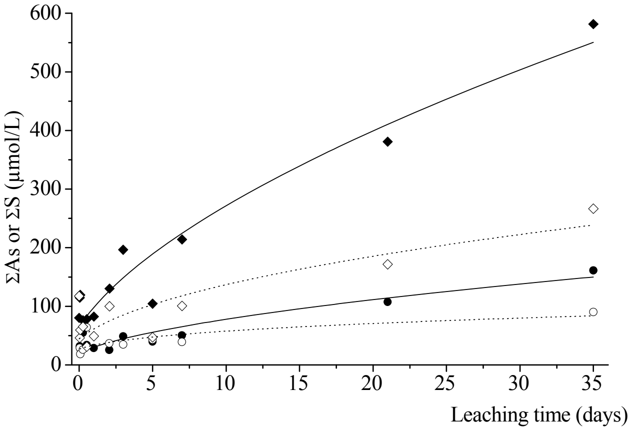
3.2. Leaching behavior of the two types of arsenopyrite

Comparing the two types of arsenopyrite used for the leaching experiments, we found that the arsenic and sulfur release from the Hartmannsdorf arsenopyrite (FeAsS$_{HA}$) exceeds that from Freiberg arsenopyrite (FeAsS$_{FG}$) for the investigated pH-values of 2, 7, 12, and 13 (Fig. 2, Table EA 3). The ratio of released arsenic ($\Sigma As_{HA}/\Sigma As_{FG}$ 3.6±0.9 (pH 2), 2.5±1.3 (pH 7), 3.3±1.5 (pH 12), 3.4±0.2 (pH 13)) and sulfur ($\Sigma S_{HA}/\Sigma S_{FG}$ 3.1± <1.1 for pH 12 and 13 and $\Sigma S_{HA}/\Sigma S_{FG}$ 2.4±0.8 at pH 2) hereby lies consistently at about 2.4 to 3.6. A lower ratio of $\Sigma S_{HA}/\Sigma S_{FG}$ 1.3±0.5 at pH 7 shows that more sulfur is released from FeAsS$_{FG}$ under neutral conditions (see section 3.3, Table EA 3). The reason for the observed differences is not entirely clear. However, while FeAsS$_{HA}$ was a solid, macroscopically pure mineral, FeAsS$_{FG}$ contained numerous impurities of white mica which could not be separated during sample preparation and thus likely diluted total arsenopyrite concentrations in the prepared sample powder. More important for us, however, the arsenic-sulfur speciation (see section 3.3., Figures in Table EA 3) showed no substantial differences in the leachates of both types of arsenopyrites. We will, thus, in the following mainly focus on the purer arsenopyrite from Hartmannsdorf (FeAsS$_{HA}$).

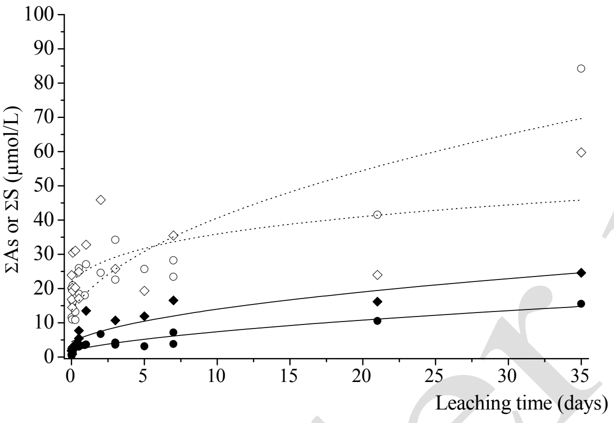
3.3. The pH-dependent total arsenic and sulfur release over time

In accordance with previous studies [15, 40, 41], we observed the highest arsenic release and fast leaching rates at highly alkaline conditions (Fig. 2, Fig. 3). At neutral conditions, arsenic concentrations were minimal and re-increased at acidic conditions (Fig. 2, Fig. 3). Dissolved arsenic concentrations generally increased substantially with time under alkaline and especially acidic conditions. From 10 minutes to 35 days, arsenic concentrations in solution increased from 80 to 580 µM at pH 2 and 200 to 2500 µM at pH 13 for FeAsS$_{HA}$ (30-160 µM at pH 2 and 60-630 µM at pH 13 for FeAsS$_{FG}$, Table EA 4). Leaching in the near neutral and weakly acidic milieu was approximately 10 to 100-times lower, reaching a minimum at pH 5.8. Arsenic concentrations were 4 µM after 10 minutes and increased very slowly during the first 3 weeks, with a finally greater increase between 21 and 35 days to a final concentration of 10 µM for FeAsS$_{HA}$ at pH 5.8 (Table EA 4).

A) Leaching kinetics at pH 2



B) Leaching kinetics at pH 7



C) Leaching kinetics at pH 13

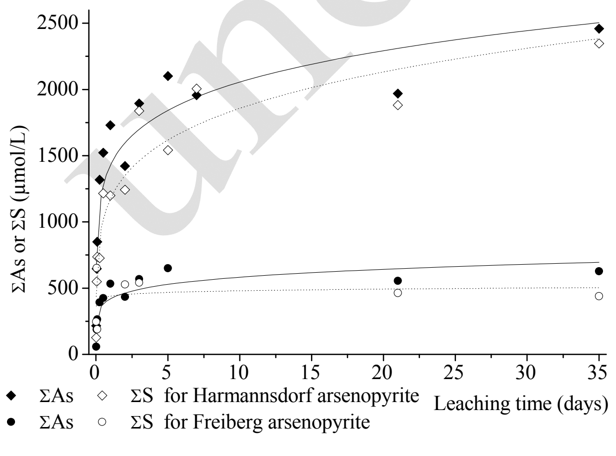


Figure 2 C: Arsenic and sulfur leaching kinetics for both arsenopyrites – Hartmannsdorf ($FeAsS_{HA}$) and Freiberg ($FeAsS_{FG}$) at pH 2, 7, and 13

The sulfur release was compared to arsenic release generally lower under acidic conditions (ΣAs/ΣS between 1.2 and 2.5; Table EA 3 and Table EA 4). Faster oxidation and release of iron and arsenic compared to sulfur in acidic media was also observed in previous studies leaving an arsenic- and iron-depleted and sulfide-enriched arsenopyrite surface [51, 54, 66]. Like arsenic, sulfur dissolution reached a minimum at near-neutral pH (Fig. 3). However, the decrease was not as significant as for arsenic. Thus, between pH 5.8 and 9, dissolved sulfur concentrations exceeded those of arsenic (ΣAs/ΣS ratios between <0.1 and 0.7, Table EA 4). Asta and co-workers [14] explained this same observation in their experiments by precipitation of secondary Fe- and As-O-containing mineral phases, e.g. iron(hydr)oxides, scorodite, pharmacosiderite, pitticite, and arsenic oxides. Under highly alkaline conditions (pH 13) a nearly stoichiometric release of arsenic and sulfur was observed over time with an average of 1.2±0.3 for both arsenopyrites and only lower ratios of ΣAs/ΣS 0.3 for initial release in case of $FeAsS_{FG}$ (Table EA 3, Table EA 4). The stoichiometric release is in line with previous reports [51, 67]. Yellow-orange precipitations were observed in our experiments which were previously characterized as ferric arsenite [51], ironhydroxides [7, 68], and AsS-phases [57]. Co-precipitation and sorption of arsenic and arsenic-sulfur species on ironhydroxides may also be important as discussed later (see section 3.6.)

3.4. The pH-dependent arsenite and arsenate speciation during oxidative arsenopyrite dissolution

Not only total releases of arsenic and sulfur showed a great dependency on pH, but also the arsenic-sulfur speciation in the leachates (Fig. 4, Table EA 3). Overall, our results showed that in the long-term arsenite and arsenate co-exist at acidic conditions, arsenite predominates under neutral to weakly acidic conditions, and arsenate under alkaline conditions. Under the most acidic conditions applied (pH 2) only arsenate formed initially. The share of arsenite increased over time (16 % after 2 days to 51 % after 35 days, Fig. 4). Even though most previous studies showed arsenite predominance under such acidic conditions [15, 20, 61]) and formation of arsenic(III)-oxides at the mineral surfaces [14], there are some that detected arsenate as in our results. Formation of both As(V)- and As(III)-oxides was shown during surface analyses of electrochemical oxidized arsenopyrite at pH 2 [54] and in leachings of 3 M H_2SO_4 arsenate even predominated [67]. According to Wedepohl [69] As(V)-oxides show a higher solubility than As(III) oxides, which might explain the initial arsenate predominance and the later increase in arsenite observed in our experiments. The predominance of arsenate was observed for both types of arsenopyrites.

At pH 5.8 and pH 7 arsenite was the dominant species already after 10 minutes with 60% and 76%, respectively, and remained predominant up to 35 days when it accounted for more than 84 % and 95% of total arsenic, respectively (Fig. 4). This is in line with former observations of > 75% arsenite in leachates over a pH-range of 1.8-12.8 [15, 20] and ~ 60% arsenite determined for leaching at pH 6.3-6.7 [19]. Walker et al. [19] proposed that initially released arsenite would further oxidize to arsenate. However, abiotic arsenite oxidation is a slow process and even though it might be important for natural systems, we could not observe oxidation of arsenite during our experimental time with a maximum of 35 days. Sulfur speciation was dominated by sulfate in all experiments from pH 2 to 7 with occurrence of some thiosulfate (only higher shares of 30-50% for pH 5 and 7 after 3-7 days, otherwise < 20%) and an unidentified sulfur species at pH 7 (retention time 290 s, max. 50%). The sulfate predominance was also reported in previous studies [14, 15, 19, 20].

Under alkaline conditions, arsenate predominated. The share of arsenite decreased with increasing pH from 50% to 41% and 33% for pH 9, 12 and 13, respectively. After 35 days, only 7 % arsenite was left at pH 9 and < 2% at pH 12. No arsenite was found at pH 13 after 35 days (Fig. 4, Table EA 3). Sulfur oxidation products of the dissolution at alkaline pH were sulfate, thiosulfate, and sulfur associated with thioarsenates (see section 3.5). Compared to leachings at lower pH the share of sulfate on total sulfur declined, while thiosulfate increased. The share of sulfate on the total released sulfur followed the overall trend pH 2 (sulfate/ΣS 0.9±0.1) > pH 5.8-7.5 (0.7±0.2) > pH 9 (decrease from 0.9 to 0.3) > pH 12-13 (< 0.3).

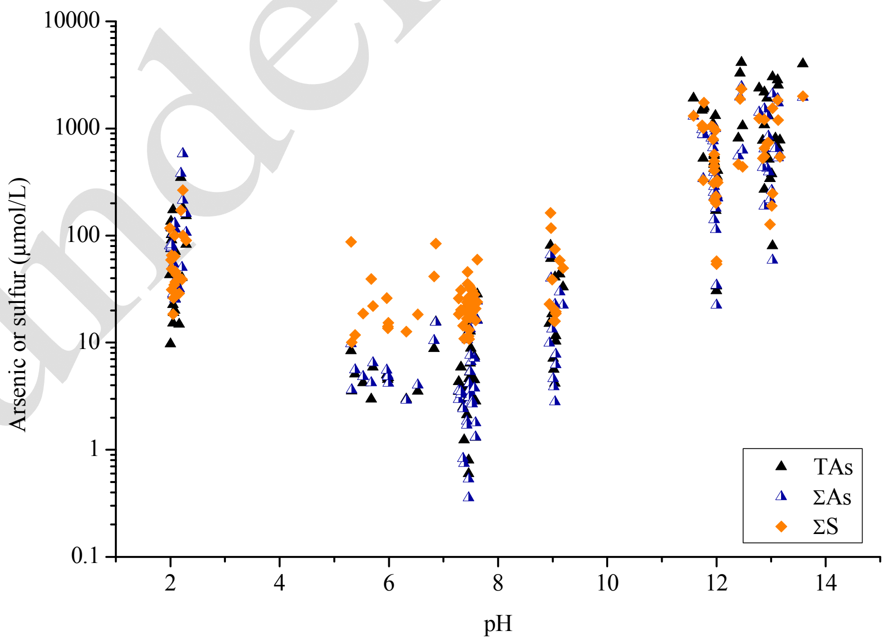


Figure 3: Arsenic and sulfur concentrations for the time- and pH-dependent arsenopyrite leachings plotted against solution pH (data of both arsenopyrites, all pH conditions, and all times)

3.5. The pH-dependent formation of thioarsenates during oxidative arsenopyrite dissolution

A maximum of 25% thioarsenates was detected at pH 13 after 35 days. In general, the share of thioarsenates increased significantly with pH and slightly over time. At acidic and neutral conditions (pH, 2, 7, and 9), some monothioarsenate formed after approximately 6-12 h, but its share was very minor with only 1-2% of total arsenic. At pH 5, with anyway the lowest leaching efficacy thioarsenate formation was negligible (< 0.3%). At highly alkaline conditions thioarsenates were formed. The share of arsenate and thioarsenate increased from equal portions of arsenate and arsenite at pH 9 (with 1% monothioarsenate) to 59% As(V)-species including 14% monothioarsenate at pH 12, and 67% at pH 13 with 15% mono- and 2% dithioarsenate. The share of thioarsenates remained stable over time at pH 12 (18±4% $FeAsS_{HA}$ and 12±2% $FeAsS_{FG}$, Table EA 3, Figure 4), while at pH 13 the initial share of 10-15% increased to 20-25% over the investigated time of 35 days. Dithioarsenate formation was < 0.5% at pH 12. At pH 13 between 2-3% dithioarsenate were formed but decreased to <0.3 % within the last 14 days of the experiment.

Thioarsenate formation upon arsenopyrite dissolution has so far only been described in a PhD study by Zhang [33]. In that study, predominately monothioarsenate was found besides arsenate and only small amounts of arsenite and dithioarsenate upon alkaline leaching. The dominant sulfur species was thiosulfate besides sulfite, sulfate, and polythionates. The occurrence of dissolved thioarsenates in arsenic-sulfur-iron systems is not trivial as strong competition exists between the formation of aqueous arsenic-sulfur species and formation of iron-sulfides or iron hydroxides which could precipitate and sorb arsenic or formation of arsenic-iron complexes [51, 68, 70, 71]. We have just recently been able to show that thioarsenates can occur in iron rich waters with a maximum of 17% monothioarsenate in waters up to 66 mg/L iron [63].

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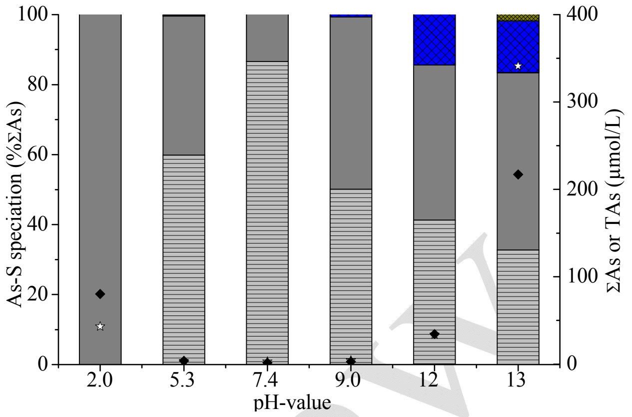
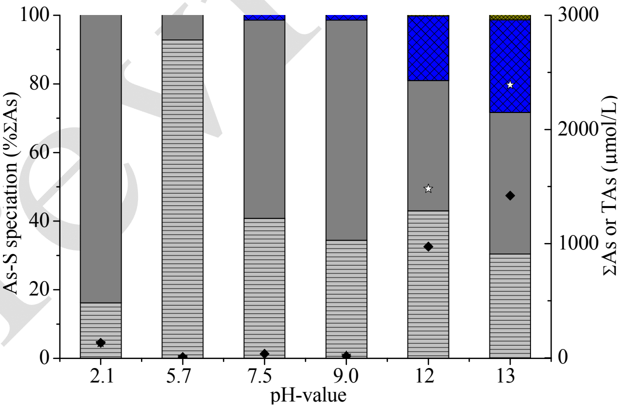
A) Arsenic speciation after 10" for the pH range 2-13



B) Arsenic speciation after 2 days for the pH range 2-13



C) Arsenic speciation after 35 days for the pH range 2-13

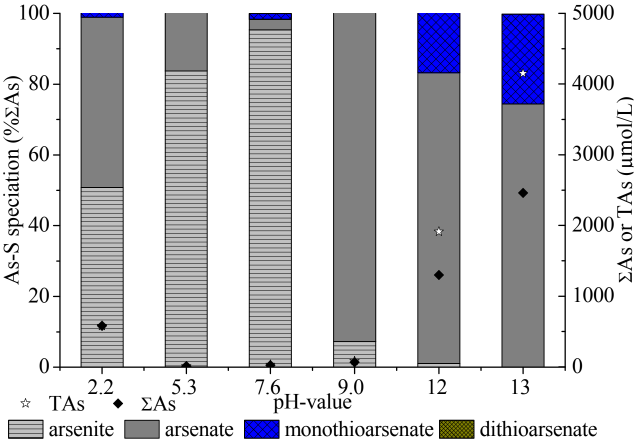


Figure 4: Arsenic speciation changes for the arsenopyrite leaches (Hartmannsdorf, $FeAsS_{HA}$) for 10" (A), 2 (B) and 35 days (C) in the pH-range 2 to 13

The fact that no thioarsenates were observed under acidic to neutral conditions even though monothioarsenate is stable over the entire pH range [43] is probably explained by the respective arsenic and sulfur species released upon arsenopyrite dissolution. Sulfate dominates the sulfur speciation and it is known not to react with the released arsenite. Reduced sulfur species, such as sulfide and polysulfides, which could react with arsenite to first form thioarsenites and quickly oxidize to thioarsenates, are obviously not released in sufficient quantities

For the formation of thioarsenates under alkaline conditions, this mechanism of arsenite and sulfide/polysulfide release and oxidative recombination to thioarsenates could be important. Thioarsenites which were already previously proposed to form upon oxidative arsenopyrite dissolution [7] would then have to be key intermediate species because we were able to show that thioarsenates only form via thioarsenites [42]. However, we were also able to show that thioarsenites are unstable when OH^- concentrations exceed the SH^- concentrations and that they transform to arsenite by competitive OH^- versus SH^- exchange and dissociation without formation of thioarsenates [42]. In our present experiments, the maximum total sulfur release was between 0.7 mM ($FeAsS_{FG}$) and 2.4 mM ($FeAsS_{HA}$) at pH 13 (OH^- 100 mM). Thus, even if all the released sulfur was in its reduced form, the OH-concentrations would still be 2 orders of magnitude higher and thus lead to competitive dissociation of thioarsenites. Thioarsenites are thus unlikely to form even as intermediate species upon arsenopyrite dissolution.

Alternatively to thioarsenate formation by oxidative recombination of arsenite and sulfide, the following mechanism has been suggested for a direct release of monothioarsenate based on an electrochemical model, i.e. anodic and cathodic reactions on the mineral surface [33].

At the cathodic sites dissolved O_2 is sorbed (1+2) with its subsequent reduction to H_2O_2 and hydroxide (3).

$$O_{2\,(aq,\ solution)} \rightarrow O_{2\,(aq,\ surface)} \qquad (1)$$

$$O_{2\,(aq,\ surface)} + FeAsS_{(s)} \rightarrow FeAsS_{(s)} \cdot O_{2(ads)} \qquad (2)$$

$$FeAsS_{(s)} \cdot O_{2(ads)} + H_2O + 2e^- \rightarrow FeAsS_{(s)} + H_2O_2 + OH^- \qquad (3)$$

At the anodic site physisorption of hydroxide and electron transfer occurs (4+5), followed by hydroxide transposition to either iron or arsenic sites (6).

$$FeAsS_{(s)} + OH^-{}_{(aq)} \rightarrow FeAsS \cdot OH^-{}_{(ads)} \qquad (4)$$

$$FeAsS \cdot OH^-{}_{(ads)} \rightarrow Fe(OH)AsS_{(ads)} + e^- \qquad (5)$$

$$Fe(OH)AsS_{(ads)} \leftrightarrow FeAs(OH)S_{(ads)} \qquad (6)$$

By further electron transfer As-OH-S complexes detach from the surface and FeOOH (7) forms. The As-OH-S complexes further form thioarsenates (8-12), arsenate by thioarsenate decomposition, and oxidized sulfur species (13-17).

$$\left[Fe(OH)AsS_{(ads)} \leftrightarrow FeAs(OH)S_{(ads)}\right] + OH^- \rightarrow Fe(OH)_3 + As(OH)_3S_{(ads)} + 5e^- \qquad (7)$$

Thioarsenate formation and decomposition:

$$As(OH)_3S_{(ads)} \leftrightarrow H_3AsO_3S_{ads} \qquad (8)$$

$$H_3AsO_3S_{(ads)} + 3OH^- \rightarrow AsO_3S^{3-} + 3H_2O \qquad (9)$$

$$2H_3AsO_3S_{(ads)} + 8OH^- \rightarrow AsO_3^{3-} + AsO_4^{3-} + S_2^{2-} + 7H_2O \qquad (10)$$

$$AsO_3^{3-} + S_2^{2-} \rightarrow AsO_3S^{3-} + S^{2-} \qquad (11)$$

$$AsO_3^{3-} + S_2^{2-} + H_2O \rightarrow AsO_2S_2^{3-} + 2OH^- \qquad (12)$$

Formation of oxidized sulfur species and arsenate:

$$S^{2-} + 6OH^- \rightarrow SO_3^{2-} + 3H_2O + 6e^- \qquad (13)$$

$$2S^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 3H_2O + 8e^- \qquad (14)$$

$$AsO_2S_2^{3-} + 10OH^- \rightarrow S_2O_3^{2-} + AsO_4^{3-} + 5H_2O + 8e^- \qquad (15)$$

$$AsO_3^{3-} + 2OH^- \rightarrow AsO_4^{3-} + H_2O + 2e^- \qquad (16)$$

$$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^- \qquad (17)$$

Summarizing, the dissolution of arsenopyrite in neutral (18) or alkaline media (19) can be written as:

$$FeAsS + 6H_2O \rightarrow Fe(OH)_3 + H_3AsO_3S + 6H^+ + 6e^- \qquad (18)$$

with reaction of oxygen and water:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + OH^- \qquad (19)$$

$$FeAsS + 6OH^- \rightarrow Fe(OH)_3 + H_3AsO_3S + 6e^- \qquad (20)$$

Thus, ironhydroxides and monothioarsenate are the initial leaching products of arsenopyrite dissolution, as a surface-controlled reaction. By subsequent decomposition of monothioarsenates into arsenate/arsenite and sulfide ions, oxidized sulfur species (sulfide ions → thiosulfate → sulfate) are formed as well as dithioarsenate which also decomposes directly into thiosulfate and arsenate.

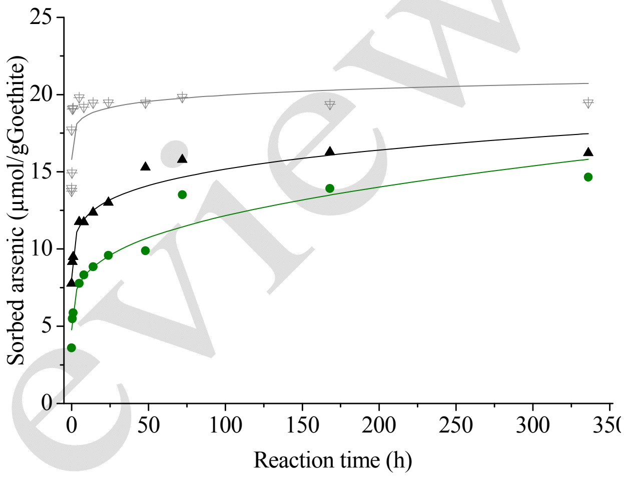
The fact that mainly monothioarsenate forms, is owed to the nearly stoichiometric release of arsenic and sulfur (ΣAs/ΣS 1.2±0.3, see section 3.2.). Dithioarsenate is only of minor importance upon arsenopyrite dissolution, either due to insufficient sulfur supply or due to its instability and transformation to monothioarsenate in the presence of iron as previously reported [63].

3.6. Re-Sorption of thioarsenates to iron hydroxides formed at alkaline conditions

At alkaline conditions, physisorption of hydroxyl anions, electron transfer and transposition of OH^- to As or Fe sites finally lead to formation of ironhydroxides as described above. We observed these ironhydroxides as orange-yellow precipitates also macroscopically in our experiments. They provide excellent sites for re-sorption of arsenic species and thus significantly influence the final aqueous arsenic speciation upon arsenopyrite dissolution. The sorption behavior of arsenate and arsenite was subject of numerous previous studies, which determined a higher sorption efficacy for arsenate on goethite and ironhydroxides compared to arsenite at pH 5-6 (sorption maxima at pH 4) and preferentially arsenite sorption at higher pH with sorption maxima between pH 8-9 [58, 59]. Although its known that the sorption efficacy is decreased at alkaline conditions, about 20% of arsenate and 30-60% of arsenite were sorbed on ironhydroxides, and 30-40% arsenate and 60-70% arsenite on goethite from solutions with 100 and 50 µM total arsenic, respectively [58].

However, so far nothing was known about the sorption behavior of monothioarsenate on iron(hydr)oxides. Our batch experiments showed that sorption efficacy and kinetics are lower for monothioarsenate than for arsenate and arsenite (Fig. 5). Initial arsenite sorption was fast and reached equilibrium conditions already after 1 h as observed previously [59, 72].

A Sorption kinetics



B Sorption isotherms

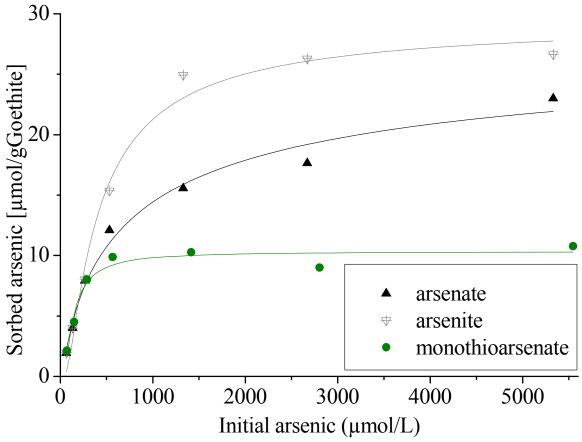


Figure 5: Sorption of arsenate, arsenite, and monothioarsenate on α-Goethite - (A) kinetics (at solution pH of 9 for arsenite and arsenate, and pH 10 for monothioarsenate) and (B) sorption isotherms For sorption isotherms solution pH increased with increasing concentrations following the same trend as the concentration curves (7-9 arsenate, 7-10 arsenite, and 8-12 monothioarsenate).

Arsenate and monothioarsenate showed slower kinetics with equilibration after 1 day and 3 days, respectively. For the sorption isotherms equilibration on the mineral surface was achieved for > 39 µM/g FeOOH initial arsenic. Maximal sorption capacities were determined with 11, 23, and 26 µmol As/g FeOOH for monothioarsenate, arsenate, and arsenite respectively. The solution pH increased in the same way as the sorption curves and yielded final values of 12, 9, and 10 for monothioarsenate, arsenate, and arsenite, respectively. In line with previous studies arsenite showed a better sorption than arsenate at higher pH [58]. Monothioarsenate sorption was only half of that of arsenite and arsenate. Considering both that only about 30% of the monothioarsenate re-sorbed to iron-hydroxides in our batch experiments and further that the amount of ironhydroxides in the batch experiments (33 g/L) was orders of magnitudes higher than what could be expected to form during arsenopyrite leaching, re-sorption of monothioarsenate upon arsenopyrite dissolution is likely to be only of minor importance. However, more detailed studies on monothioarsenate-FeOOH surface species formation using XAS are currently underway.

3.7. Influence of ionic strength on net total arsenic release and thioarsenate formation

To determine whether thioarsenate formation really is mainly a function of pH as shown in section 3.4. or also depends on solution ionic strength and net total arsenic release, leaching experiments were conducted in 4 mM to 800 mM solutions of $NaHCO_3$ and NaOH, yielding final pH of 8.1 to 8.8 and 11.3 to 13.4, respectively. Fig. 6 shows the results for net total arsenic release and arsenic speciation.

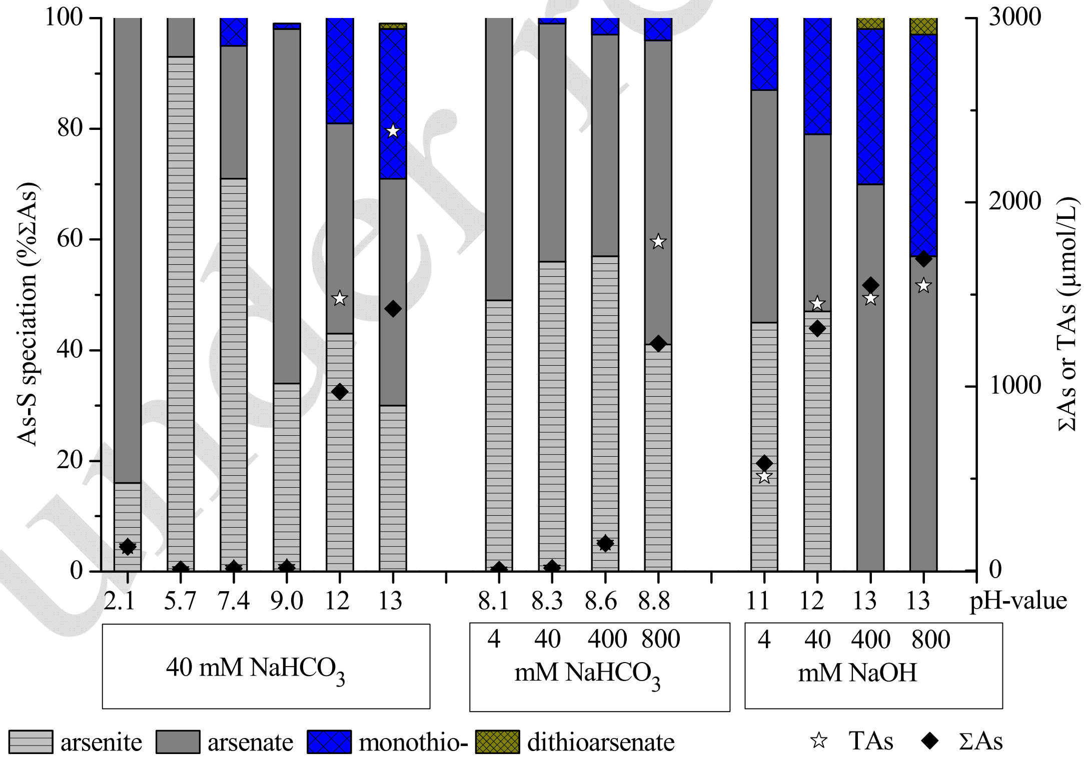


Figure 6: Leaching of arsenopyrite (Hartmannsdorf, $FeAsS_{HA}$) in different concentrated matrices of $NaHCO_3$ and NaOH compared to leaching in 40 mM $NaHCO_3$ at pH 2-12 for overall reaction times of 48 hours

Applying increasing concentrations of NaOH, total arsenic and sulfur release increased about 2-3 fold from 4 to 40 mM NaOH (Fig. 6, Table EA 5). Higher concentrations of NaOH (400 and 800 mM) did not further affect dissolution significantly. As shown before (Fig. 4), the share of arsenite decreased with increasing NaOH concentrations, i.e. increasing pH, and was completely transformed in 400 and 800 mM NaOH leachates. Arsenate and thioarsenate increased accordingly. Thioarsenates finally accounted for 43% at pH 13.4 (40% mono-, 3% dithioarsenate). The sulfur speciation shifted from thiosulfate predominance in low ionic strength solutions (4-40 mM NaOH) to nearly equal shares of sulfate, thiosulfate, and sulfur associated with thioarsenates in higher concentrated solutions.

Applying increasing concentrations of $NaHCO_3$ for dissolution, arsenic and sulfur release increased significantly from 4 mM to 800 mM $NaHCO_3$ by a factor of ~200 (Fig. 6, Table EA 5). At 400 mM $NaHCO_3$ and a pH of 8.6 total arsenic release was comparable to that normally observed under acidic conditions and at 800 mM $NaHCO_3$ and a pH of 8.8 the release was comparable to the maximum dissolution yields at highly alkaline conditions (pH 12 and 13, Fig. 4). Formation of relatively weak mono- and bicarbonate As(III)-complexes was suggested to explain increased arsenic leaching ([73]. If these complexes formed they are probably only meta-stable, fully converted to arsenite and/or arsenate in our experiments and were thus not detectable with our IC-ICP-MS method. Thioarsenates increased slightly with increasing $NaHCO_3$ concentration. However, their share was only 4% even at the highest concentration of $NaHCO_3$ applied. For sulfur, a shift from sulfate dominance to thiosulfate predominance in solutions with 800 mM $NaHCO_3$ was observed, similar to what was observed under highly alkaline conditions (section 3.4.).

Summarizing, though total net arsenic release could be increased by addition of high-ionic strength $NaHCO_3$ to levels comparable to those at highly alkaline leaching conditions, the share of monothioarsenate was significantly lower at pH 8.8 (4%) than at pH 11 (13%) and 13 (40%). This refutes thioarsenate formation to depend on net total arsenic or sulfur release and lends further support to the proposed direct release mechanism by physisorption of hydroxyl anions, electron transfer and transposition of OH to As or Fe sites.

3.8. The effect of thiosulfate, sulfide, and polysulfides on arsenopyrite dissolution and thioarsenate formation

Thiosulfate is used a lixiviant in industrial leaching processes to increase total dissolution and was observed to become more important for sulfur speciation with increasingly alkaline conditions at which also thioarsenates occurred (see section 3.4. and 3.7.). To determine potential effects of thiosulfate on thioarsenate formation, experiments were conducted in the presence of two different thiosulfate concentrations (3 and 30 µM). As Fig. 7 shows thiosulfate had no significant effects either on total arsenic and sulfur dissolution or on speciation changes at pH 7 or pH 12. A slight increase was observed for total arsenic release at highly alkaline conditions (1.1 times more compared to leaching without thiosulfate) and a slight decrease at neutral conditions (0.8 times less than without thiosulfate). The addition of different thiosulfate concentrations yielded no significant differences. The observed speciation was similar to experiments in the absence of thiosulfate with a predominance of arsenite at neutral conditions (Fig. 7) and 22% monothioarsenate, 35% arsenate and 42% arsenite at alkaline conditions (Fig. 7) after 2 days (compare also to Fig. 4B). Similar observations were made in Zhang's studies adding 50 µM thiosulfate to 50 g/L arsenopyrite leaching in 1.25 M NaOH [33]. The fact that thiosulfate did not increase the net leaching rate nor the formation of thioarsenates confirms that surface or solution complexation of thiosulfate with arsenite is not a significant pathway for thioarsenate formation upon oxidative arsenopyrite dissolution.

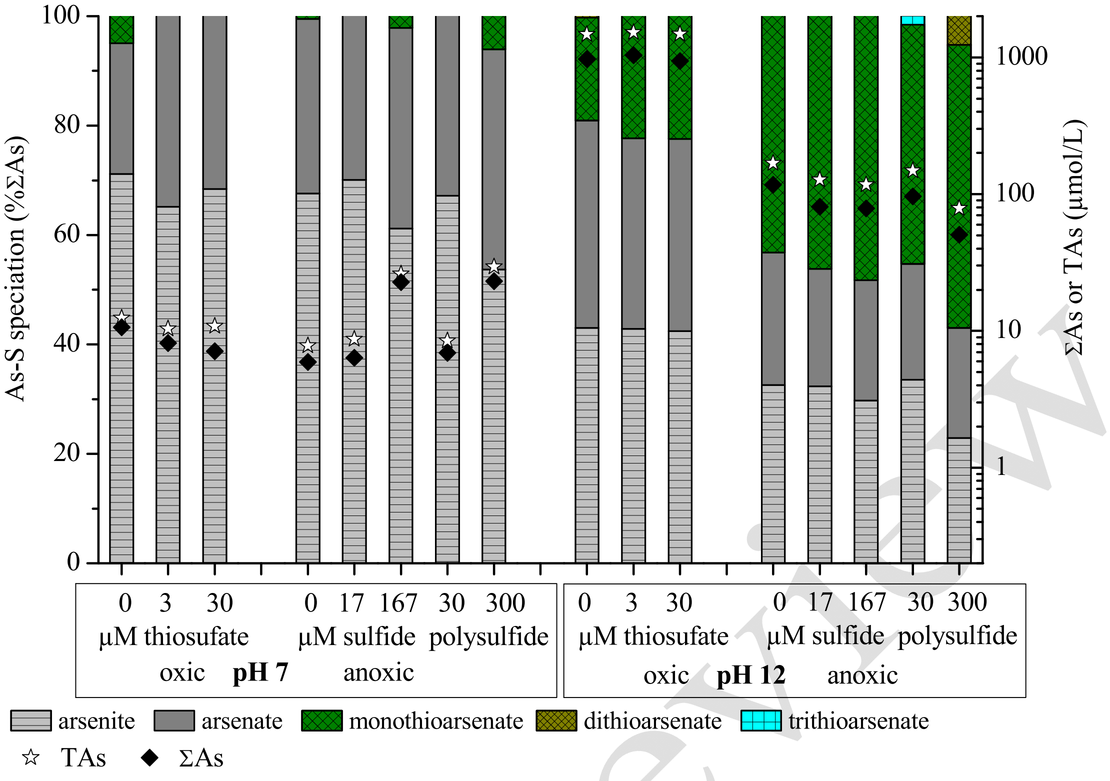


Figure 7: Arsenic speciation in arsenopyrite leachates ($FeAsS_{HA}$) depending on redox-state and solution composition

The effects of sulfide and polysulfides on net arsenic release and thioarsenate formation had to be tested under anoxic conditions to prevent premature oxidation to thiosulfate or sulfate. As it is known that reductive arsenopyrite dissolution is significantly lower than oxidative dissolution [14, 18, 40], comparative leaching experiments were first carried out with oxygen exclusion in the absence of additional sulfur species. Under neutral conditions, total arsenic concentrations in solution decreased by a factor of approximately 2 (Fig. 7). There was no redox-controlled preference for arsenic or sulfur leaching after 2 days. As observed under oxic conditions, more sulfur than arsenic was released (ΣAs/ΣS ratio ~0.4). The arsenic speciation compared well to that under oxic conditions with approximately 70% arsenate and 30% arsenite. The formation of thioarsenates was of minor importance at both, oxic and anoxic conditions (< 5%). The share of sulfide and the non-identified sulfur species increased from 0 and 12% (oxic) to 6 and 14% (anoxic), respectively. At alkaline conditions, the redox-effect was even stronger with a decrease by a factor of 7 under anoxic conditions (Fig. 7). The substantial decrease corresponds to previous observations that oxygen is the main oxidation agent at high pH, while it is ferric iron at low pH [15]. Compared to arsenic, more sulfur was released (ΣAs/ΣS decreased from 0.9 (oxic) to 0.4 (anoxic)). Especially the share of the non-identified sulfur species increased (from 4% to 33%) under anoxic conditions. While arsenite remained stable around 30%, the share of monothioarsenate increased under anoxic conditions (20% to 40%) at the expense of arsenate (Fig. 7, Table EA 5). The higher share of thioarsenates under anoxic conditions could be the result of thioarsenate instability under oxic conditions [64] or an indication for additional formation in solution due to greater release of reduced sulfur species [42].

The presence of sulfide or polysulfides under anoxic conditions enhanced arsenopyrite dissolution at neutral conditions, but suppressed it at highly alkaline conditions (Fig. 6, Table 3). Increasing sulfide or polysulfide concentrations aggravated the effects and in general, polysulfides had a slightly more pronounced effect than sulfide. At neutral conditions, total released arsenic increased by approximately 1.1 at low and 3.9 at high (poly)sulfide concentrations. These observations compare to previous studies in which sulfide was shown to enhance arsenopyrite dissolution under near neutral conditions [30], but only in the presence of at least 2% oxygen, not under anoxic conditions. Since the authors did not study arsenic speciation, they could only speculate that formation of thioarsenic species should drive the dissolution under both (hyp)oxic and anoxic conditions. From the results of the present study we can state, that thioarsenates are neither at oxic nor anoxic conditions predominant arsenic species under neutral conditions. The underlying mechanism for the observed increase in dissolution is thus not clear, yet. Potentially, reduced sulfur species decreased or impeded the formation of arsenic and iron-oxide surface species and thus increased arsenic dissolution. Speciation remained fairly stable with formation of some monothioarsenate (max. 6%) at the expense of arsenite which could be attributed either to solution reactions between arsenite and excess sulfide or polysulfides as reported before [42] or to increased stabilization of released monothioarsenate by excess sulfide in the presence of iron.

At alkaline conditions, dissolution was reduced by a factor of approximately 0.7; at higher polysulfide concentrations even by 0.4 (Fig. 7, Table EA 5). Addition of sulfide and polysulfides leads to a slight increase in thioarsenates from 43% (at pH 12 under anoxic conditions) to 46% and 57%, respectively. Addition of polysulfides induced the formation of dithioarsenate (5%) and trithioarsenate (2%) traces besides monothioarsenate (52%). Since the net total arsenic release decreased at high pH we can assume that neither sulfide nor polysulfide anions trigger the same effect of physisorption, electron transfer and transposition with release of thioarsenates as hydroxyl anions do. On the contrary, competition seems to decrease hydroxyl anion sorption. The increase in thioarsenate species at the expense of arsenite can in this case not be explained by solution reactions between arsenite and excess sulfide or polysulfides as thioarsenites, the necessary intermediate species for thioarsenate formation, cannot form at the highly alkaline conditions. Only a stabilizing effect of the reduced sulfur species in solution on the released thioarsenates seems to explain our observations.

4. Conclusion

In the present study, the formation of aqueous arsenic(V)-sulfur species, so called thioarsenates during dissolution of the sulfide minerals orpiment and arsenopyrite was investigated time-, pH-, and redox-dependent. Special focus was laid on the behavior and thioarsenate formation mechanisms upon arsenopyrite leaching under restricted oxic and anoxic conditions and depending on the composition of the leaching solution in terms of ionic strength, pH, and the presence of aqueous thiosulfate and (poly)sulfide species.

In line with prior knowledge, arsenopyrite showed the lowest leaching rate at near neutral pH, while orpiment dissolution increased base-promoted, yielding the 10-100 fold arsenic release at pH > 7 compared to arsenopyrite. No thioarsenate formation was observed for leaching of both sulfide minerals at acidic conditions which can be explained by precipitation of arsenic-sulfides, instability of thioarsenic complexes, or the release of oxidized sulfur and arsenic species which do not interact to form thioarsenates. At highly alkaline conditions thioarsenates accounted for up to 43% of the arsenic speciation. Thereby orpiment dissolution yielded approximately equal shares of mono-, di-, and trithioarsenate, while only monothioarsenate was formed upon arsenopyrite leaching. From orpiment, thioarsenates were formed already at neutral conditions (50%) with a predominance of the higher SH-substituted trithioarsenate (31%).

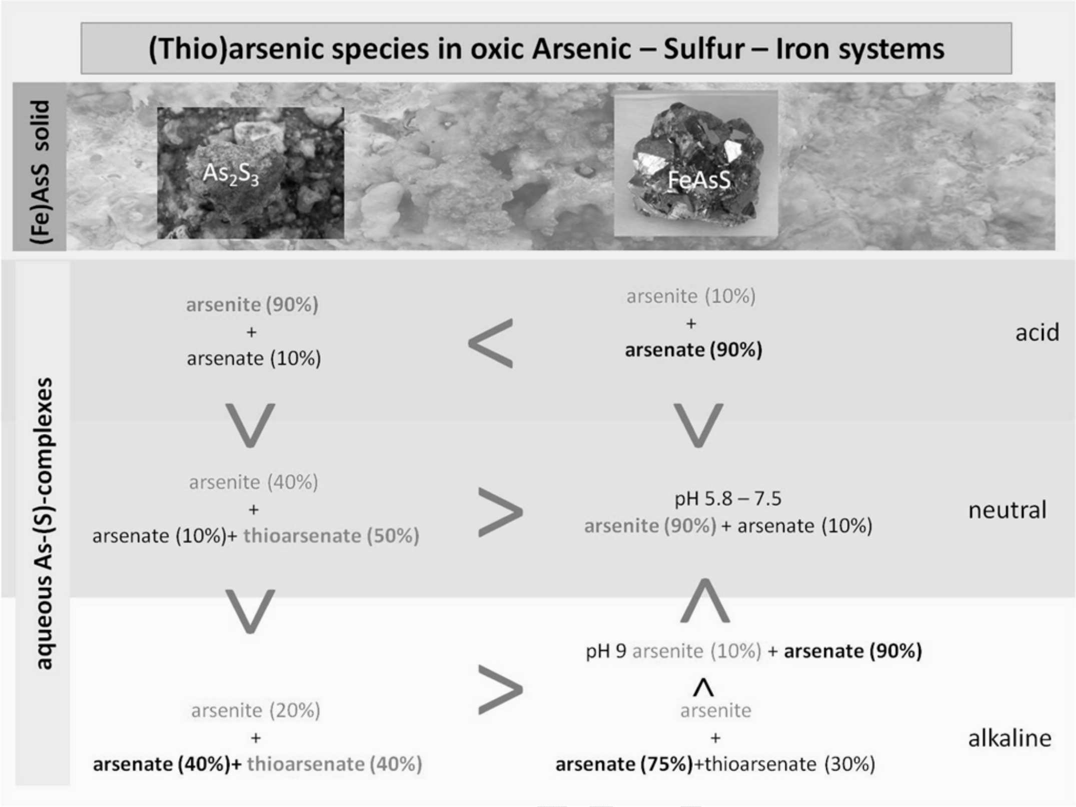


Figure 8: Summary of orpiment vs. arsenopyrite leaching

Different leaching mechanisms cause the observed speciation differences between arsenopyrite and orpiment at neutral and alkaline conditions. Thioarsenate formation from orpiment leaching occurs via recombination of sulfide and arsenite to thioarsenites or direct release of thioarsenites, transforming to thioarsenates under oxic conditions. The speciation pattern matches the recently observed formation of thioarsenates in oxic arsenite-sulfide mixes, with the species distribution depending on the SH:As and OH:SH ratios. In case of arsenopyrite dissolution, physisorption of hydroxyl anions, electro transfer and transposition of hydroxyl to As or Fe sites finally leading to release of monothioarsenate is postulated At neutral conditions possibly iron-arsenic oxide complexation is kinetically favored, which become unstable with increasing pH, where physisorption prevails. The formation of ironhydroxides upon arsenopyrite dissolution under alkaline conditions provides possible sorption sites for the released arsenic species. However, batch experiments showed that sorption efficacy and kinetics follow the order arsenite > arsenate > mono-thioarsenate, revealing the highest mobility for monothioarsenate and a much less effective retention compared to arsenate and arsenite.

Under completely anoxic conditions, arsenopyrite dissolution is significantly reduced. However, in the presence of (poly)sulfides, leaching could be increased at least for neutral conditions by approximately a factor of 4 at the highest applied concentrations of 167 and 300 µM sulfide and polysulfide, respectively. The share of monothioarsenate increased slightly, probably due to a stabilizing effect of the reduced sulfur species in solution. However this slight increase cannot explain the general increase in total released arsenic as previously speculated. Thiosulfate, an industrial lixiviate for gold leaching, did not change speciation or total arsenic release for neutral and alkaline oxic leaching. Total arsenic release was increased by increasing the ionic strength of the leaching solution from 4 to 800 mM $NaHCO_3$ (pH 8-9). Thereby, total arsenic release was comparable to that upon NaOH addition (40-800 mM) at pH 12-13, potentially due to formation of arsenic-carbonate or iron-carbonate complexes. However, while at high pH substantial thioarsenate formation was observed (maximum 40%), the share of thioarsenate remained low in the high-ionic-strength $NaHCO_3$ solutions which further supports the hypothesis of thioarsenate formation as a result of physisorption of hydroxyl anions.

Overall the present study has shown that thioarsenates, even the higher sulfur-substituted trithioarsenate, are potential species released during dissolution of arsenopyrite and orpiment at (highly) alkaline conditions as well as at neutral conditions for orpiment. Apart from natural settings, such conditions also exist e.g. in calcite-treated tailings or industrial alkaline leaching facilities. As the released monothioarsenate shows lower potential for re-sorption onto secondary ironhydroxides compared to arsenate and arsenite its environmental mobility and toxicity must be taken into account for future assessment studies in sulfidic environments.

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Appendix E - Stabilization of thioarsenates in iron-rich waters

Elke Suess, Dirk Wallschläger, and Britta Planer-Friedrich

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Appendix F - Enrollment Form

PhD program for

Ecology and Environmental Research

Erklärungen zur Promotionsarbeit **„Investigations towards a better understanding of arsenic-sulfur speciation in aquatic environments: Formation, stability, structural characterization, and conflicting analyses“**

Eingereicht von **Frau Elke Süß**, geb. **23.03.1980**

Hiermit erkläre ich, dass ich die vorliegende Promotionsarbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Bayreuth, 15.02.2011 Elke Süß

(Elke Süß)

Hiermit erkläre ich, dass ich nicht bereits anderweitig versucht habe, diese Dissertation ohne Erfolg einzureichen oder mich einer Doktorprüfung zu unterziehen.

Bayreuth, 15.02.2011 Elke Süß

(Elke Süß)

Hiermit erkläre ich, dass ich die Hilfe von gewerblichen Promotionsberatern bzw. -vermittlern weder bisher in Anspruch genommen habe, noch künftig in Anspruch nehmen werde.

Bayreuth, 15.02.2011 Elke Süß

(Elke Süß)