Fe-As-S systems (E. Suess)

As-S complexes in solution

Natural systems:
* Alkaline springs YNP, ≈ 80% thioarsenates
  ~ 30-50 % AsS\_3O\_3\_3\_3, TA\_s 2.5 mg/L
* Mono Lake, ≈ 45% thioarsenates,
  ≈ 30% AsS\_3O\_3\_3\_3, TA\_s 15 mg/L
* Bengal GW, ≈ 10 % AsSO_3^-\_3, TA\_s 0.15 µg/L

Synthetic solutions:
* arsenite-sulfide mixes
* thioarsenate solutions

(Thio)arsenic species in Arsenic – Sulfur – Iron systems

(Fe)AsS-solid phases
Minerals As\_2S\_3, AsS, FeAsS, precipitates, surface complexes

* arsenite-sulfide mixes
* thioarsenate solutions

* oxidative dissolution = Fe, As, S and As-S-complex formation? S
* stability/ stabilization of thioarsenates in presence of iron

Stability of thioarsenates and preservation strategies for Fe-containing systems
Submitted:
Thioselenates in iron-rich waters
Suess, E., Wallschlaeger, D., and Planer-Friedrich, B.

**SPECIATION AFFECTS:**
- mobility \(\rightarrow\) environmental behavior
- toxicity, biotic metabolism

**EVALUATION \(\gg\) \(\gg\) ACURATE SPECIATION AFFECTED BY:**
- microorganisms
- precipitation/sorption/colloids
- redox agents ((photo)oxidation, reduction)

> > > SAMPLE STABILIZATION/PRESERVATION

**Common preservation strategies for arsenic speciation**
(key-papers)

- preservation of redox-sensitiv species (e.g., As) \(\rightarrow\) filtration, acidification, storage – cool+light exclusion (e.g., McCleskey 2004 (Review), Samanta 2006a (AWWA Publication), Daus 2002)

**PROBLEMS:**
- radical formation/photo-oxidation \(\rightarrow\) HCl, HNO\(_3\), Fe(III) \(\rightarrow\) light exclusion (e.g., Emmett and Khoe, 2001)
- H\(_3\)PO\(_4\) / H\(_2\)SO\(_4\) precipitation with metal cations
- As-S precipitation in sulfidic systems (Smeja 2003, Samanta 2006b)
- thioarsenate instability (Planer-Friedrich 2009, Suess 2009)
  \(\rightarrow\) FLASH-FREEZING (N\(_2\)(aq.), DRY-ICE)

Suess et al. (submitted): Thioselenates in iron-rich waters
Fe-As-S systems (E. Suess)

Experimental set-up to test thioarsenate preservation strategies: flash-freezing and headspace influence

Suess et al. (submitted): Thioarsenates in iron-rich waters

Stabilization of thioarsenates by flash-freezing

- arsenite/arsenate >98% recovery over 21 days N₂/O₂
- best preservation small headspace, N₂ → variability < 3%
- di- and tetrathioarsenate best stability, also O₂/N₂ → variability < 3%, but: matrix 1% EtOH, 0.1 M NaOH
- EtOH and NaOH → improved monothioarsenate stability (variability <1%)
- effect: NaOH → protection against “attack” of H⁺
  EtOH → preference for reaction with O₂

>>> organic solvents and high ionic strength may increase stability of thioarsenates

>>> test for BSc-thesis: EtOH, MeOH, NaOH, NaCl (references + mixes + concentrations)
Common preservation strategies for arsenic speciation (key-papers)

- preservation of redox-sensitive species (e.g., As) → filtration, acidification, storage – cool+light exclusion (e.g., McCleskey 2004 (Review), Samanta 2006a (AWWA Publication), Daus 2002)

**PROBLEMS:**

- radical formation/photo-oxidation → HCl, HNO₃, Fe(III) → light exclusion (e.g., Emett and Khoe, 2001)
- $\text{H}_2\text{PO}_4$/ $\text{H}_2\text{SO}_4$ precipitation with metal cations
- **As-S precipitation in sulfidic systems** (Smeja 2003, Samanta 2006b)
- thioarsenate instability (Planer-Friedrich 2009, Suess 2009)

→ **FLASH-FREEZING (LN, DRY-ICE)**

**but:** Fe containing systems → FeOOH precipitation + co-adsorption

→ EDTA + acidification (e.g., McCleskey 2004, Gallagher 2001, Polya 2003, Bednar 20043) OR acidification+CEC –resins (Fe³⁺) (Oliveira 2006, Samanta 2006) ⇝ thioarsenate stability

- sulfidic systems → Fe-S complexes

→ **OCCURRENCE OF THIOARSENATES IN FE-RICH WATERS?**

→ **STABILITY OF THIOARSENATES TOWARDS Fe(II) AND EDTA**

→ **PRESERVATION STRATEGY: EDTA + FLASH-FREEZING**

→ **SUMMARY + IDEAS FOR FUTURE WORK**

Suess et al. (submitted): Thioarsenates in iron-rich waters

Thioarsenates in iron-rich waters?

- pH-dependence of thioarsenates
- formation of Fe-S complexes

**but:** → mineral spring waters in Czech Republic up to 17% thioarsenates (mono-, di-)

→ pH 5.5 – 6.1, 0.02 – 1.2 mM Fe

stabilization of field water samples (Maria’s work):

- 65% HNO₃ → no precipitation, “true” totals
- arsenic loss HCl > EDTA >> flash-freezing

>>> thioarsenates occur in Fe-systems

>>> TAS-preservation with HNO₃

>>> speciation = challenge

Suess et al. (submitted): Thioarsenates in iron-rich waters

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Experimental set-up to test thioarsenate stability in iron-rich waters: influence of Fe(II), EDTA, Fe(II)+EDTA+flash-freezing

Tests to evaluate effects of:
- EDTA-addition (pH 4.5, pH 7, 12.5 mM for ca. 9 mM Fe, Bednar et al. 2002)
- Fe(II) (1.8 mM ≈ 100 mg Fe/L)

preservation Fe(II)-thioarsenate systems by:
- EDTA + flash-freezing

Influence of Fe(II) on thioarsenates

- decrease of ΣAs
- conversion to arsenite, lower SH-substituted thioarsenates
- monothioarsenate least affected
- trend increased by flash-freezing (11 days) 33% (mono-) – 77% (di-) = arsenite TAs ≈ 50% initial, without Fe(II)

>>> preservation required
>>> use of EDTA+flash-freezing

but: EDTA = acid application  test on thio’s

Suess et al. (submitted): Thioarsenates in iron-rich waters
Fe-As-S systems (E. Suess)

**EDTA application to thioarsenate solutions**
- pH 4.5 conversion dithioarsenate → arsenite (~20%)
- strongest Fe-EDTA complex at acidic conditions

>>> EDTA-neutralization

>>> stability for at least 7 days flash-frozen

- variabilities < 3% (mono-dithioarsenate), < 10% (trithioarsenate)

**Stabilization of thioarsenates in Fe(II) solutions by EDTA (pH 7) & flash-freezing**
- initially:
  - species and ΣAs preservation for mono- and dithioarsenate
  - tri- 47% vs. 22% without EDTA

- flash-freezing 11 days:
  - slight decrease for ΣAs
  - speciation preserved for mono- and dithioarsenate (variability < 1%, di- → mono-fraction! → arsenite)
  - tri- 29% vs. 5% without EDTA

>>> improvement of thioarsenate preservation by > 50% (systems with Fe)
Summary

- Acidification → destruction of thioarsenates → but HNO₃ for TAs!
- Stability of thioarsenates by flash-freezing (best N₂, SHS) up to 21 days
  → sampling → exclusion of O₂ – gas-bags, septum-vials or “septum-vial-like” flow-trough cell + syringe
  → need of flash-freezing vs. anoxic storage
- Matrix stabilizing effect (EtOH, NaOH) → test thioarsenate stability + mixes with MeOH, EtOH, NaOH, NaCl → METHOD ICP-MS!!!!
- Thioarsenates occur in Fe-rich waters (Czech mineral spring waters)
- TAs (HNO₃), species preservation high variable depending on method → day 0 sample!, sampling strategies as stated above/below (after lab tests, e.g. storage, sampling under N₂ – unfrozen/flash-frozen, ! exclusion of light is important!)
  + Fe(II) → conversion to arsenite, increasing effect with time/cryo-storage
  + Fe(III) + EDTA → at least immediately stability thioarsenates → Czechs samples
- Increase of EDTA, test other complex agents HIDS, siderophores (Chaston 2003, Rahman 2009), ferrozin → pre-tests with thio’s, Fe(II)/Fe(III)/mixes, O₂/N₂, sample matrix (NaCl, ...)

OVERALL:

→ minimizing O₂ influence

→ TAs for totals, speciation as %TAs, improvement of species preservation method

Suess et al. (submitted): Thioarsenates in iron-rich waters
Thioarsenate formation through oxidative dissolution of (Fe)AsS-minerals

Background

- arsenic association with sulfides: arsenian pyrite, arsenoyprie, Engarite CuAsS$_4$, orpiment, realgar
  - natural leaching $\rightarrow$ release of sulfide, arsenic, iron $\ldots$ $\rightarrow$ effect GW, surface water
- sulfides "hosts" for Au and other valuable metals/minerals
  - mining, recovery/leaching $\rightarrow$ tailings $\rightarrow$ effect mine drainage, remain leaching solutions
- gold recovery $\rightarrow$ alkaline oxidation (high pH, also tailings pH $>$ 10 (calcite), CN-leaching $\rightarrow$ flotation, bio-oxidation/bio-leaching (acidic pH) $=$ pre-step’s

>>> necessity to understand leaching process
  * "natural" weathering in tailings/aquifers/soil $\rightarrow$ acidic to neutral conditions
  * industrial recovery plants – remaining leacheates $\rightarrow$ acidic and high alkaline conditions

>>> influence factors
  * redox-conditions (oxic, anoxic), agents increases/inhibit leaching (sulfur species)

>>> to evaluate effects for:
  * natural systems (weathering – aquifer, mine drainage)
  * recovery processes (increase efficacy, precipitation/complexes)
  * subsequent steps to remove toxic metals (arsenic) from the leachates
  * protection of tailings against weathering
Fe-As-S systems (E. Suess)

In preparation:
**Formation of thioarsenates during oxidative dissolution of arsenopyrite and orpiment**
Suess, E. and Planer-Friedrich, B.

**FeAsS dissolution**
- alkaline oxidation as refractory technique for Au
- acid mine drainage – pyrite weathering
- thioarsenate/thioarsenite formation suggested by Bou et al. 1998, Rosovsky 1993
- Zhang 2004 → determination of thioarsenates during oxidative alkaline leaching
- further publications of FeAsS dissolution → mainly kinetics & surface analyses, no investigations of As-S speciation

**Key-papers:**

- **Suess & Planer-Friedrich in preparation**
**Formation of thioarsenates during oxidative dissolution of arsenopyrite and orpiment**

**As$_2$S$_3$ dissolution**
- Eary et al. 1992, Webster et al. 1990, Helz & Tossel 2008 propose thioarsenite formation
- Helz & Tossel 2008 concede thioarsenate formation
- Planer-Friedrich et al. 2010 – thioarsenites redox-instable!

Further publications with focus on kinetics, minor species detection:

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Fe-As-S systems (E. Suess)

**Experimental set-up - Batch and open vessel leachings**

**FeAsS batch leaching (Canada)**
- 0.025g FeAsS (< 10 µm)
- 40 mL solution (0.04 M NaHCO₃/0.1 M NaOH)

Variables: pH (2-13), kinetics (10⁻⁵-35d), additional amendments thiosulfate/(poly)sulfide, matrix strength NaOH, NaHCO₃

**FeAsS & As₂S₃ open vessel leaching (Bayreuth)**
- 0.19 g FeAsS / 0.14 g As₂S₃
- 300 mL solution (0.1 M NaOH (pH 12), 0.04 M NaHCO₃ (for pH 2 and 6), natural water (NW, pH 6, Erzgebirge)

Variables: pH (2, 6, 12), temperature (room temperature (RT) and 30°C), air conditions (open and closed system)

Suess & Planer-Friedrich (in preparation): Oxidative As-S mineral dissolution

**Oxidative dissolution of FeAsS:**
**Modeling ▲ vs. leaching experiments (24 h ▲, 5 days ▼)**

modeling → strong dissolution high alkaline / acid milieu

experiments → 30-40% total dissolvable As (TDₐs) at high alkaline cond., pH < 12 TDₐs < 1%

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Fe-As-S systems (E. Suess)

Results oxidative dissolution experiments – FeAsS
Sulfur and arsenic release for pH 2-13

Results oxidative dissolution experiments – FeAsS
Release of sulfur vs. arsenic

As>Fe>S
metal depleted S-rich surface

As, Fe<S
precipitates/surface coatings– iron and arsenic oxides, sulfates (solubility increases with pH)

As:Si:1
Fe(hydr)oxides, surface coatings thick but porous, solubility of iron -arsenic oxides
Results oxidative dissolution experiments - FeAsS:
Dissolution kinetics & comparison of two different FeAsS's

• **FG < HA** (small mineral in matrix vs. solid block,
  factor As(S)_{HA} / As(S)_{FG} ≈ 3)
• sharp increase pH 2 – nearly no slow down
• only pH 12/13 “equilibrium” (2-3 days), pH 5-9 slow down of leaching rates after 2-3 days
• max release 160/580 µM/L pH 2, 10-70 µM pH 5-9, 600/2500 µM pH 13

Results oxidative dissolution experiments – FeAsS:
arsenic-sulfur speciation

initially
• arsenite predominance (pH 5, 7),
  +arsenite pH 9-13 (+ thios), arsenate pH 2 = initial release of arsenite, iron(II) → reduced species
  = pH 2 dissolution of surface AsV-oxides?, oxidation by Fe(III)? = also at pH 2-9 thios, but (< 2%)
  with increasing reaction time:
• arsenic share increases for pH’s 2-7.5 → release of surface As(III), reduction by Fe(II)
  • minimum pH 5-7 → switch of main oxidant from O_{2} to OH
  = release As(V) species + thioAs(V)-species = increase with time (≈ + 10%)

>>> “long-term view” As(III) predominates in acid and neutral conditions
>>> As(V) species with thioarsenates (25% mono-) in weak alkaline to high alkaline conditions, e.g. high alkaline leaching and calcite treated tailings!
Fe-As-S systems (E. Suess)

Results oxidative dissolution experiments – FeAsS

pH- and ionic strength depending As-S dissolution and speciation

- NaHCO₃, pH 8-9
- NaOH, pH 11-13

- TAs ↑ (factor > 200) = NaOH
- Speciation 50-60% arsenite, 50-40% arsenate,
- High ionic strength → monothioAs(V) (3%)
- Speciation agrees with pH pH 5-7(9)

- No influence TAs
- Thioarsenate-formation ↑
- NaOH ≤ 0.04 M → As(III), As(V) ≈ 50%
- NaOH > 0.4 M → As(V)-species (30-40% thio’s)
- Agrees with "long-term" pH 12/13 speciation = faster oxidation process by OH

Results oxidative dissolution experiments – FeAsS

Addition of sulfur species

- Decrease of dissolution under N₂ (minor extensive at pH 7) → higher pHs – O₂ impact on dissolution greater
- Addition of (poly)sulfide → enhanced FeAsS dissolution under N₂ (pH 7), no effect at pH 12, slight increase thio’s
- Thiosulfate no effect TAs, speciation (cf. gold-leaching) – Zhang same results, but low concentrations (< 30 µM S)
Results oxidative dissolution experiments – FeAsS

SUMMARY

- bimodal leaching behavior; pH2 > pH 5 <pH 7-9<pH12
- slow down of dissolution rates after 2-3 days, not for acidic conditions, pH 12/13 equilibrium after 2 – 3 days
- speciation (long-term) >>> arsenite pH 2-7.5 (8); AsV-species pH > 9; thio’s pH 12/13 up to 25%
- avoidance of O2 reduced release sharply \(\rightarrow\) under anoxic (neutral) conditions enhanced dissolution in presence of sulfide
- thiosulfate no leaching effect
- increasing matrix strength \(\rightarrow\) increases dissolution (with NaHCO3) comparable to pH 12/13, no thioarsenates species – arsenite vs. AsV-species (+thios) with NaOH

Does orpiment (=system with only As and S) show a similar leaching behavior?

Oxidative dissolution of FeAsS vs. As\(_2\)S\(_3\) – TAs-relaease

>>> FeAsS minimum pH 7 \(\leftrightarrow\)As\(_2\)S\(_3\) increase with pH
>>> efficacy FeAsS < As\(_2\)S\(_3\) (pH 7, 12)
>>> FeAsS leaching \(\rightarrow\) time depending \(\leftrightarrow\) As2S3 only pH 7
(pH 2 slow and pH 12 fast kinetics – no time effects for observed time frame)
- both experiments: open system > closed system
- only slight T influence (RT vs. 30°C)
Fe-As-S systems (E. Suess)

Oxidative dissolution of FeAsS vs. As$_2$S$_3$ – speciation

FeAsS leaching
• pH 2 AsIII > AsV
• neutral cond. AsIII > AsV
• at high alkaline conditions – thioarsenates + AsV (oxidative dissolution)
• pH 12 – with time thioarsenate formation (better with less O$_2$)

As$_2$S$_3$ leaching
• pH 2 AsIII
• neutral cond. formation of thioarsenates (tri-)
• at high alkaline conditions – thioarsenates (mono-, di-, tri-) + AsV
• with time AsV ↑ at pH 12

(Thio)arsenic species in oxic Arsenic – Sulfur – Iron systems

(Fe)AsS solid

arsenite (90%)
arsenate (10%)

arsenite (10%)
+ arsenate (90%)

arsenite (40%)
+ arsenate (10%) + thioarsenate (50%)

arsenite (90%)
+ arsenate (10%)

arsenite (40%)
+ thioarsenate (50%)

arsenite (20%)
+ arsenate (40%)
+ thioarsenate (40%)

arsenite (10%) + arsenate (90%)

pH 5.8 – 7.5

arsenite (90%) + arsenate (10%)

arsenite
+ arsenate

pH 9 arsenite (10%) + arsenate (90%)

arsenite (75%) + thioarsenate (30%)

pH ≥ 14

aqueous As-(S)-complexes

acid

neutral

alkaline