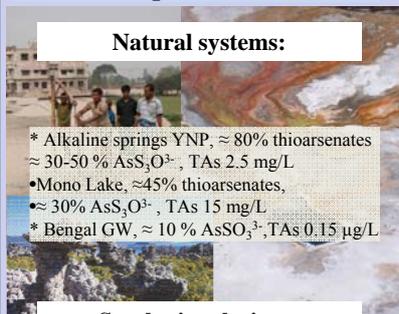


As-S complexes in solution

Natural systems:



- * Alkaline springs YNP, ≈ 80% thioarsenates
≈ 30-50 % AsS_3O_3^- , TAs 2.5 mg/L
- Mono Lake, ≈ 45% thioarsenates,
≈ 30% AsS_3O_3^- , TAs 15 mg/L
- * Bengal GW, ≈ 10 % AsSO_3^3- , TAs 0.15 $\mu\text{g/L}$

Synthetic solutions:

- * arsenite-sulfide mixes
- * thioarsenate solutions

oxic → thioarsenates



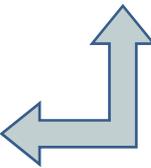
IC-ICP-MS

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

(Fe)AsS-solid phases



Minerals As_2S_3 , AsS, FeAsS, precipitates, surface complexes

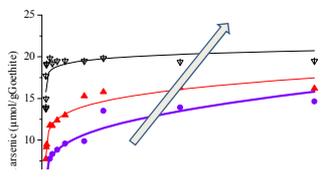


- ▶ **(oxidative) dissolution = Fe, As, S and As-S-complex formation? S**
- ▶ **stability/ stabilization of thioarsenates in presence of iron**

Stability of thioarsenates and preservation strategies for Fe-containing systems

Submitted:
Thioarsenates in iron-rich waters
 Suess, E., Wallschlaeger, D., and Planer-Friedrich, B.

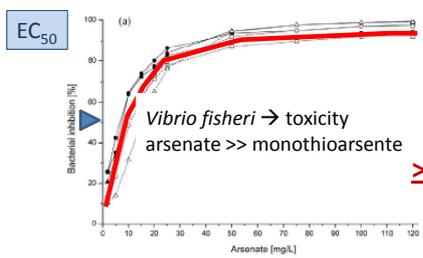




sorption increase
 arsenite > arsenate > monothioarsenate

SPECIATION AFFECTS:

- * mobility → environmental behavior
- * toxicity, biotic metabolism



EC₅₀

Vibrio fischeri → toxicity
 arsenate >> monothioarsenate

AFFECTED BY:

- * microorganisms
- * precipitation/sorption/colloids
- * redox agents ((photo)oxidation, reduction)

>>> SAMPLE STABILIZATION/PRESERVATION

from: Planer-Friedrich et al., ETCJ, 2008

Common preservation strategies for arsenic speciation (key-papers)

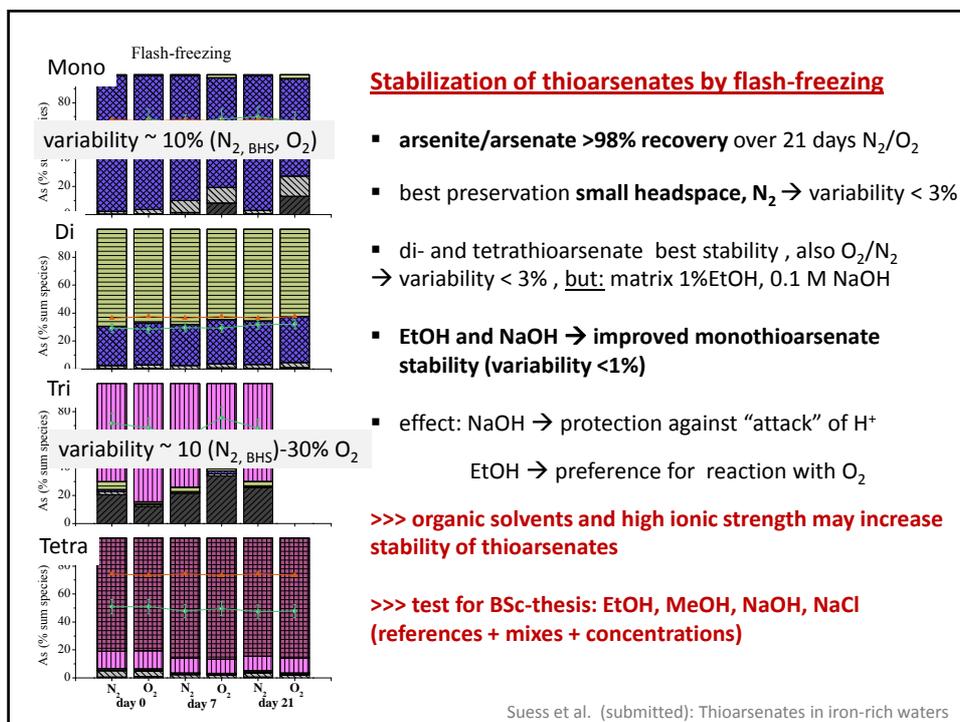
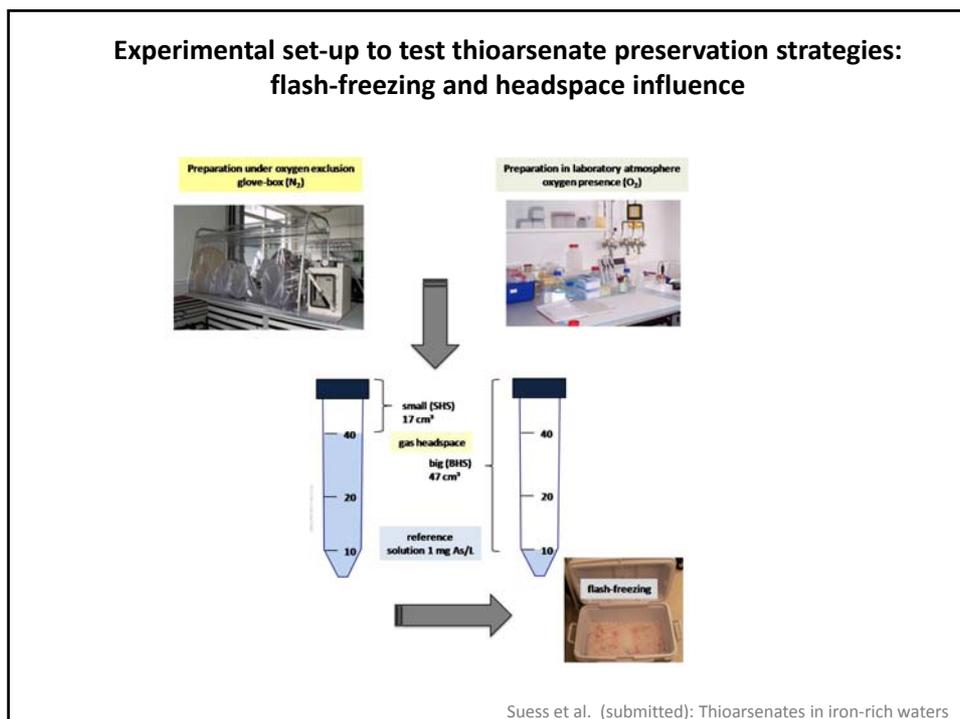
- preservation of redox-sensitiv species (e.g., As) → filtration, acidification, storage – cool+light exclusion (e.g., McCleskey 2004 (Review), Samanta 2006a (AWWA Publication), Daus 2002)

PROBLEMS:

- radical formation/photo-oxidation → HCl, HNO₃, Fe(III) → light exclusion (e.g., Emmett and Kloe, 2001)
- H₃PO₄ / H₂SO₄ precipitation with metal cations
- **As-S precipitation in sulfidic systems** (Smeja 2003, Samanta 2006b)
- **thioarsenate instability** (Planer-Friedrich 2009, Suess 2009)

→ FLASH-FREEZING (N₂(aq.), DRY-ICE)

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



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- **thioarsenate instability** (Planer-Friedrich 2009, Suess 2009)

→ FLASH-FREEZING (LN, DRY-ICE) ✓

→ BEST N₂, SHS, + STRONG MATRIX

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

→ EDTA + acidification (e.g., McCleskey 2004, Gallagher 2001, Polya 2003, Bednar 20043) Or

acidification+CEC –resins (Fe²⁺ !) (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

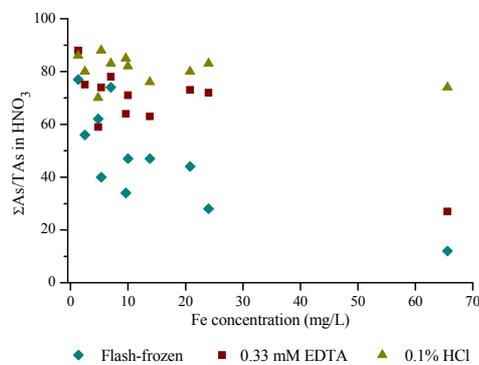
Thioarsenates in iron-rich waters?

- 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

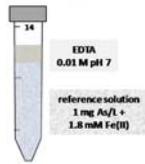
>>> TAs-preservation with HNO₃

>>> speciation = challenge

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

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

Preparation under oxygen exclusion
glove-box (N₂)



Tests to evaluate effects of:

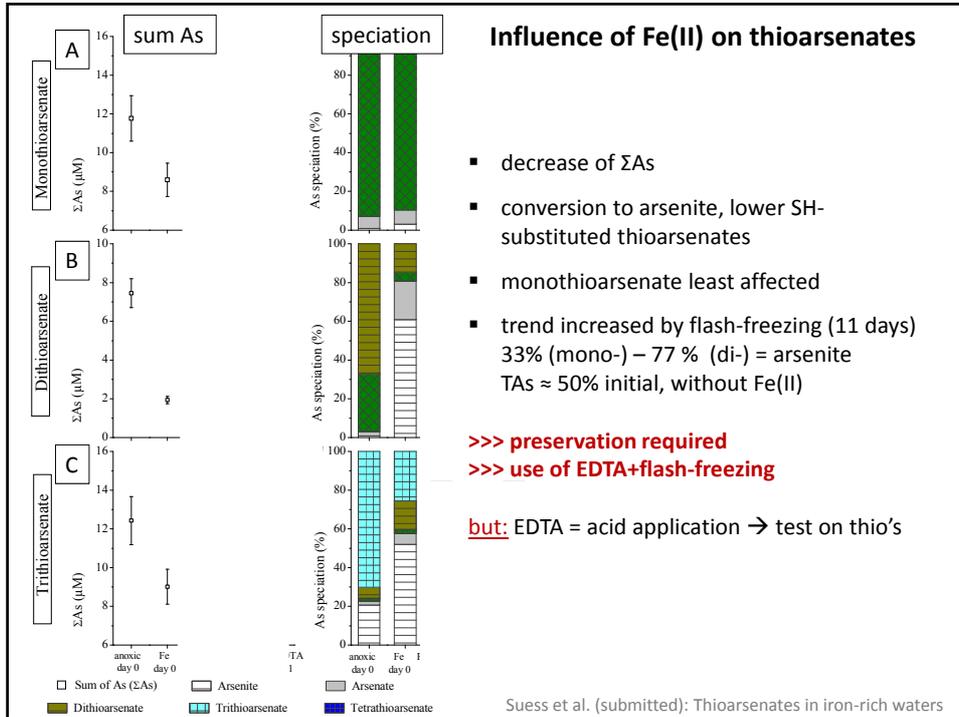
- EDTA-addition (pH 4.5, pH 7, 12.5 mM for ca. 9 mM Fe, Bednar et al. 2002)
- Fe(II) (1.8 mM \pm 100 mg Fe/L)

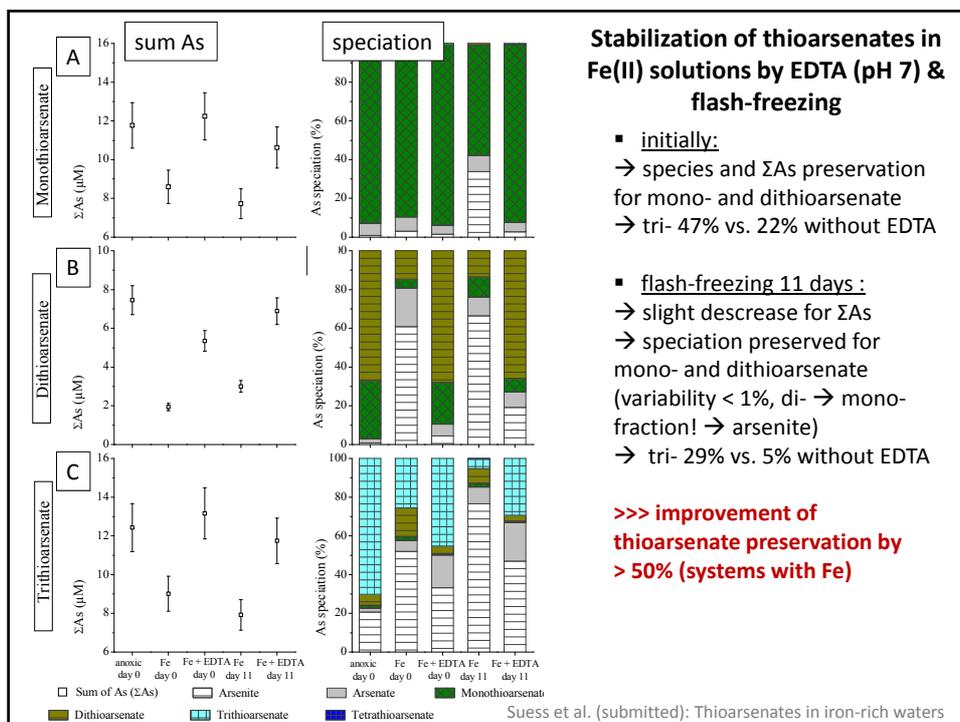
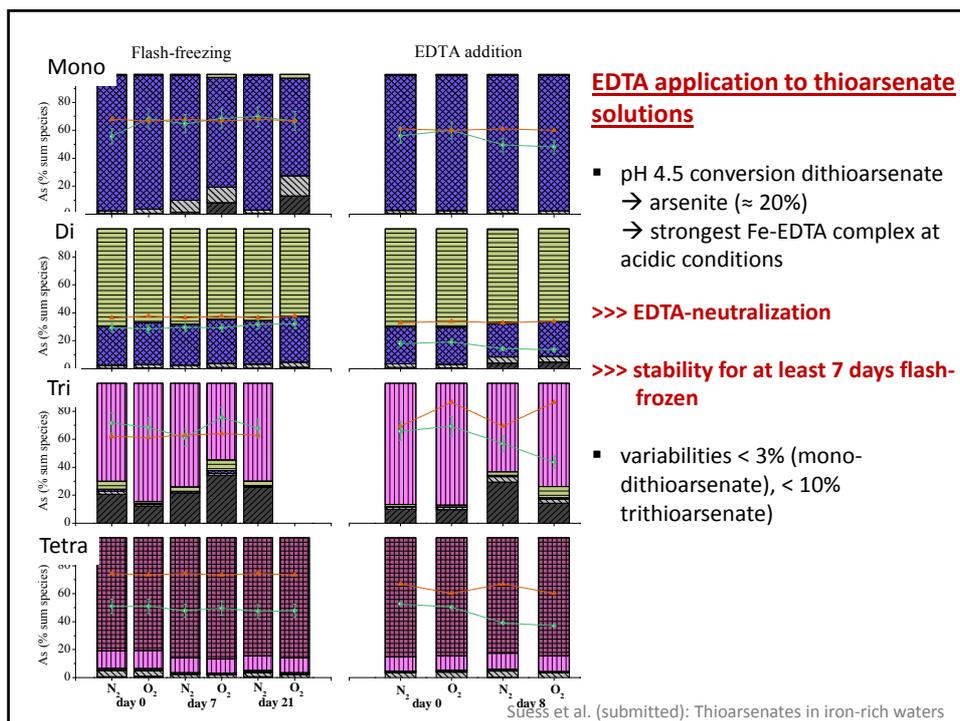
preservation Fe(II)-thioarsenate systems by:

- EDTA+ flash-freezing



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





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(II) + 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, ...)**

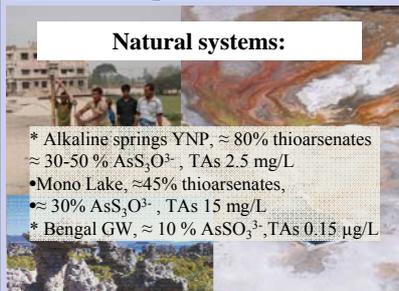
OVERALL:

- **minimizing O₂ influence**
- **TAs for totals, speciation as %TAs, improvement of species preservation method**

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

As-S complexes in solution

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IC-ICP-MS

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

(Fe)AsS-solid phases



Minerals As₂S₃, AsS, FeAsS, precipitates, surface complexes

▶(oxidative) dissolution = Fe, As, S and As-S-complex formation?

▶stability/ stabilization of thioarsenates in presence of iron

Thioarsenate formation through oxidative dissolution of (Fe)AsS-minerals

Background

- arsenic association with sulfides: arsenian pyrite, arsenopyrite, Enargite CuAsS_4 , orpiment, realgar
- = natural leaching → release of sulfide, arsenic, iron → effect GW, surface water

- sulfides “hosts” for Au and other valuable metals/minerals

- = mining, recovery/leaching → tailings → effect mine drainage, remain leaching solutions
- gold recovery → alkaline oxidation (high pH, also tailings pH > 10 (calcite), CN-leaching → flotation, bio-oxidation/bio-leaching (acidic pH) = pre-step's

- >>> **necessity to understand leaching process**
 - * “natural” weathering in tailings/aquifers/soil → acidic to neutral conditions
 - * industrial recovery plants – remaining leachates → 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

In preparation:
Formation of thioarsenates during oxidative dissolution of arsenopyrite and orpiment

Suess, E. and Planer-Friedrich, B.



FeAsS
 = 34% Fe, 46% As, 20% S

FeAsS dissolution

- alkaline oxidation as refractory technique for Au
- acid mine drainage – pyrite weathering
- thioarsenate/thioarsenite formation suggested by Bou et al. 1998, Rossovsky 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**

Yu	2007	Rates of Arsenopyrite Oxidation by Oxygen and Peroxide at pH 1.8, 12.6 and 15-45 °C
Rossovsky	1993	Alkaline Leaching of Refractory Gold Arsenosulfide Concentrates
Walker	2006	Kinetics of arsenopyrite oxidative dissolution by oxygen
Buckley	1988	The surface composition of arsenopyrite exposed to oxidizing environments
Nesbitt	1995	Oxidation of arsenopyrite by air and air-saturated, distilled water, and implications for mechanism
Nesbitt	1998	Oxidation states and speciation of secondary products on pyrite and arsenopyrite reacted with H ₂ O ₂
Bou	1998	Kinetics of the interaction of gold chloride solutions on arsenopyrite
Yu	2004	A kinetic study of the oxidation of arsenopyrite in acidic solutions. Implications for the environment
Rutenberg	1999	The ferric leaching kinetics of arsenopyrite
Potterovskii	2002	Stability and solubility of arsenopyrite, FeAsS, in crustal fluids
Liang	2008	Reoxidation of arsenopyrite
McKibben	2008	Kinetics of inorganic arsenopyrite oxidation in acidic aqueous solutions
Rawlings	2008	High level arsenic resistance in bacteria present in biooxidation tanks used to treat gold-bearing ores
Zhu	2008	Sulfide-driven arsenic mobilization from arsenopyrite and black shale pyrite
Corkhill	2009	Arsenopyrite oxidation - A review
Lengke	2009	The oxidation and dissolution of arsenic-bearing sulfides
Ma	2009	Rejection of arsenic minerals in sulfide flotation - A literature review
Acta	2010	Arsenopyrite dissolution rates in O ₂ -bearing solutions
Zhang	2004	The effect of arsenopyrite concentration on the kinetics of arsenopyrite dissolution
Zhang	2004	Oxidation of refractory gold concentrates and simultaneous dissolution of gold in alkaline solutions

Key-papers:

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

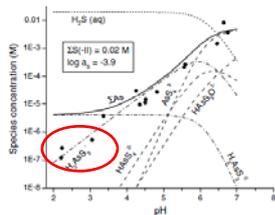
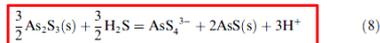


Fig. 3. Solubility of orpiment (Webster, 1990) compared to predictions from the model. Activity of zero-valent sulfur (a_S) controlled by orpiment + realgar. Concentrations of 32 species in equilibrium with H₂AsO₄ (given by reaction LL) were computed, but only those that contribute significantly to the solubility are shown.

As₂S₃ 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:

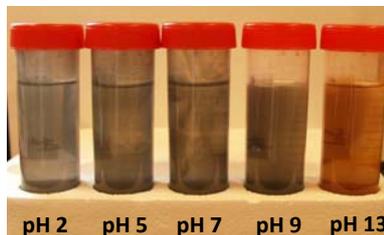
Eary	1992	The solubility of amorphous As ₂ S ₃ from 25 to 90°C (revised)
Webster	1990	The solubility of As ₂ S ₃ and speciation of As in dilute and sulphide-bearing fluids at 25 and 90°C
Lengke	2005	Geochemical modeling of arsenic sulfide oxidation kinetics in a mining environment
Lengke	2010	Reaction rates of natural orpiment oxidation at 25 to 40°C (revised) and pH 6.8 to 8.2 and on
Weissberg	1966	Solubility of orpiment (As ₂ S ₃) in H ₂ S-H ₂ O at 50-200°C and 100-1500 bars, with geological ap
Mironova	1990	The solubility of orpiment in sulfide solutions at 25-150°C and the stability of arsenic sulfide comp...
Lengke	2009	The oxidation and dissolution of arsenic-bearing sulfides

Experimental set-up - Batch and open vessel leachings

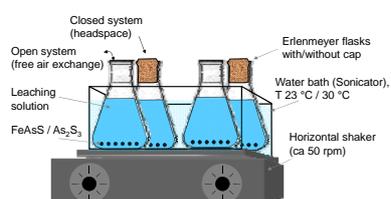
FeAsS batch leaching (Canada)

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

Variables: pH (2-13), kinetics (10''-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)

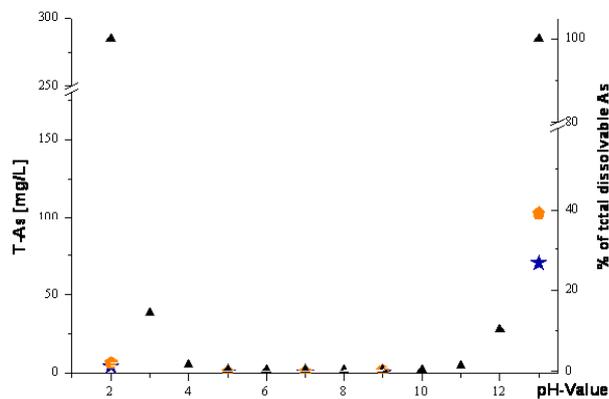
Suess & Planer-Friedrich (in preparation): Oxidative As-S mineral dissolution

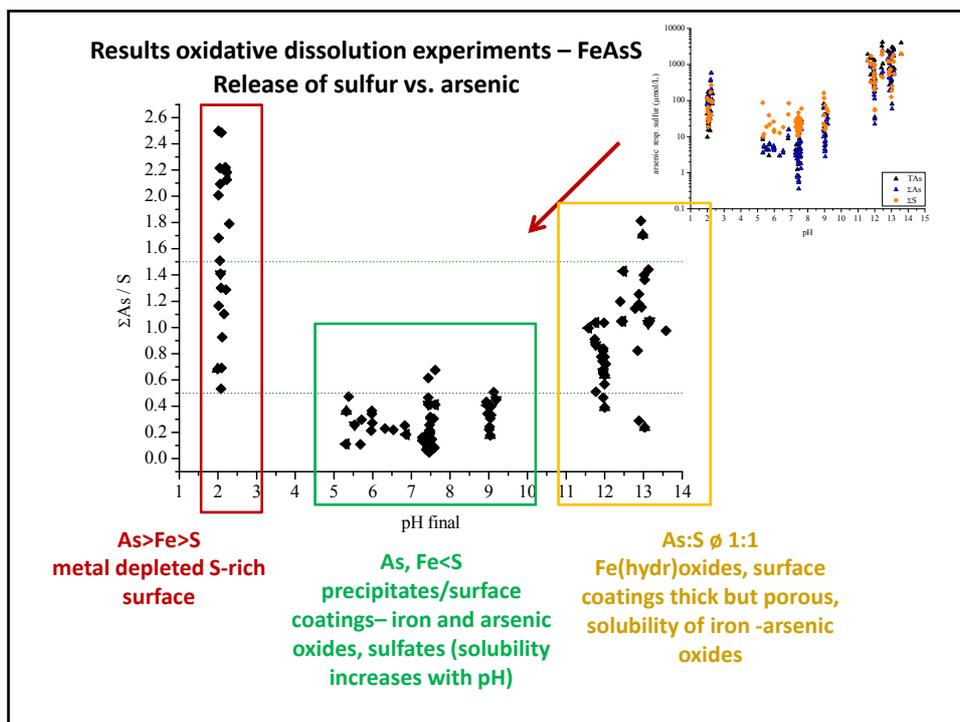
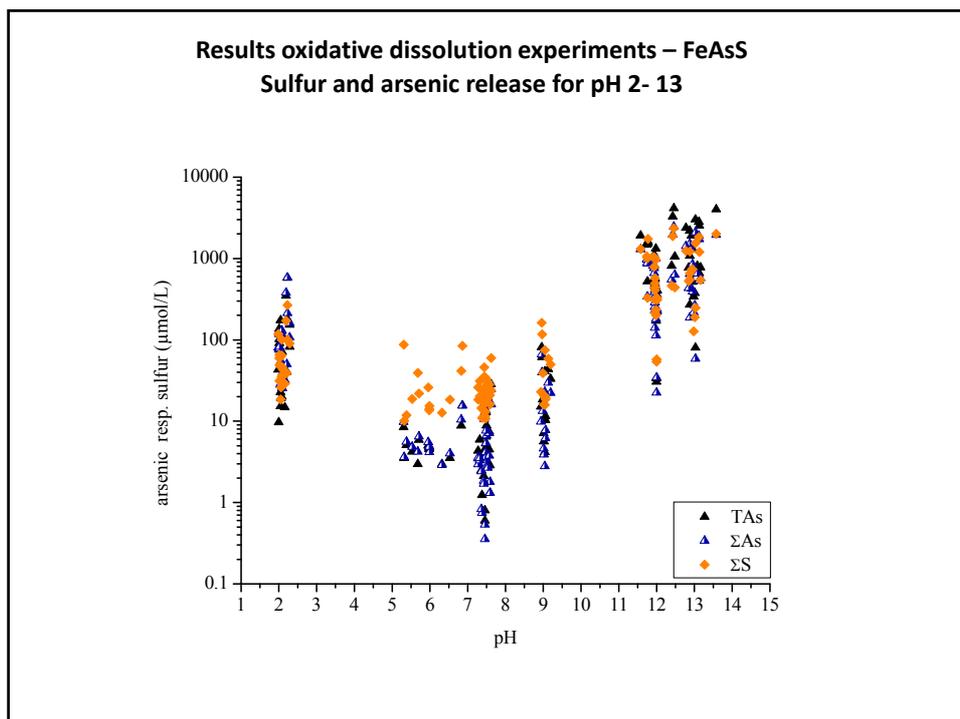
Oxidative dissolution of FeAsS:

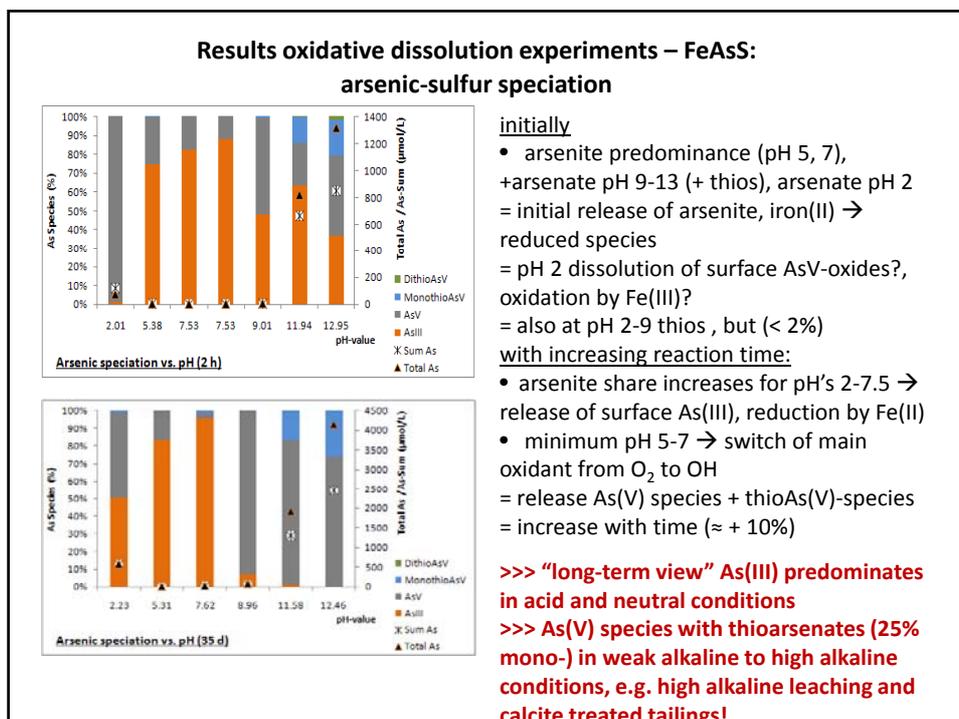
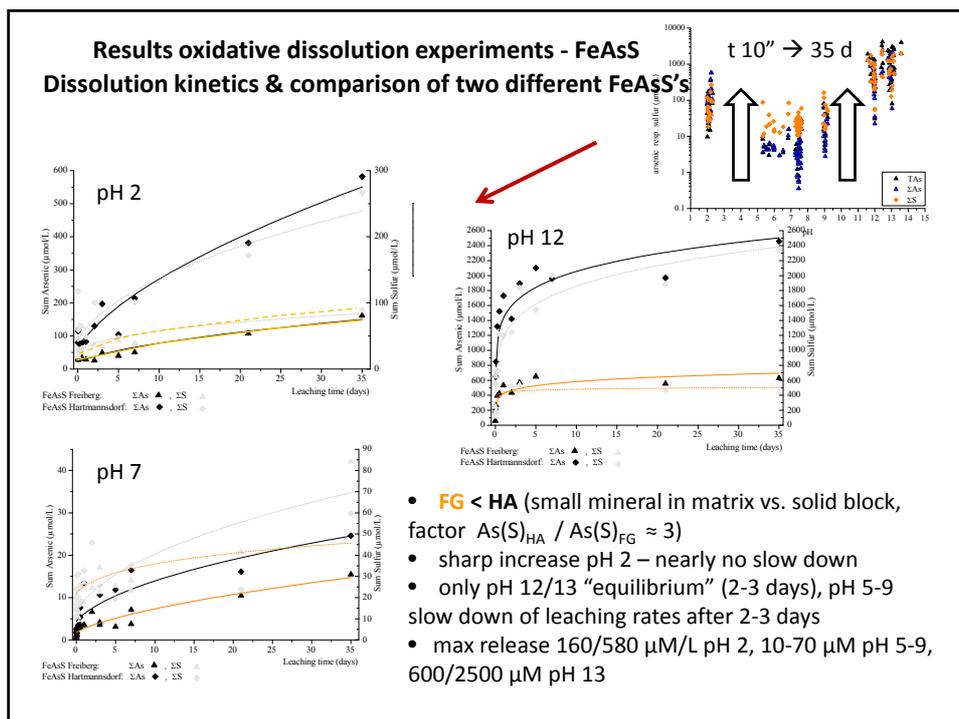
Modeling ▲ vs. leaching experiments (24 h ★, 5 days ◆)

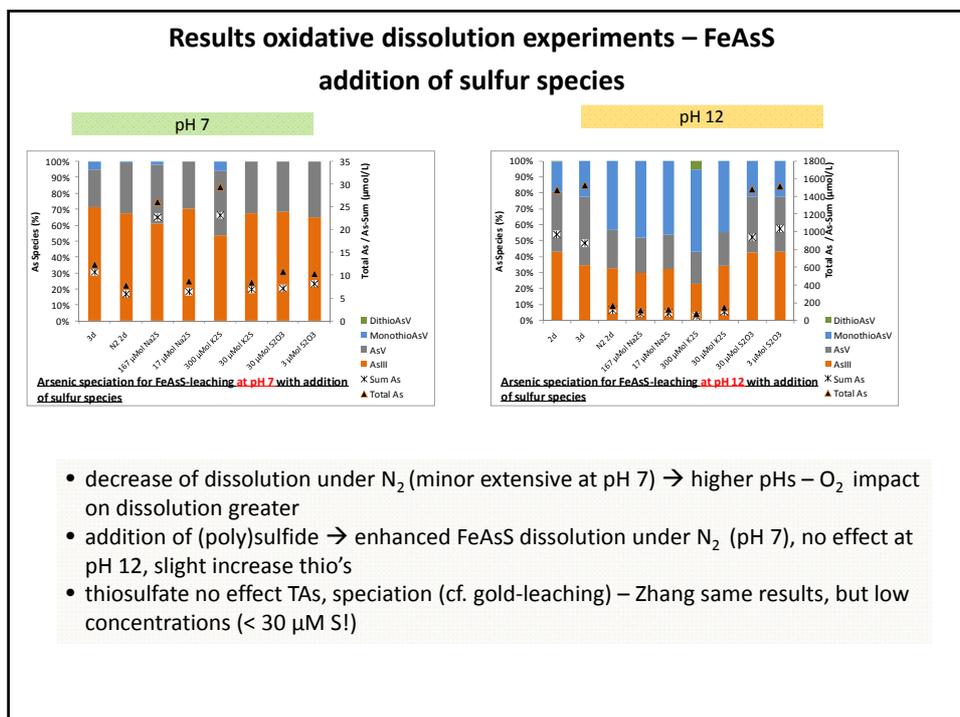
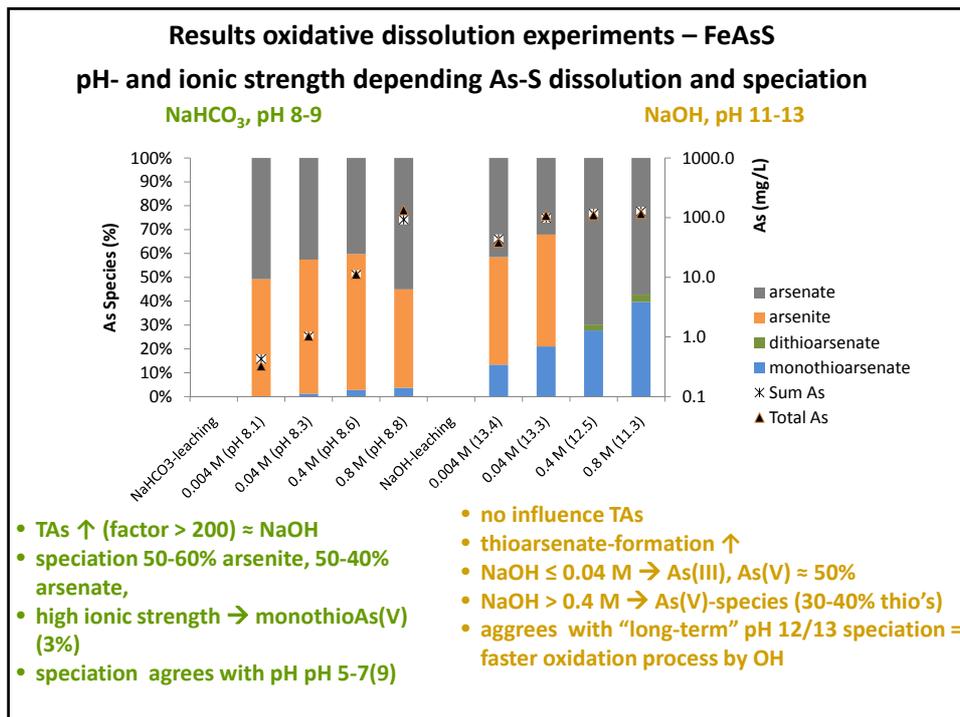
modeling → strong dissolution high alkaline / acid milieu

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







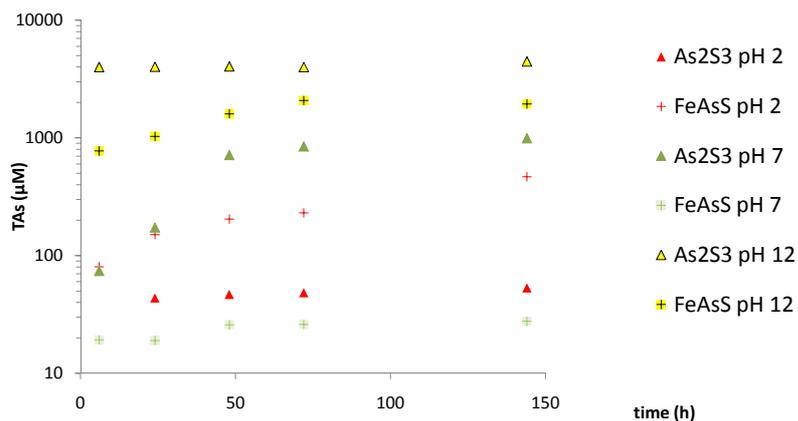


**Results oxidative dissolution experiments – FeAsS
SUMMARY**

- bimodal leaching behavior; pH 2 > pH 5 < pH 7-9 < pH 12
- 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 → under anoxic (neutral) conditions enhanced dissolution in presence of sulfide
- thiosulfate no leaching effect
- increasing matrix strength → 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. As₂S₃ – TAs-release



- >>> FeAsS minimum pH 7 ↔ As₂S₃ increase with pH
- >>> efficacy FeAsS < As₂S₃ (pH 7, 12)
- >>> FeAsS leaching = time depending ↔ 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)

