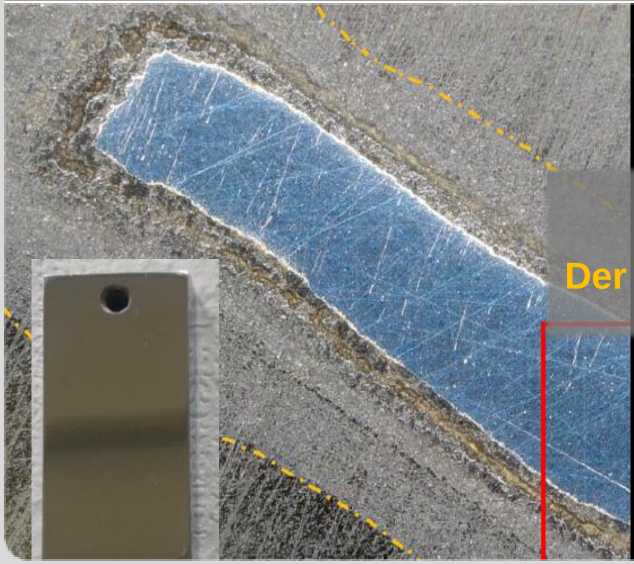
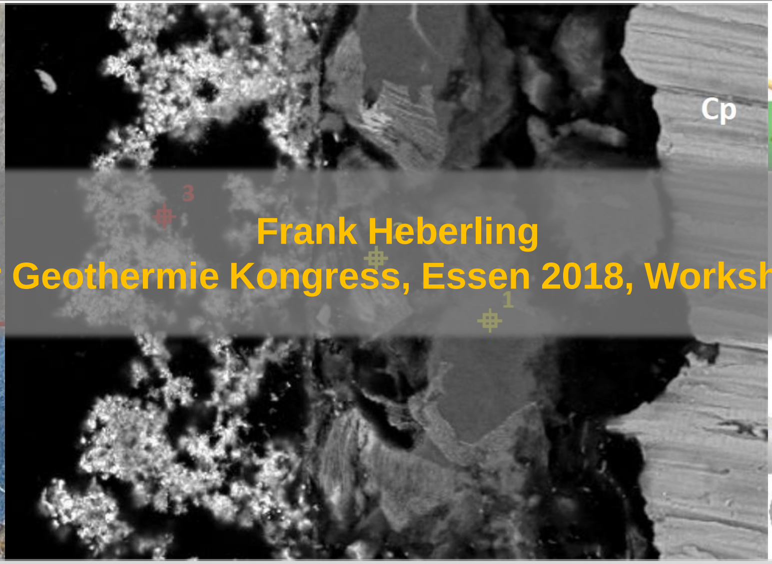
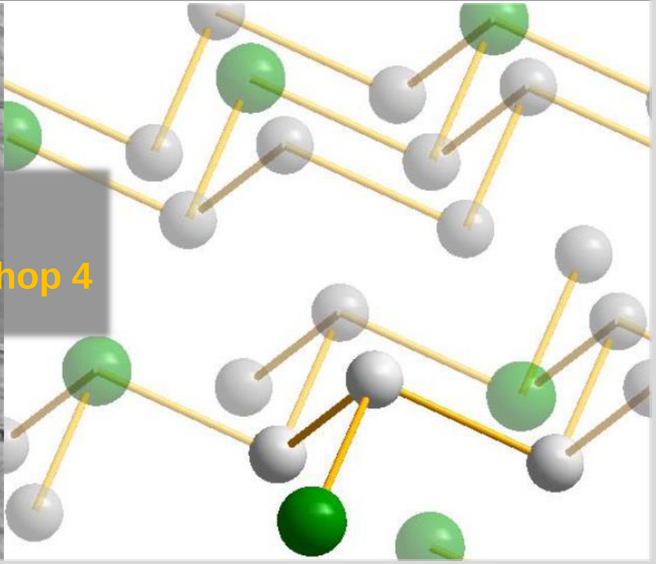
Karlsruhe Institute of Technology

Mineralogical characterization of scalings formed in the presence of a sulfate inhibitor – links between scale formation and corrosion

Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (INE)







Frank Heberling
Der Geothermie Kongress, Essen 2018, Workshop 4

Collaborators

- KIT-INE
  - **Fabian Duske**
  - Dieter Schild
  - Christian Marquardt
  - Jörg Rothe
  - Kathy Dardenne
- KIT-AGW
  - Elisabeth Eiche
  - Ruth Haas-Nüesch
  - Jochen Kolb

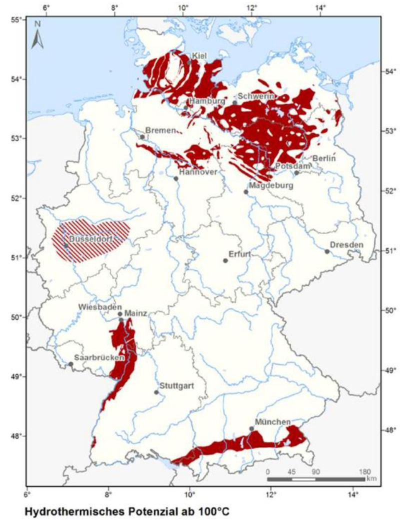
Collaborative Project **SUBITO** (BMWi)

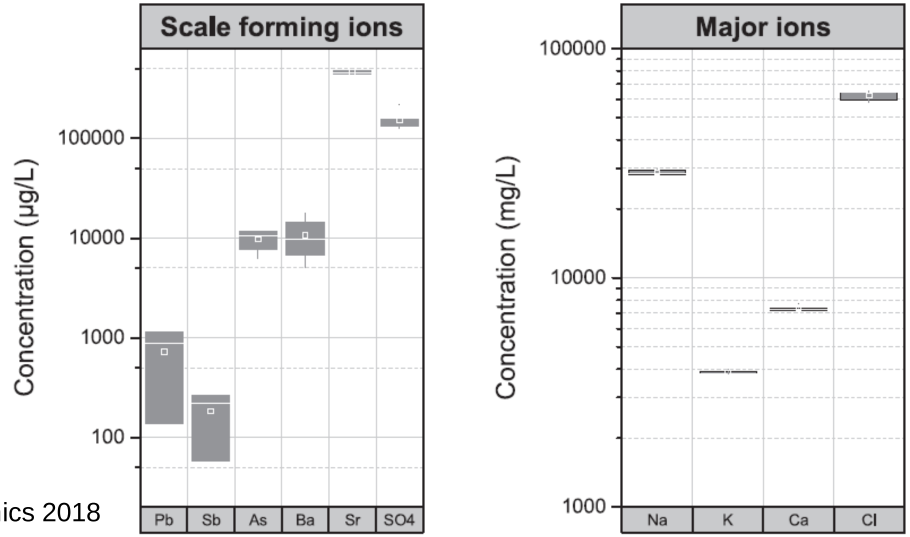
- Bestec GmbH
  - Julia Scheiber
  - Gitta Wahl
- VKTA Dresden
  - Sabine Jähnichen
  - Detlev Degering
- Aqua-Titan, Umwelttechnik GmbH
  - Tobias Otto
- BWG, Geochemical Consulting
  - Andrea Seibt
- GTN, Geothermie Neubrandenburg GmbH
  - Christian Buse
- Pfalzwerke, Geofuture GmbH
  - Jörg Uhde

Conditions in the Upper Rhein Graben

- The Upper Rhein Graben is known for its potential for deep geothermal energy production with Temperatures ≥ 150°C in ≥ 3000 m depth.
- Carboniferous granite aquifers (Sanjuan et al., Chem. Geol., 2016)
- Brines are dominated by NaCl (~2 mol/L)
- Main scale forming ions: Sr^{2+}, SO_4^{2-}, Ba^{2+}(sulfate phases); As, Pb, Sb (sulfidic / elementary phases)
- Dissolved CO_2 + Ca^{2+} could form $CaCO_3$ scalings. These can, however, efficiently be avoided by pressure control

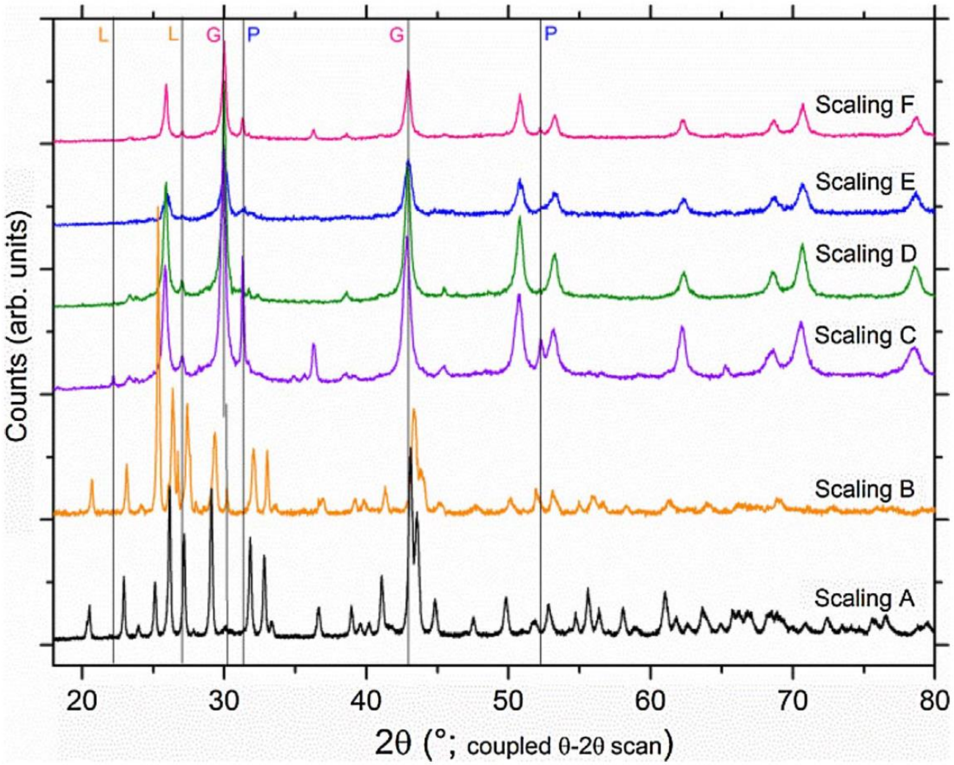
Agemar et al. 2018



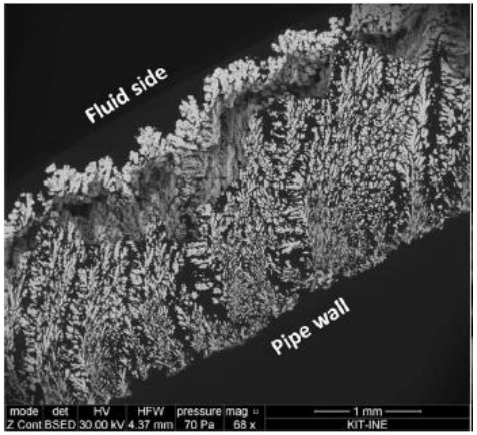


Haas-Nüesch et al.,Geothermics 2018

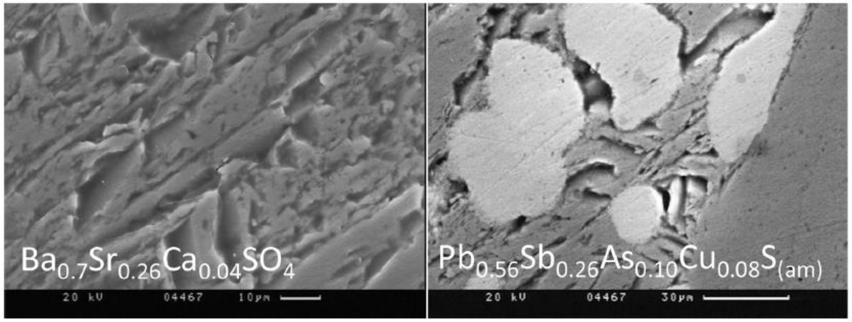
Scalings before and after sulfate inhibition



Since application of a phosphonic acid based inhibitor, scales dominated by Galena (PbS) and amorphous (Sb, As) with minor Pb(0)

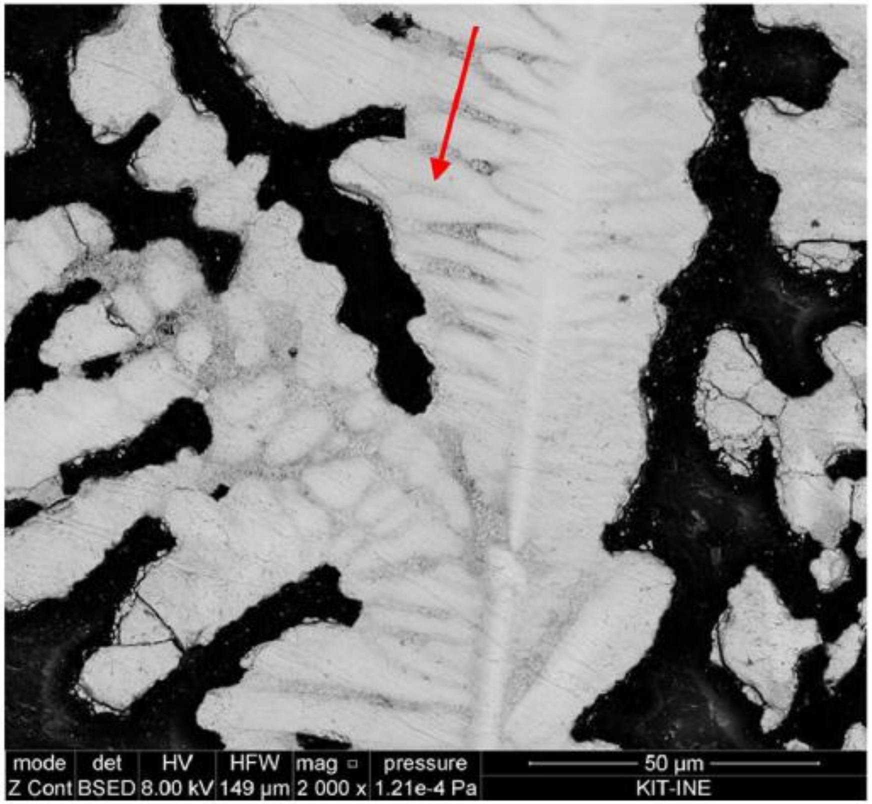


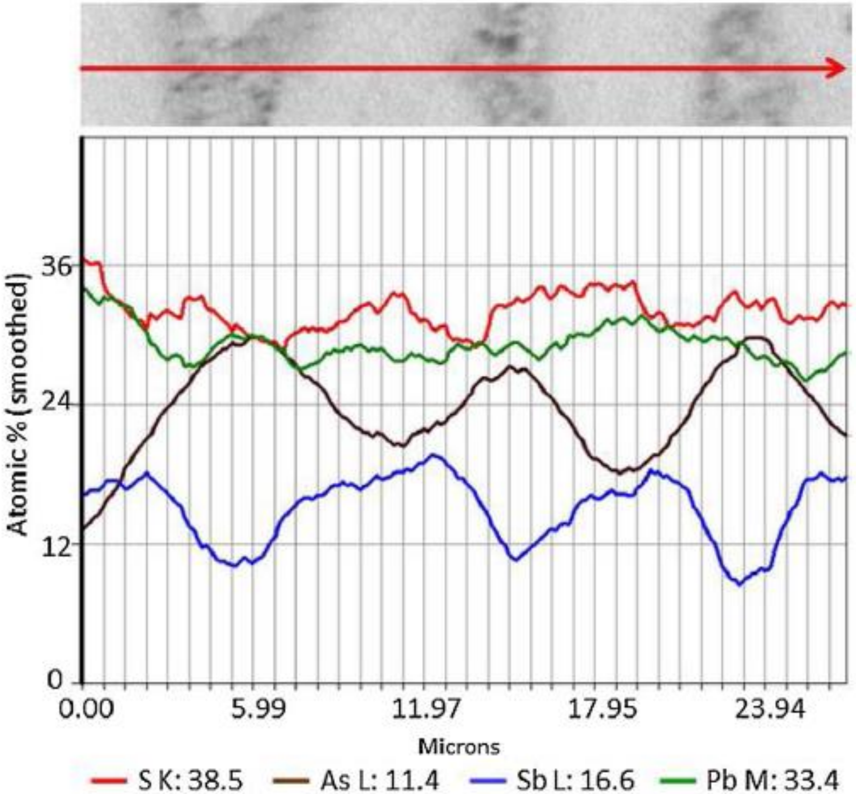
Before application of an inhibitor scalings dominated by a $(Ba,Sr,Ca)SO_4$ solid-solution + minor (ca. 14 %) sulfide minerals (Pb,Sb,As,Cu)S or Galena (PbS)



Figures from: Haas-Nüesch et al.,Geothermics 2018

What do the dendritic structures consist of?

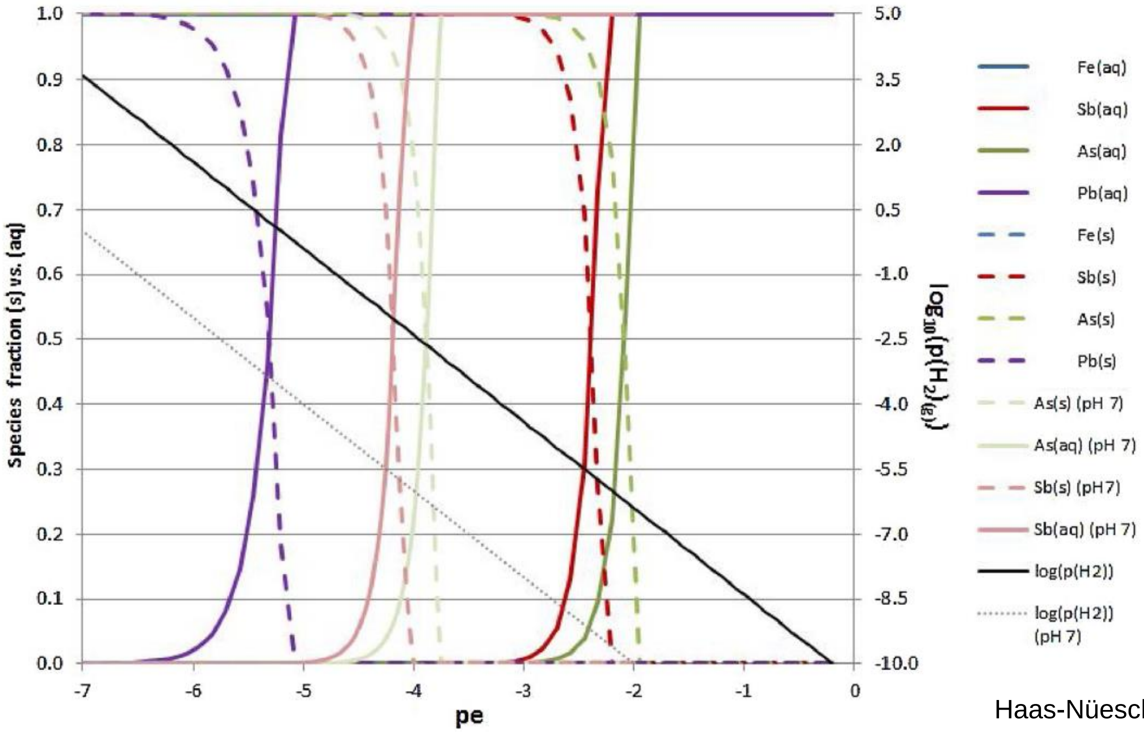




Haas-Nüesch et al.,Geothermics 2018

- Pb and S ca. 1:1; As and Sb with variable content; clearly not as sufides
- No separate PbS and (As,Sb) phases discernible

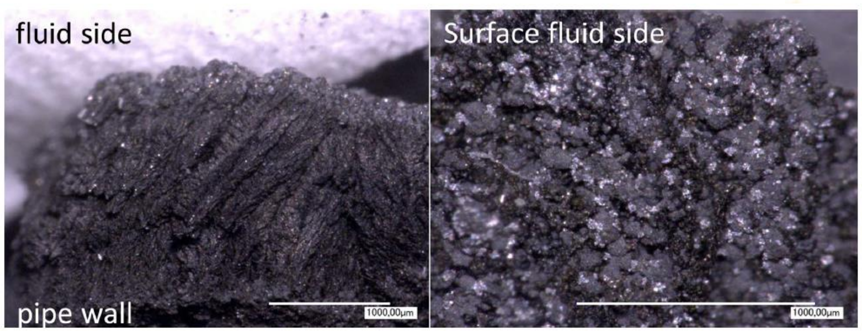
Redox-Reactions of Pb, Sb, As (and Fe)



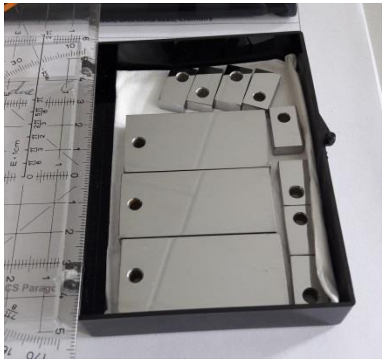
Haas-Nüesch et al.,Geothermics 2018

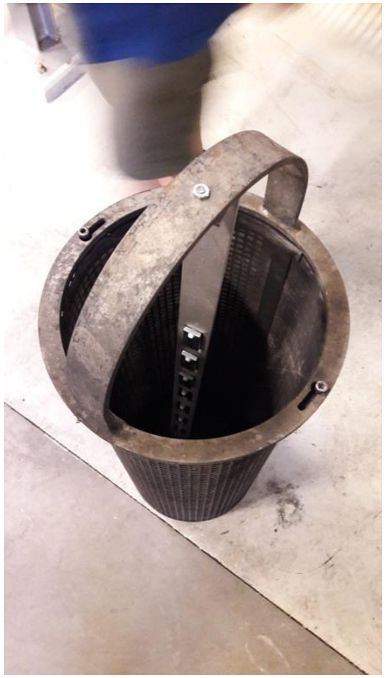
- As and Sb reduced before Pb at pH 5 (and 7) in 2 M NaCl; all three far more noble compared to Fe.
- Electrochemical reduction of As, Sb, Pb in conjunction with Fe-Corrosion?

Scaling sampling campaign



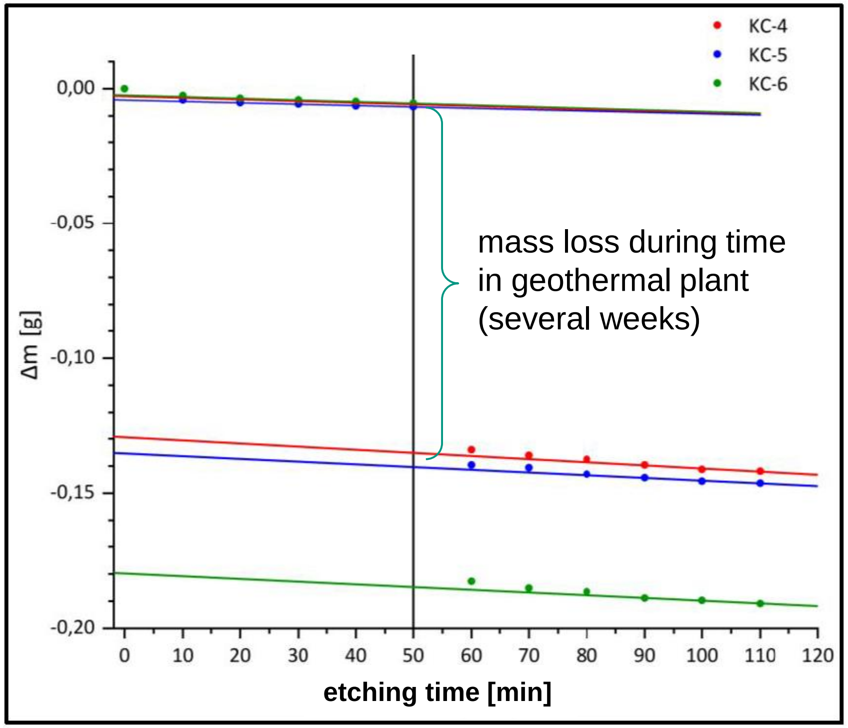
Combined corrosion and scaling analysis





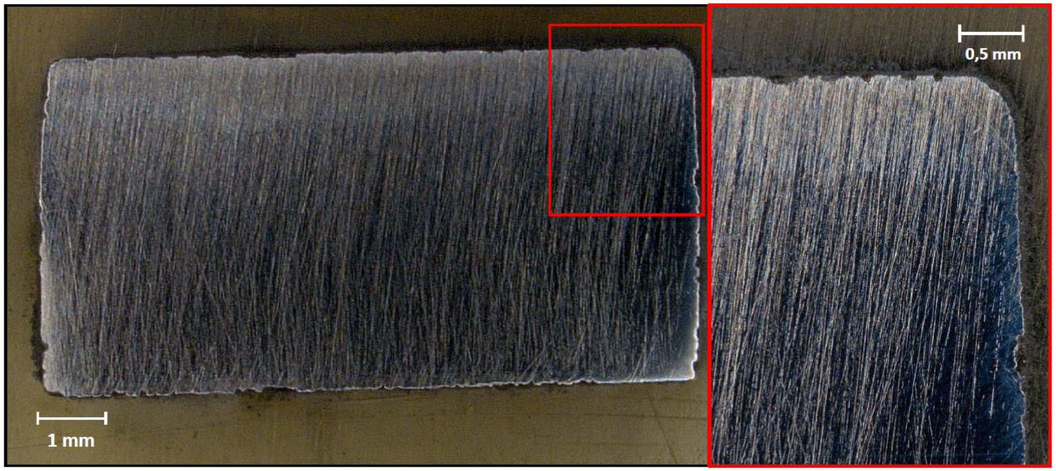
- Polished mild steel coupons (pipe material from geothermal power plant)
- Introduced into the thermal water circuit (low temperature side) for several weeks
- Most coupons mounted with electric isolation, some in contact to test galvanic / contact corrosion

Coupon mass loss (ASTM)



- Low corrosion rates (on isolated coupons!)
- Range from 0.06 mm/a to 0.27 mm/a
- Average: 0.08 ± 0.02 mm/a (n=5)

Severe effect of contact corrosion

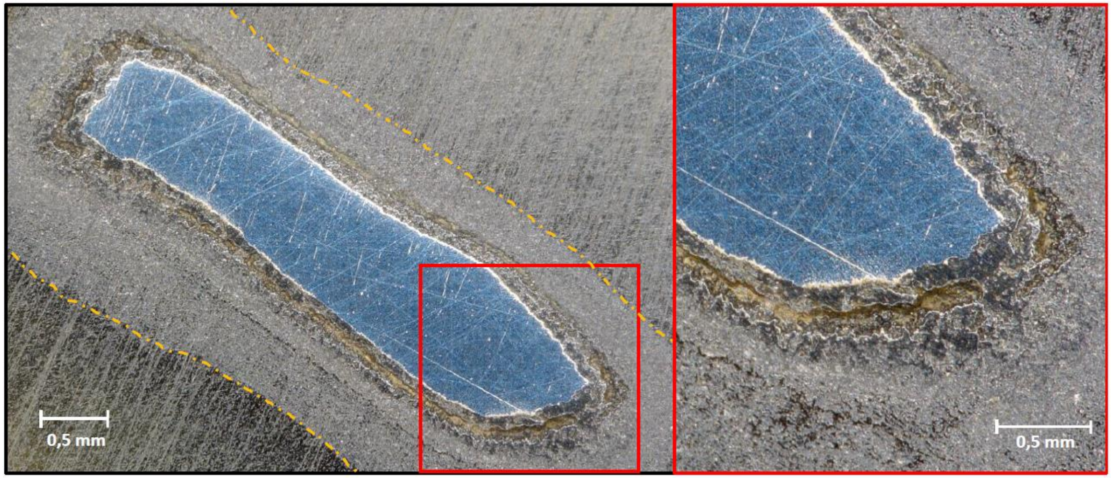


Duske, 2018

- Isolated coupon

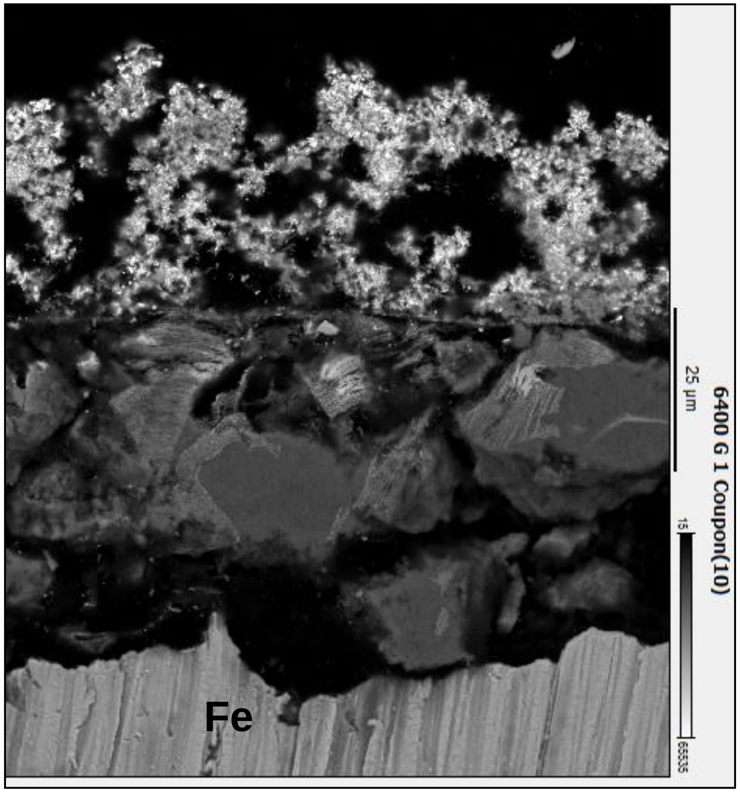
Orig. coupon size 5 mm x 10 mm

- Coupon in contact with stainless steel



Duske, 2018

Corrosion & Scales at isolated Coupons

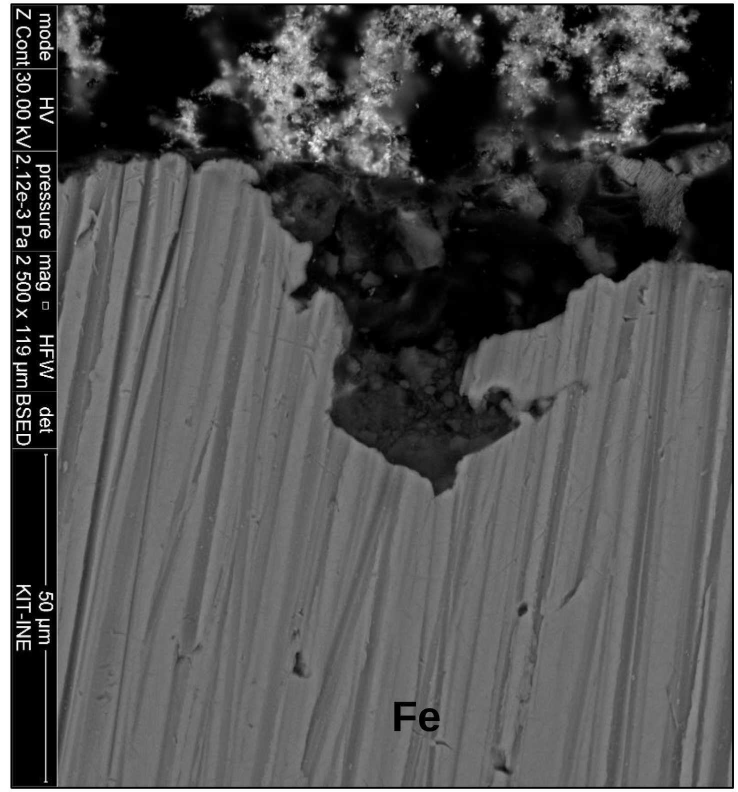


Duske, 2018

Pb,As,Sb ± S

As-rich Fe-platelets, As:Fe 1:1 – 1:4

$(Fe_xCa_{1-x})CO_3$

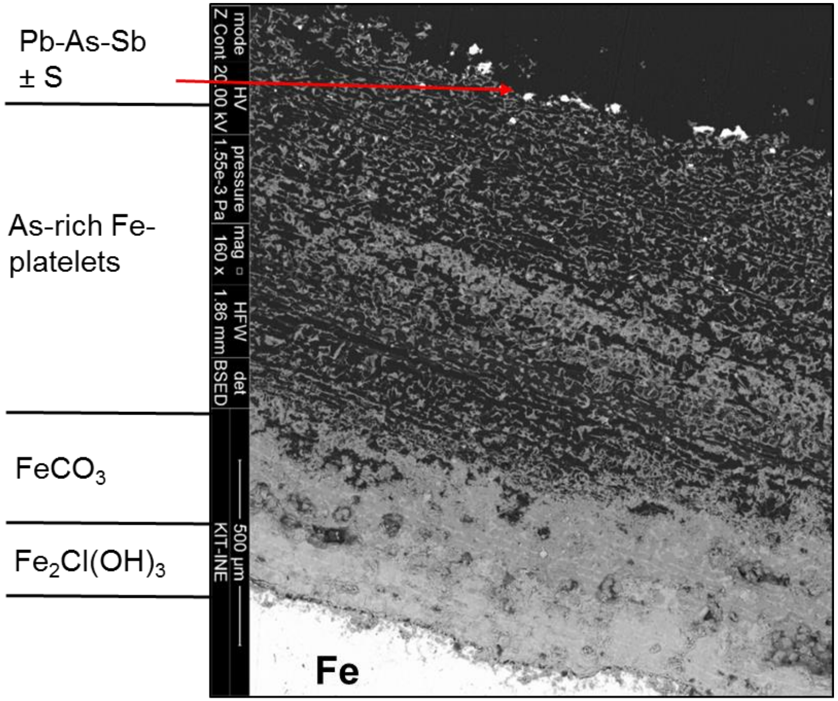


Duske, 2018

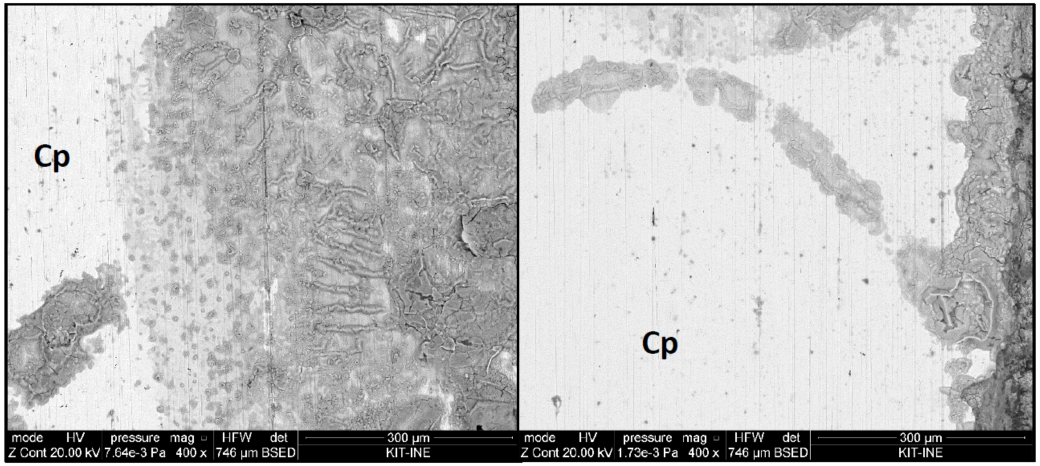
- Corrosion + Scaling layer ca. 50 µm – 130 µm
- Shallow corrosion pits, occasional small forms of local pitting corrosion

Corrosion & scales after contact corrosion

- Scaling layer up to 1.5 mm thick
- Inner-layer with Hibbingite like stoichiometry
- Otherwise very similar scaling chemistry
- Pb, As, Sb phases forming a separated layer
- Occurrence of filiform corrosion (up to 800 µm)



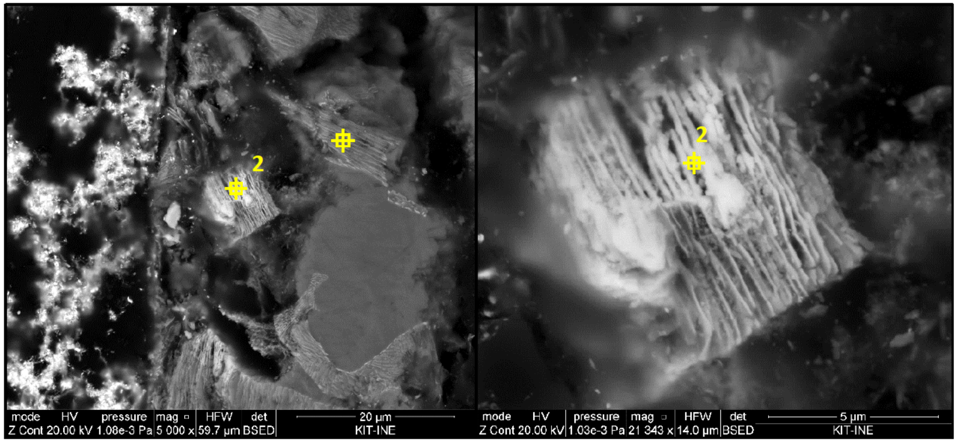
Duske, 2018



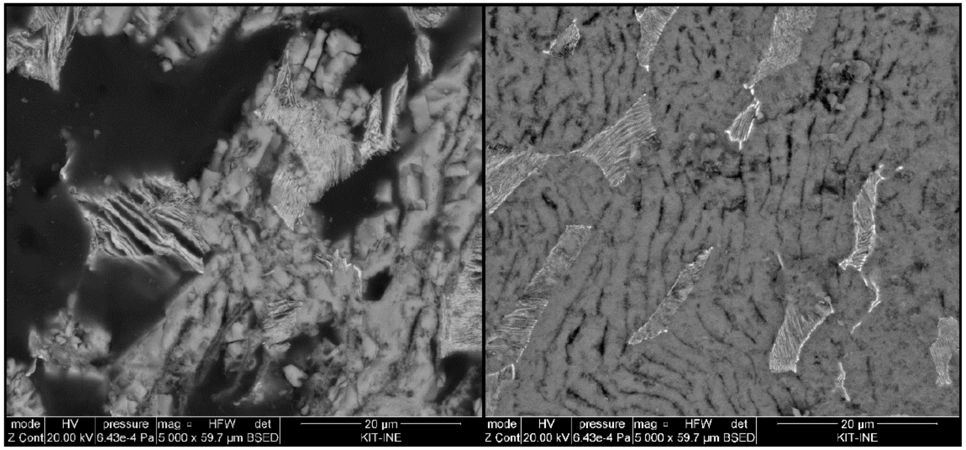
Duske, 2018

Secondary Fe-phases

- Hibbingite $Fe_2(OH)_3Cl$ possible after contact corrosion
- Siderite (partly containing Ca) $(Fe,Ca)CO_3$, also confirmed by XRD
- As-rich Fe platelets:
  - As:Fe ratio 1:4 – 1:1
  - No indication for formation of crystalline stoichiometrc Löllingite ($FeAs_2$) or Westerveldit (FeAs)
  - Texture of corrosion products indicates preferred ferrite dissolution and As precipitation between remaining cementite lamellae



Perlitic texture conserved in As-rich lamellae

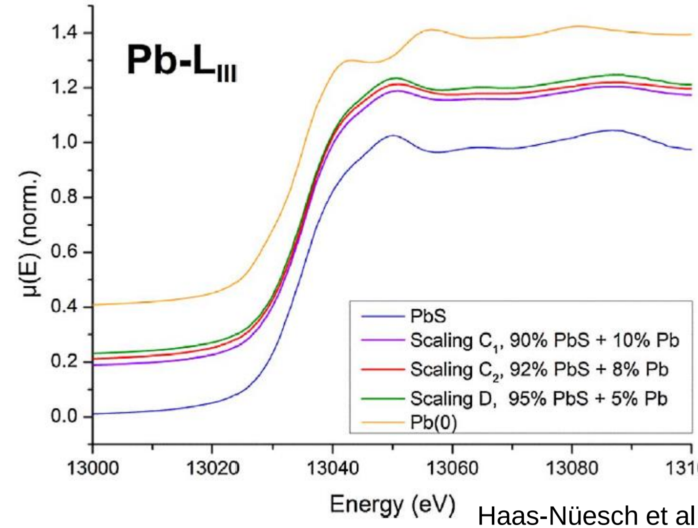


As-rich cementite lamellae embedded in Siderite

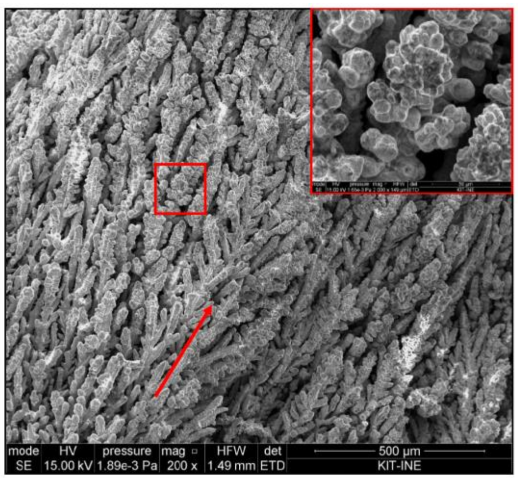
after Duske, 2018

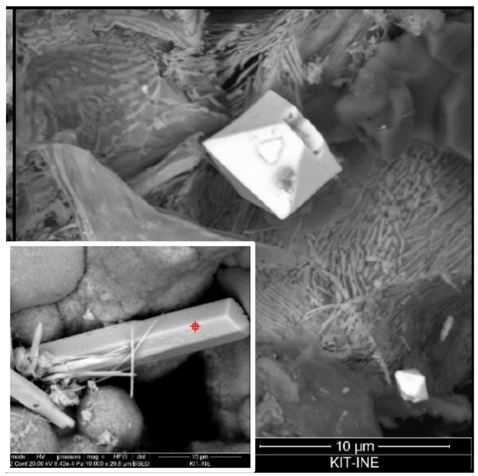
Secondary Pb-phases

- Mainly Galena (PbS)
  - Mostly dentritic and tightly mingled with an (As,Sb) phase
  - rarely idiomorphic crystals
  - significantly enlarged unit cell (~0.03Å / ~0.5 %) → incorporated impurities
- Pb(0) (0 – 10 %)
- Accessory Laurionite (PbCl(OH))

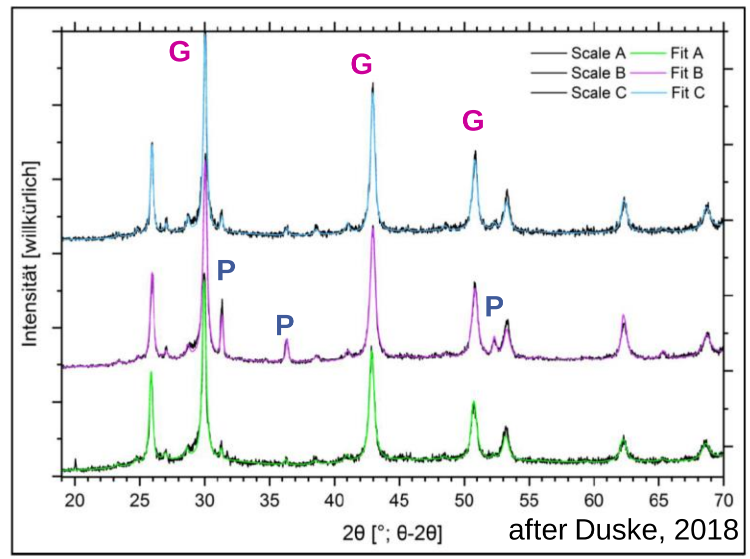


Haas-Nüesch et al., 2018



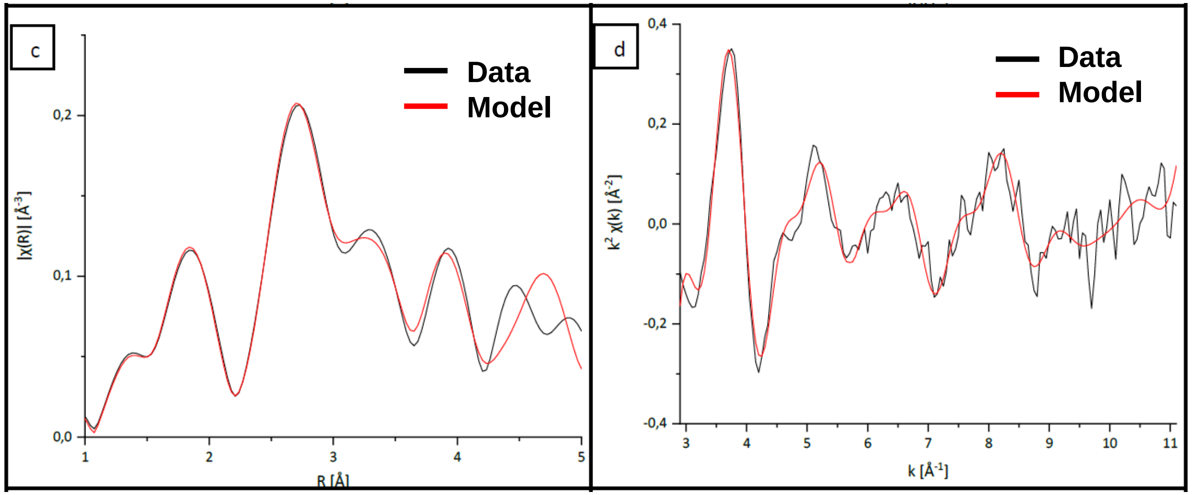


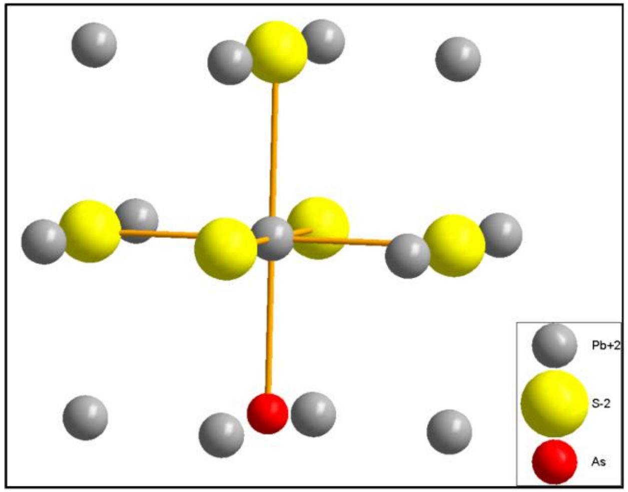
after Duske, 2018



after Duske, 2018

Pb(S, As)

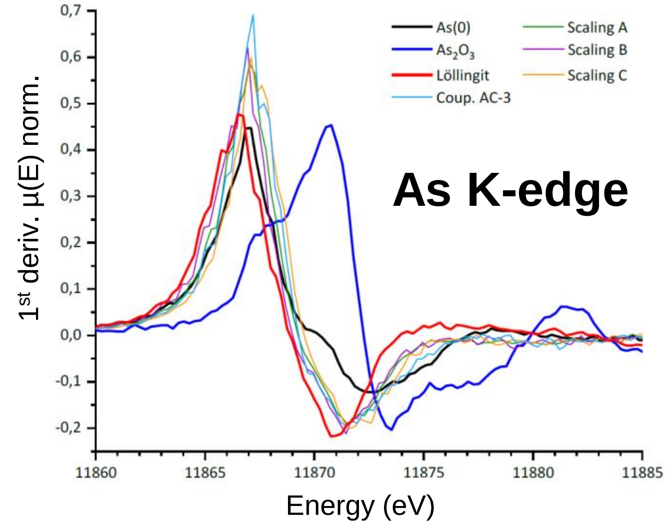


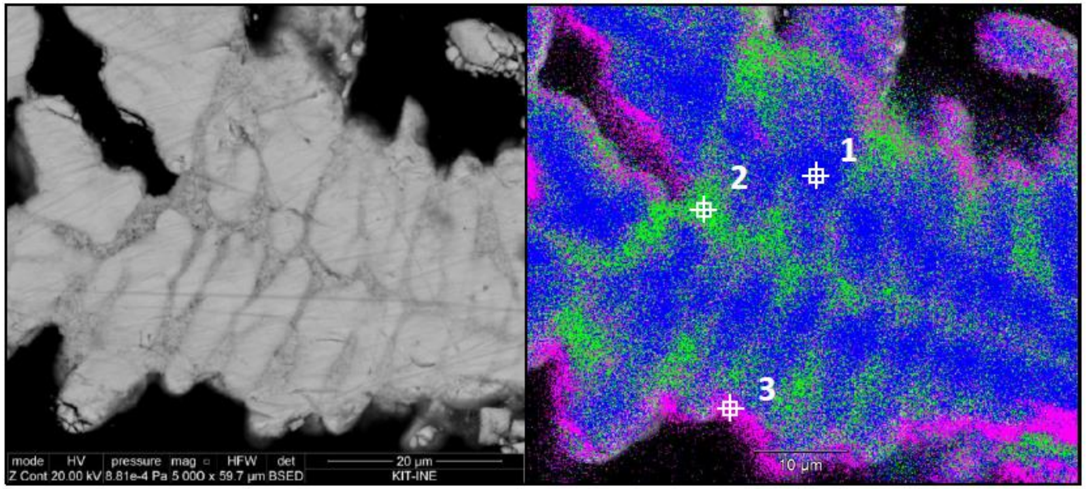


- EXAFS analysis of three scaling samples indicates that considerable amounts of S in PbS may be replaced by As (up to 8 % (mass))
- It is unclear if such high As contents are realistic, but the measured bond distances could explain the observed unit cell enlargement.

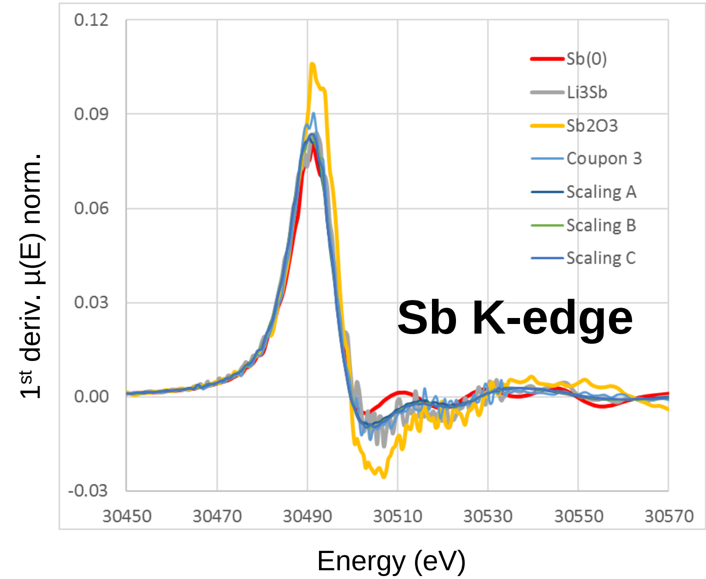
(As,Sb)

- As and Sb in elementary / intermetallic form
- Mostly in x-ray amorphous (As,Sb) mixed phase
- As additionally in Fe/As-platelets and Pb(S,As)



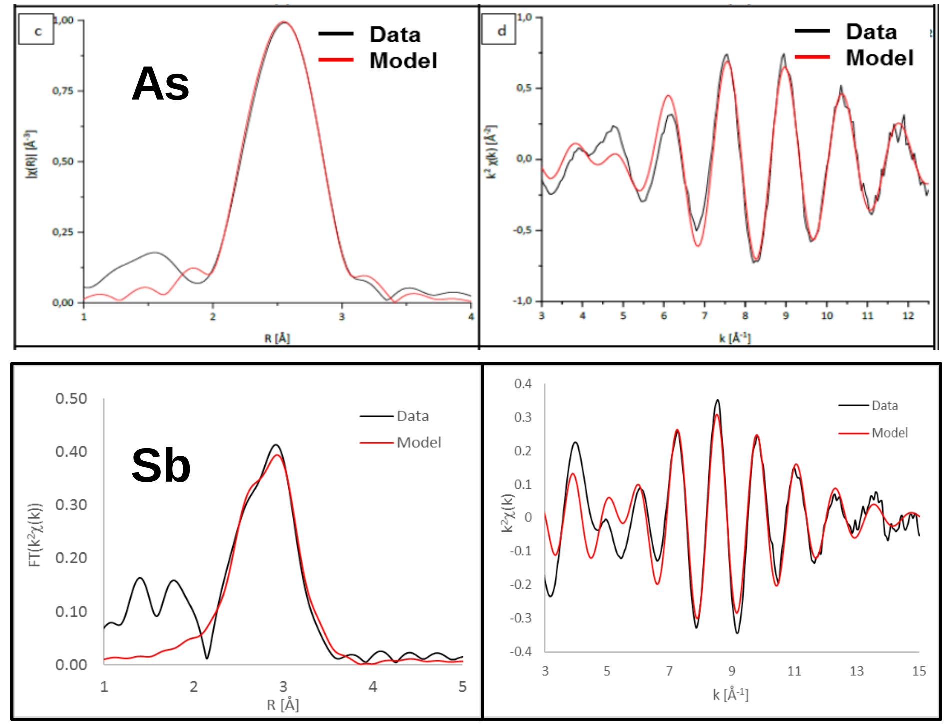


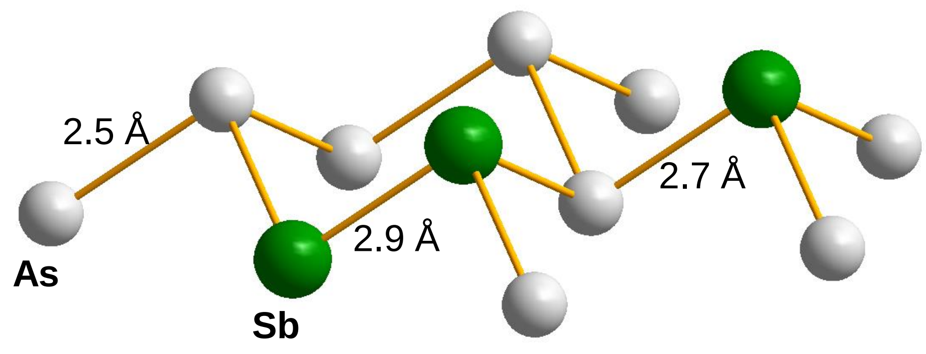
Cross section through dendrites. Phases 1,2 & 3 Pb(S,As) – (As, Sb) mixtures with 3 different compositions



(As,Sb)

- As EXAFS (n=4)
  - Distance (As-As): 2.45 ± 0.02 Å (cf. 2.51 Å crystallographic data)
  - Distance (As-Sb): 2.65 ± 0.01 Å
- Sb EXAFS (n=4)
  - Distance (Sb-As): 2.68 ± 0.02 Å
  - Distance (Sb-Sb): 2.87 ± 0.01 Å (cf. 2.91 Å crystallographic data)
- Coordination numbers ~3
- Short range order corresponding to As(0), (As,Sb), or Sb(0) ($R\bar{3}c$)





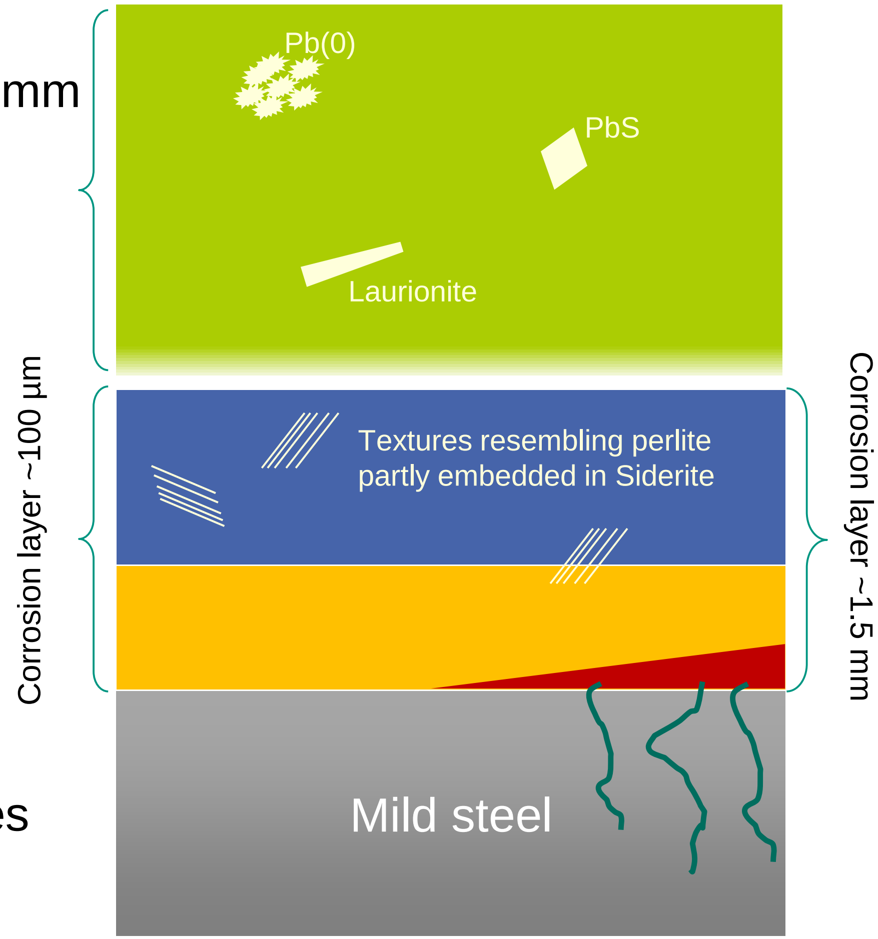
Summary

Scaling layer, up to 4-6 mm
Dendritic growth of
Pb(S,As) + (As,Sb)
varying compositions

Fe/As-platelets

Ca-rich Siderite

Shallow corrosion pits;
Moderate corrosion rates
0.08 mm/a



Aqueous corrosion

Contact / galvanic corrosion

Formation triggered by redox milieu (brine, Fe^{2+} flux, & inhibitor?)
rather than
direct conduction from steel into scaling

Fe/As-platelets

Siderite
Hibbingite (high Fe^{2+}-flux)

Filiform corrosion;
Strongly increased rates

Summary

- Redox conditions:
  - Anoxic milieu
  - oxidizing with respect to iron corrosion: Fe(0) → Fe^{2+}
  - reducing with respect to toxic heavy metals: As^{3+}, Sb^{3+}, Pb^{2+} → As(0), Sb(0), Pb(0)
  - Thermodynamic catch-22: modifications of the redox state will either enhance corrosion or scale formation

- Exploiting kinetic inhibition effects is the best choice to mitigate the formation of elemental / sulfide scales and corrosion (similar to the successfully applied sulfate inhibitors)

- Final disposal of elemental scaling waste poses a serious challenge

References

- Haas-Nüesch, R.; Heberling, F.; Schild, D.; Rothe, J.; Dardenne, K.; Jähnichen, S.; Eiche, E.; Marquardt, C.; Metz, V.; Schäfer, T.; Mineralogical characterization of scalings formed in geothermal sites in the Upper Rhine Graben before and after the application of sulfate inhibitors. *Geothermics* **2018,** *71*, 264-273.

- Duske, F. (**2018**), Master's Thesis: 'Mineralogische Charakterisierung von geothermalen Scalings und Korrosionsproben…' Institute of Applied Geosciences, Karlsruhe Institute of Technology (confidential)

- Sanjuan, B., Millot, R., Innocent, C., Dezayes, C., Scheiber, J. and Brach, M.; Major geochemical characteristics of geothermal brines from the Upper Rhine Graben granitic basement with constraints on temperature and circulation. *Chemical Geology* **2016,** 428, 27-47.

- Agemar, T., Suchi, E., Moeck, I.: Positionspapier: Die Rolle der tiefen Geothermie bei der Wärmewende, LIAG **2018**, Archivnr. 0135181

Acknowlegement

- Thanks to all collaborators for their support

- This research received partial funding from VKTA through the collaborative Project **Subito** (BMWi)

- Thanks to the Cat-**ACT**- and INE-Beamlines at the KIT Synchrotron Light Source for providing Beamtime

Thank you for your attention…