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Mineralogy and leaching behavior of mineralized rocks excavated near tunnel construction sites

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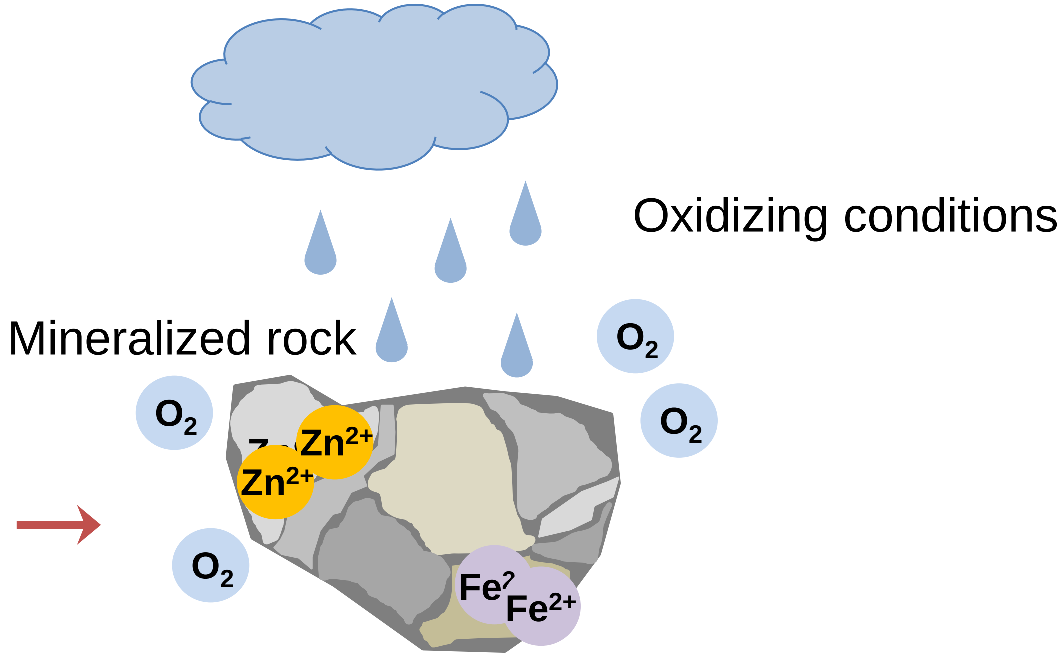
Background and purpose



$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

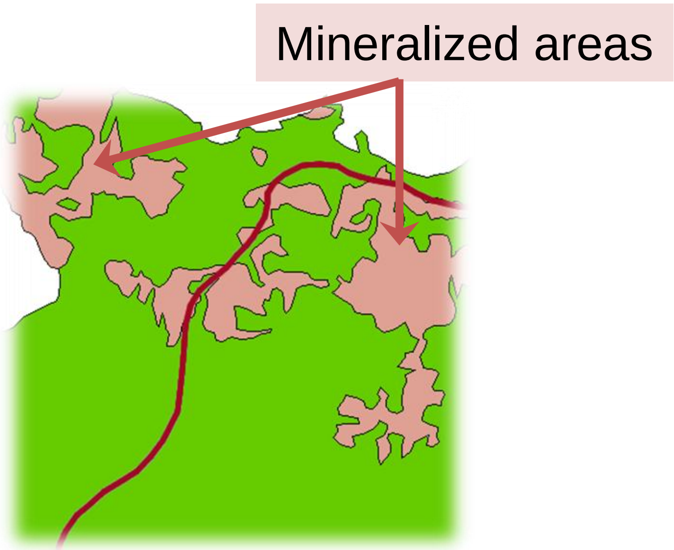
$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$

Release heavy metals and generate high acidity

Background and purpose

Mineralized areas are widespread in Hokkaido, Japan.

Background and purpose



Mineralized areas are widespread in Hokkaido, Japan.

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Several tunnels for the Hokkaido Bullet Train Line are being planned for construction in mineralized areas.

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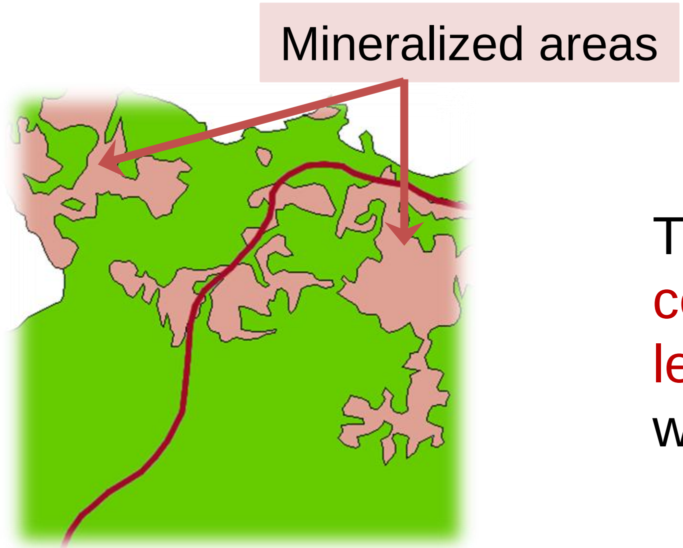
When mineralized rocks are excavated, they become potential sources of acid rock drainage (ARD), as well as heavy metals/metalloids.

Background and purpose

The objectives are
- to evaluate the chemical and mineralogical properties of the mineralized rocks
- to investigate the leaching characteristics of heavy metals from the mineralized rocks



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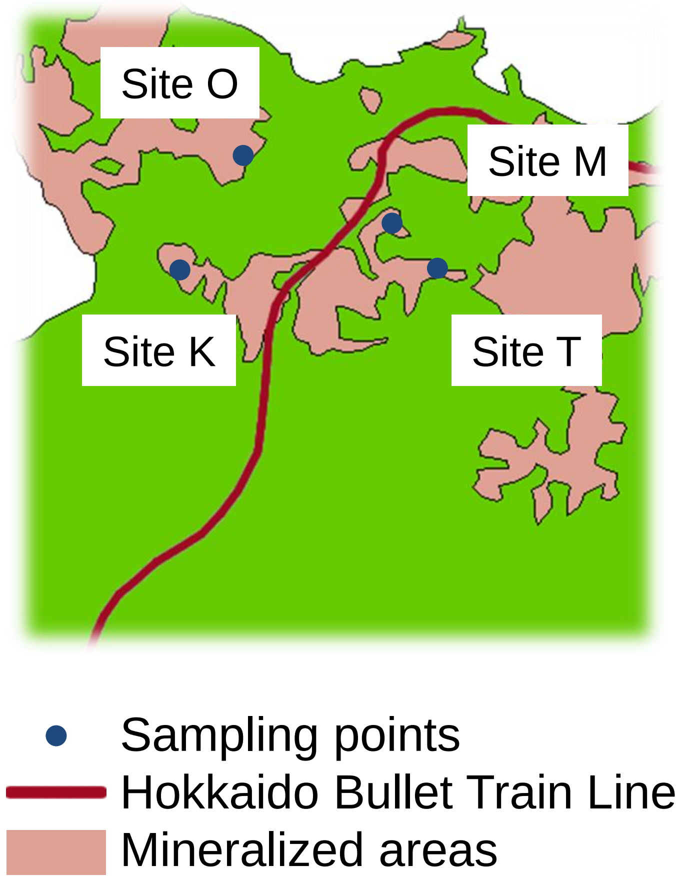
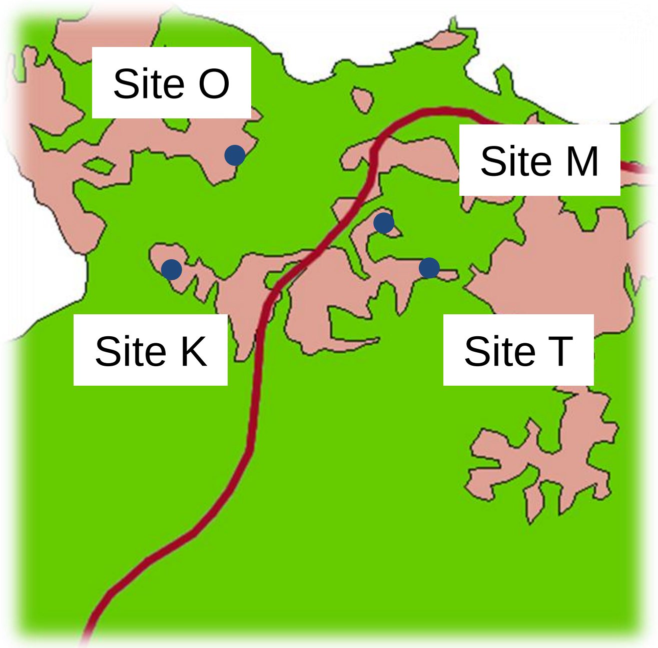
The relationships between the mineral composition of the rocks and the leaching characteristics of heavy metals were investigated.

Site and sample description



Site	Sample	Feature
K	K1	Barite rich
	K2	White siliceous rock
	K3	Siliceous rock
	K4	Black ore
	K5	Siliceous rock
M	M1	Siliceous sulfide ore
	M2	White siliceous rock
O	O1	Rhodochrosite
T	T1	Quartz vein

Site and sample description



● Sampling points
Hokkaido Bullet Train Line
Mineralized areas

Site	Sample	Feature
K	K1	Barite rich
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	K5	Siliceous rock
M	M1	Siliceous sulfide ore
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Methods -Characterization of samples-

Characterization of samples

Mineral identification
using
Microscopy and XRD

Chemical analysis
using
XRF and EPMA

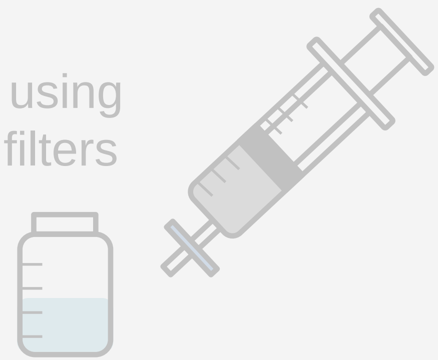
Batch leaching experiments

Mixing time: 6, 24,168 h

Solid to liquid ratio:10
Speed: 120 rpm

pH, EC, ORP
and
temperature
measurements

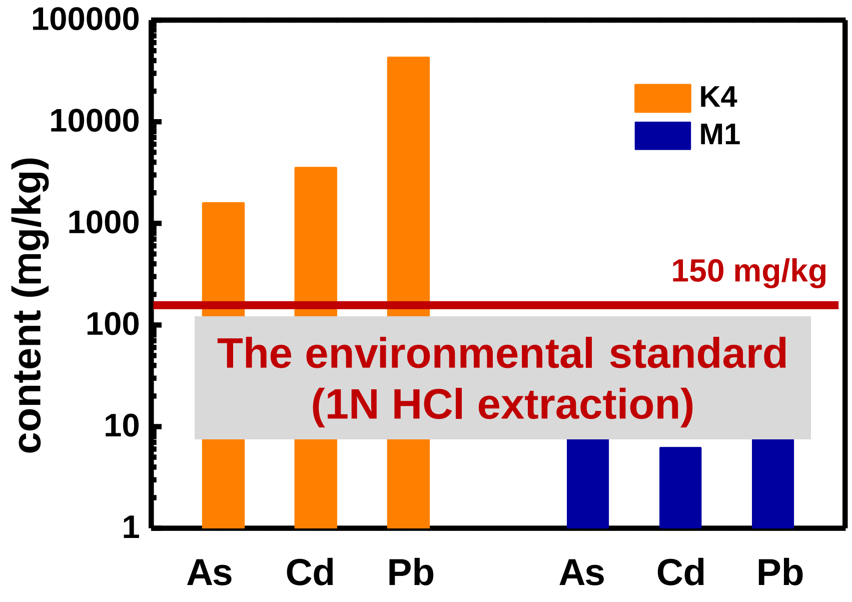
Filtration using
0.45 μm filters



Measuring
As, Cd, Fe, Pb, Zn and SO_4^{2-}
in filtrates
using ICP-AES, ICP-MS and IC

Results -Mineralogical analysis-

K4	Sphalerite (ZnS) Galena (PbS) Barite ($BaSO_4$) Cerussite ($PbCO_3$)
M1	Quartz (SiO_2) Pyrite (FeS_2)



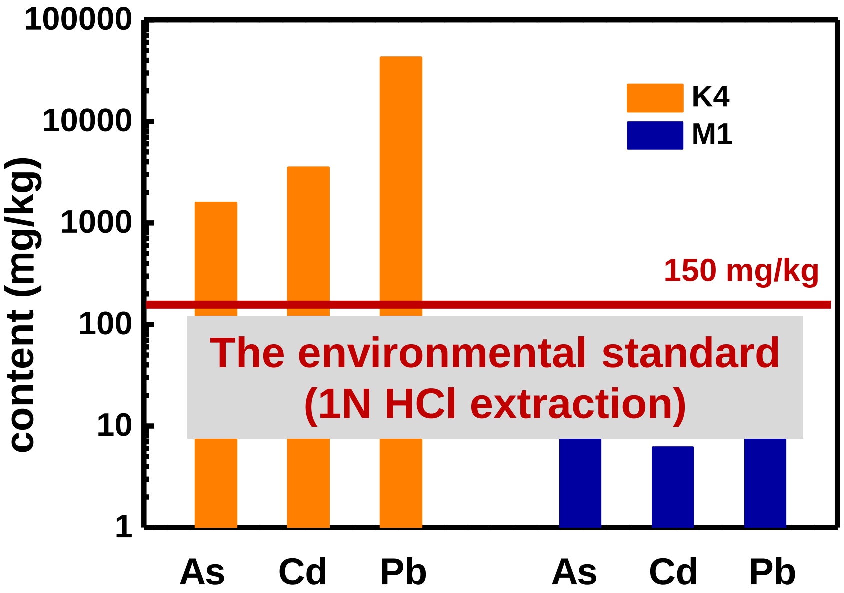
Average of As: 1 – 10 mg/kg
Cd: 0.1 – 0.2 mg/kg
Pb: 11 – 32 mg/kg

K4 contained substantial amounts of As, Cd and Pb.

As-bearing and Cd-bearing minerals were not detected by the XRD analysis.

Results -Mineralogical analysis-

K4	sphalerite (ZnS) galena (PbS) barite ($BaSO_4$) cerussite ($PbCO_3$)
M1	quartz (SiO_2) pyrite (FeS_2)



Average of As: 1 – 10 mg/kg
Cd: 0.1 – 0.2 mg/kg

These toxic elements are found in the rocks most probably as impurities in the crystal matrix of other minerals like sphalerite or pyrite.

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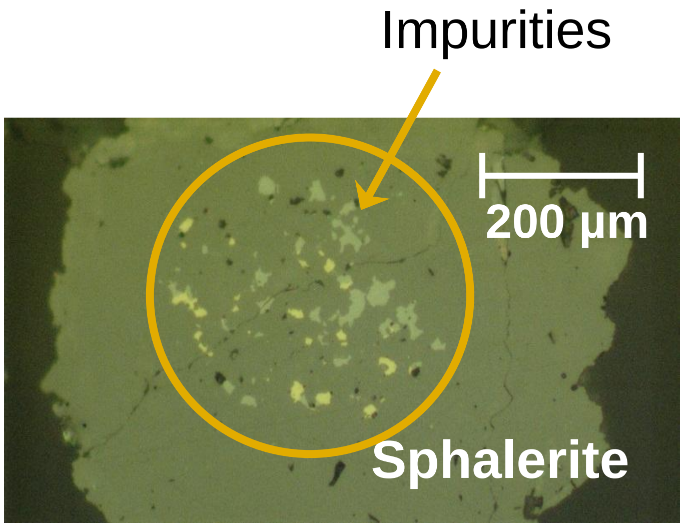
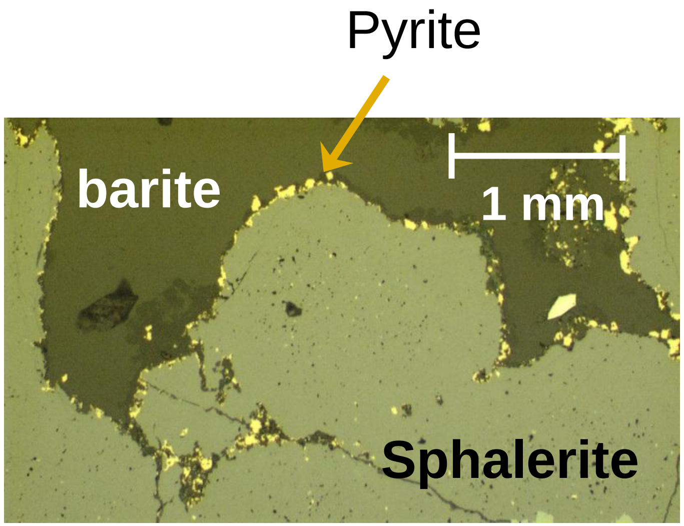
Results -Mineralogical analysis-

Photomicrographs of K4

Transmitted polarized light



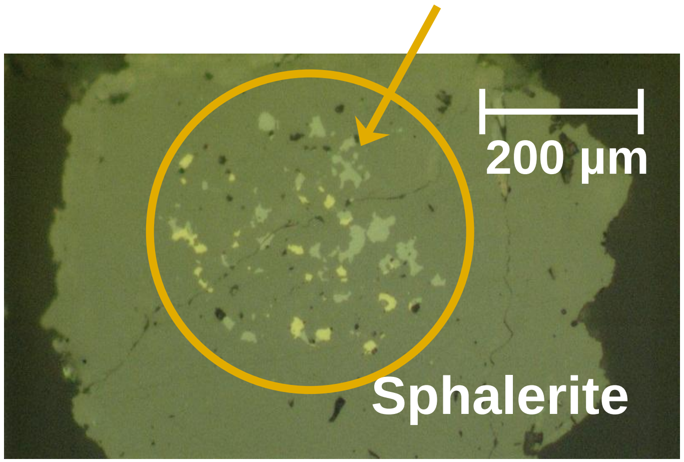
Transmitted polarized light



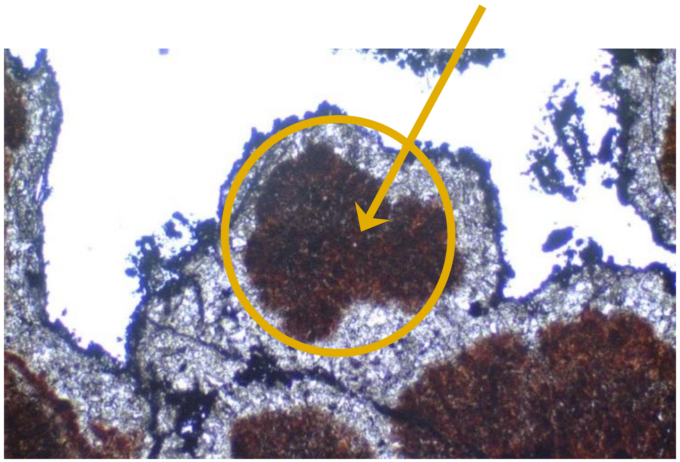
Results -Mineralogical analysis-

Photomicrographs of K4

Transmitted polarized light



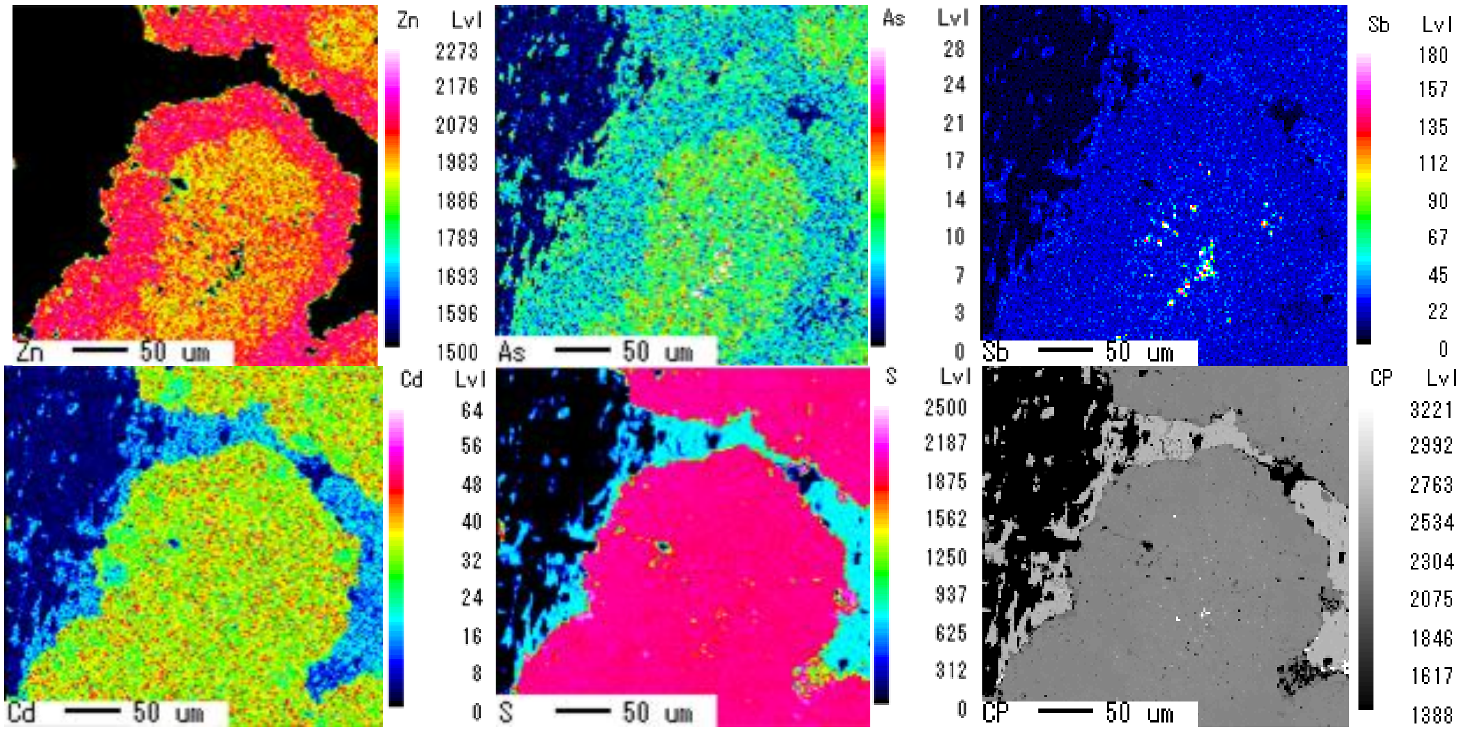
Reflected polarized light



Sphalerite crystal contained impurities.

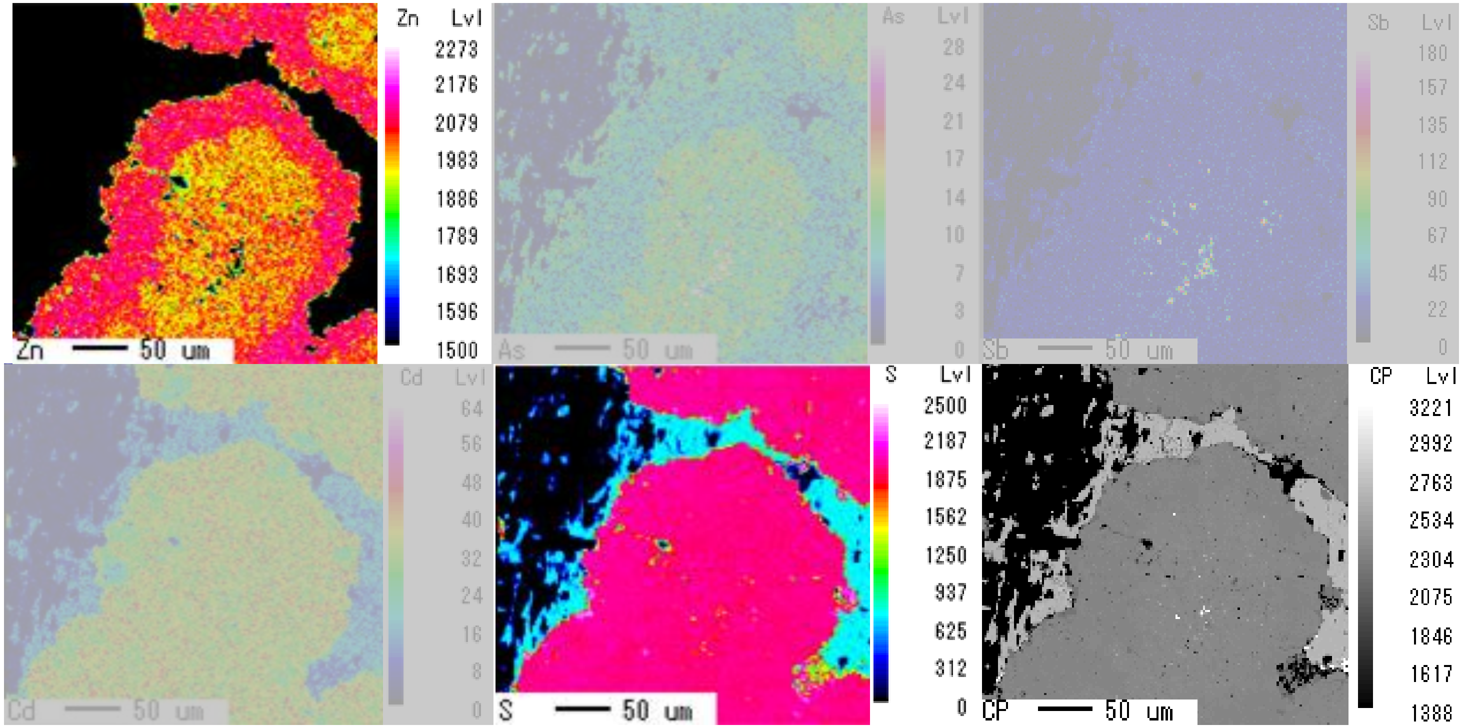
Results -Mineralogical analysis-

Mapping analysis of K4



Results -Mineralogical analysis-

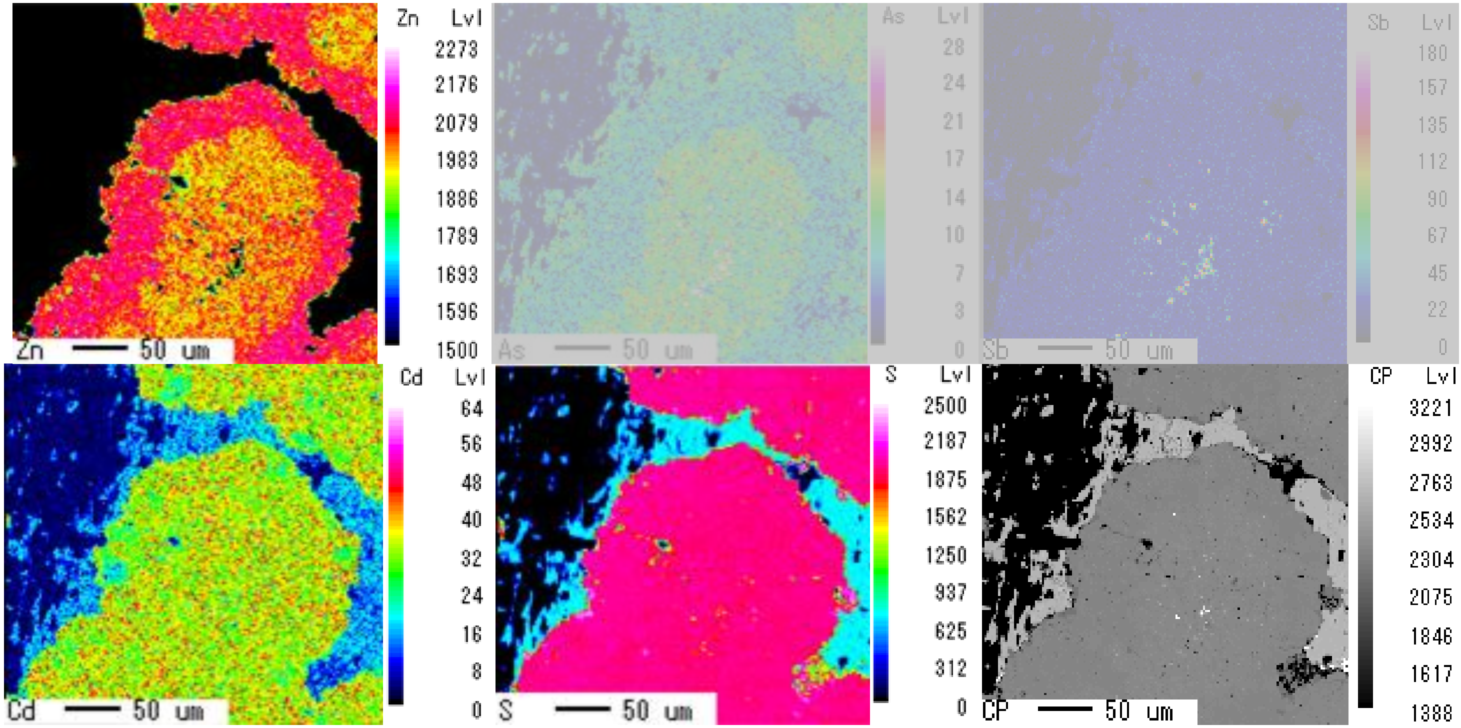
Mapping analysis of K4



The part of red zone was identified as sphalerite.

Results -Mineralogical analysis-

Mapping analysis of K4

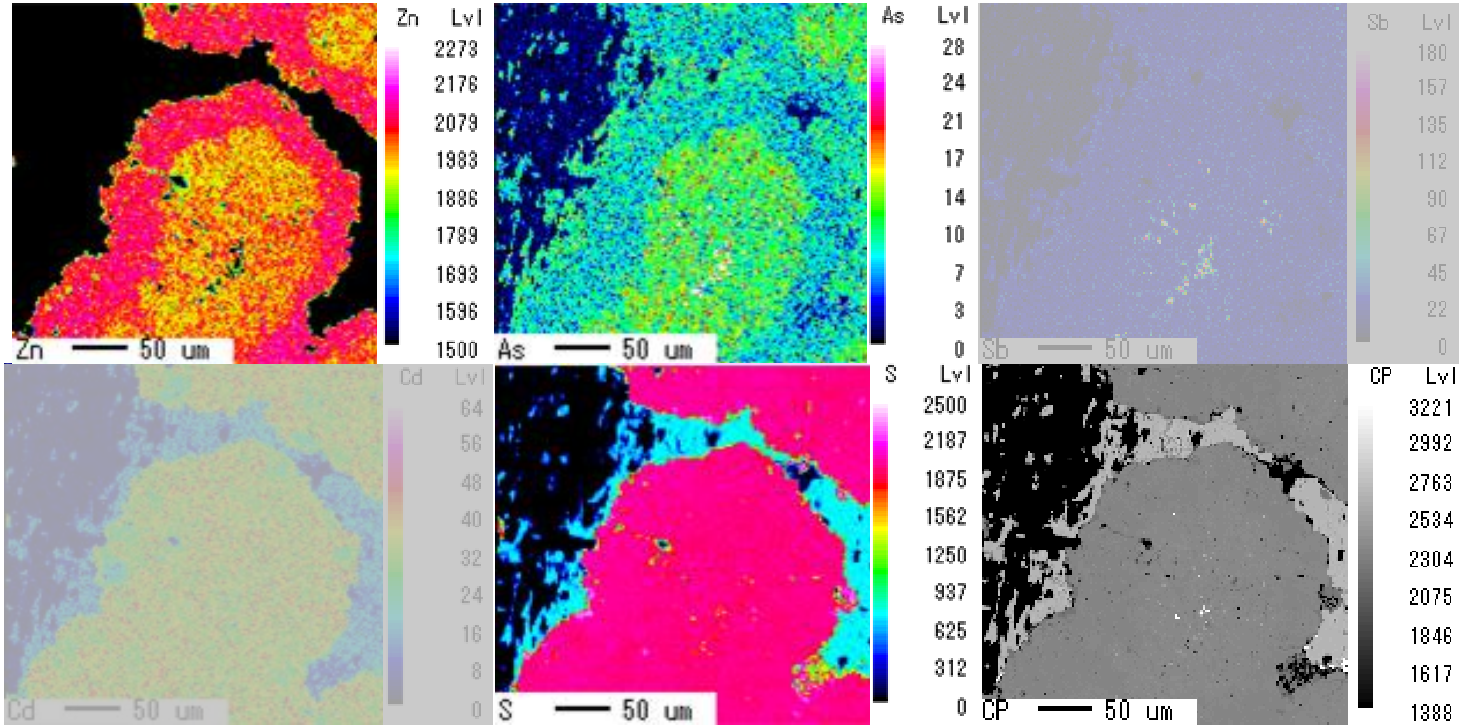


Cd, Zn and S elemental maps coincided with each other.

Cd is predominantly partitioned with sphalerite.

Results -Mineralogical analysis-

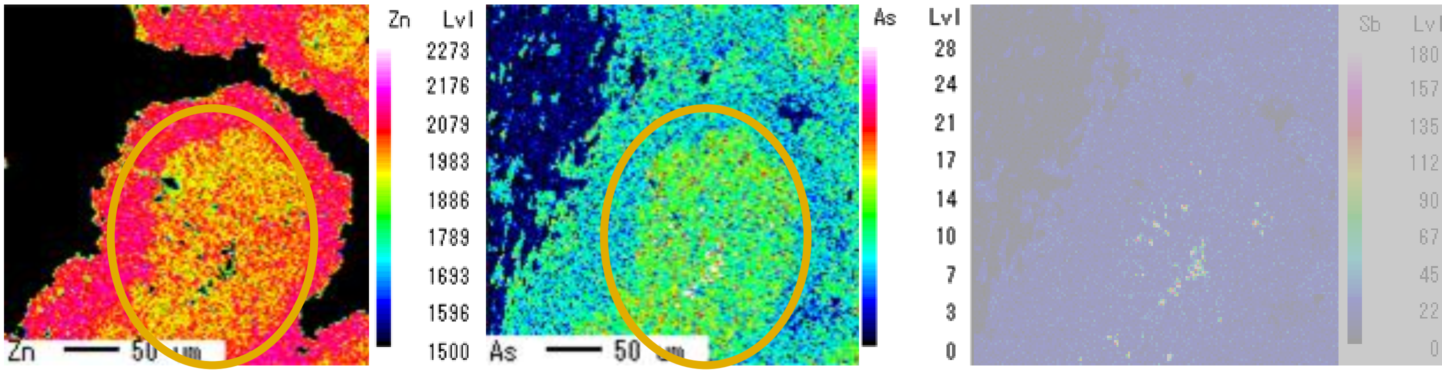
Mapping analysis of K4



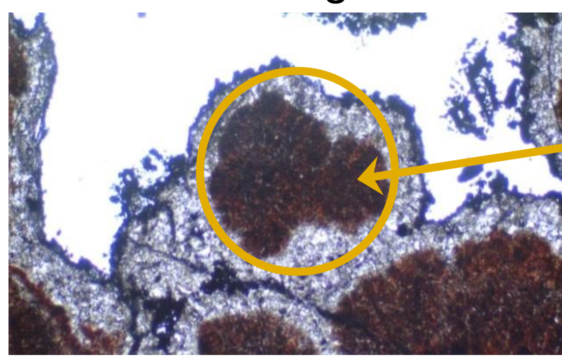
As was also concentrated in the sphalerite crystal.

Results -Mineralogical analysis-

contents lower than that of surrounding area



contents higher than that of surrounding area

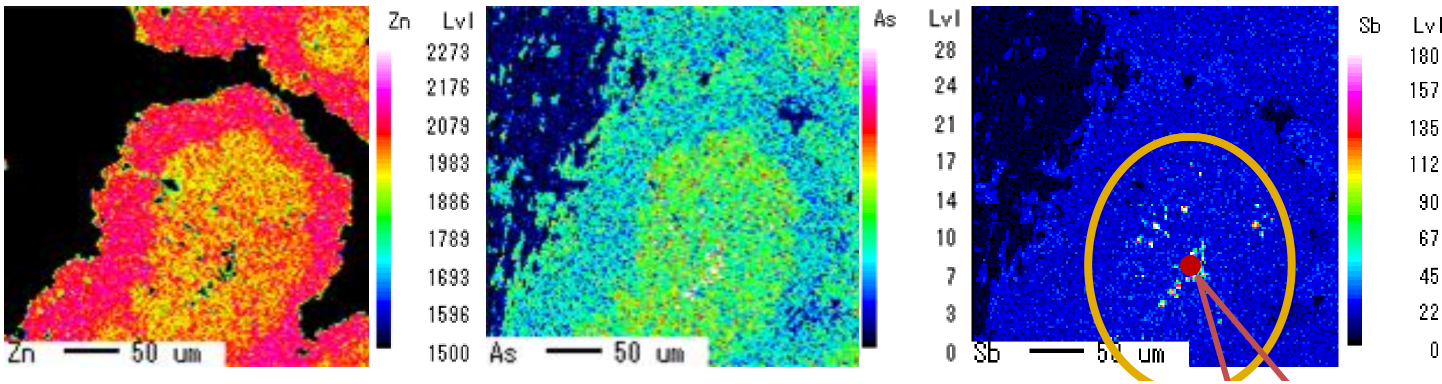


Impurities

The distribution of impurities in sphalerite and the distribution of As coincided well with each other.

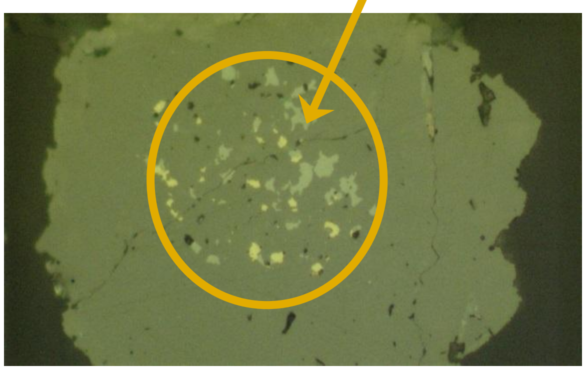
Results -Mineralogical analysis-

Minerals that contain Sb



Single point quantitative analysis

Impurities



tennantite $((Cu, Fe, Zn)_{12}As_4S_{13})$

displace ↕

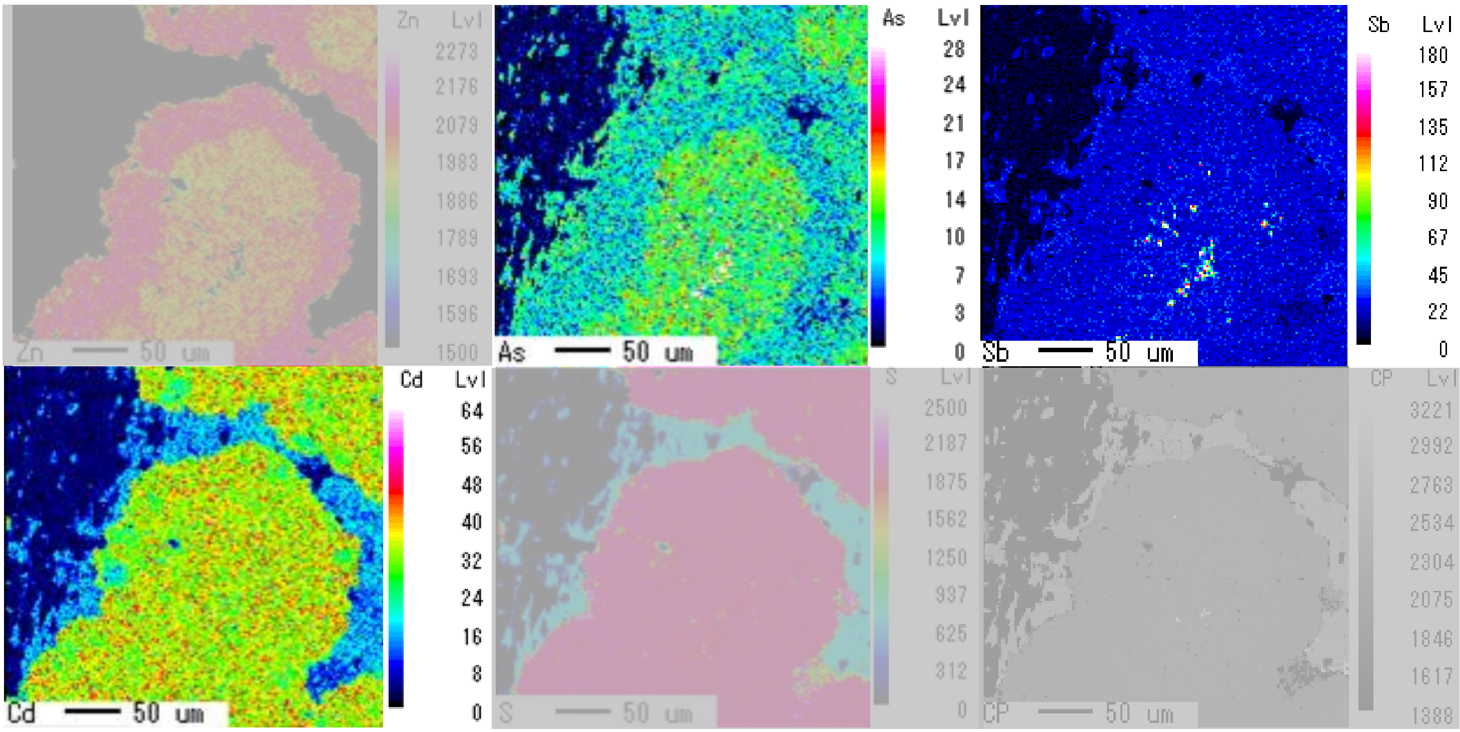
tetrahedrite $((Cu, Fe, Zn)_{12}Sb_4S_{13})$

S (wt %)	27.9
Pb (wt %)	1.09
Cd (wt %)	0.199
Sb (wt %)	0.829
As (wt %)	17.3
Fe (wt %)	0.578
Cu (wt %)	40.3
Zn (wt %)	7.88

As may exist as the mineral tennantite.

Results -Mineralogical analysis-

Mapping analysis of K4



There is a possibility that As and Cd are released with the oxidation of sphalerite.

Methods -Batch leaching experiments-

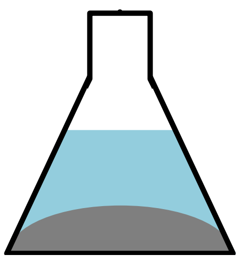
Characterization of samples

Mineral identification
using
Microscopy and XRD

Chemical analysis
using
XRF and EPMA

Sphalerite might be largely related to the dissolution of toxic elements.

Batch leaching experiments

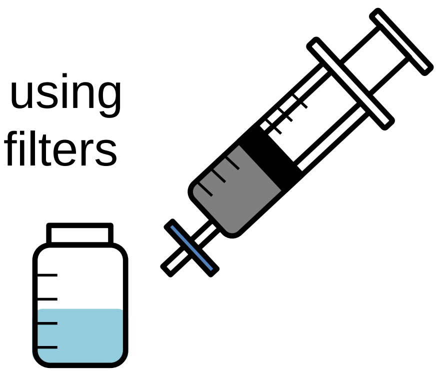


Solid to liquid ratio: 10
Speed: 120 rpm

Mixing time: 6, 24,168 h

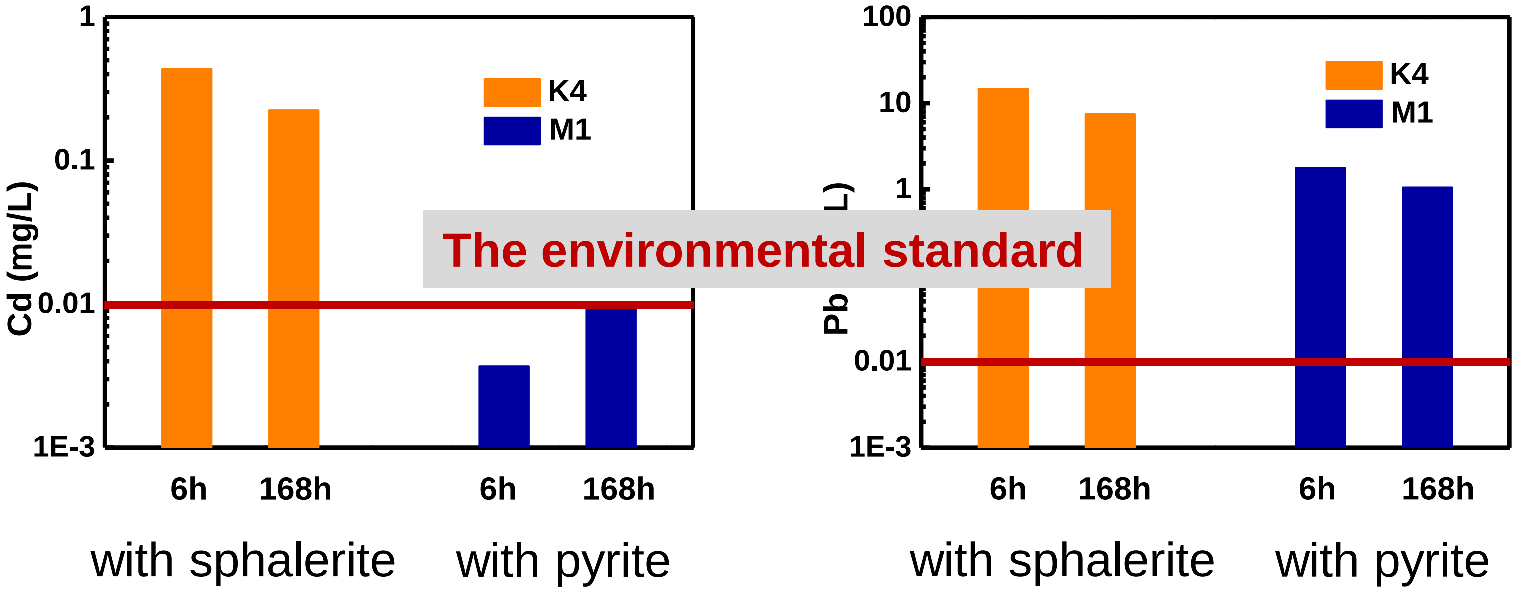
pH, EC, ORP
and
temperature
measurements

Filtration using
0.45 μm filters



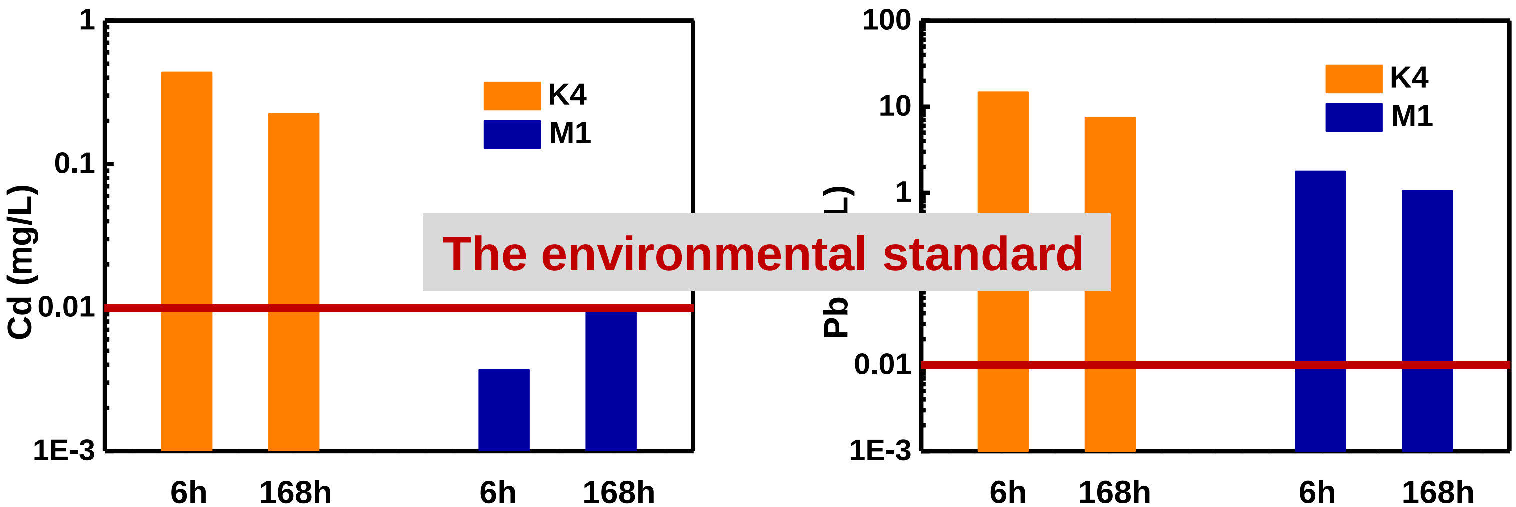
Measuring
As, Cd, Fe, Pb, Zn and SO_4^{2-}
in filtrates
using ICP-AES, ICP-MS and IC

Results -Leaching behavior of As, Cd and Pb-



The concentrations of Cd leached from M1 were lower than the environmental standard of Japan (0.01 mg/L).

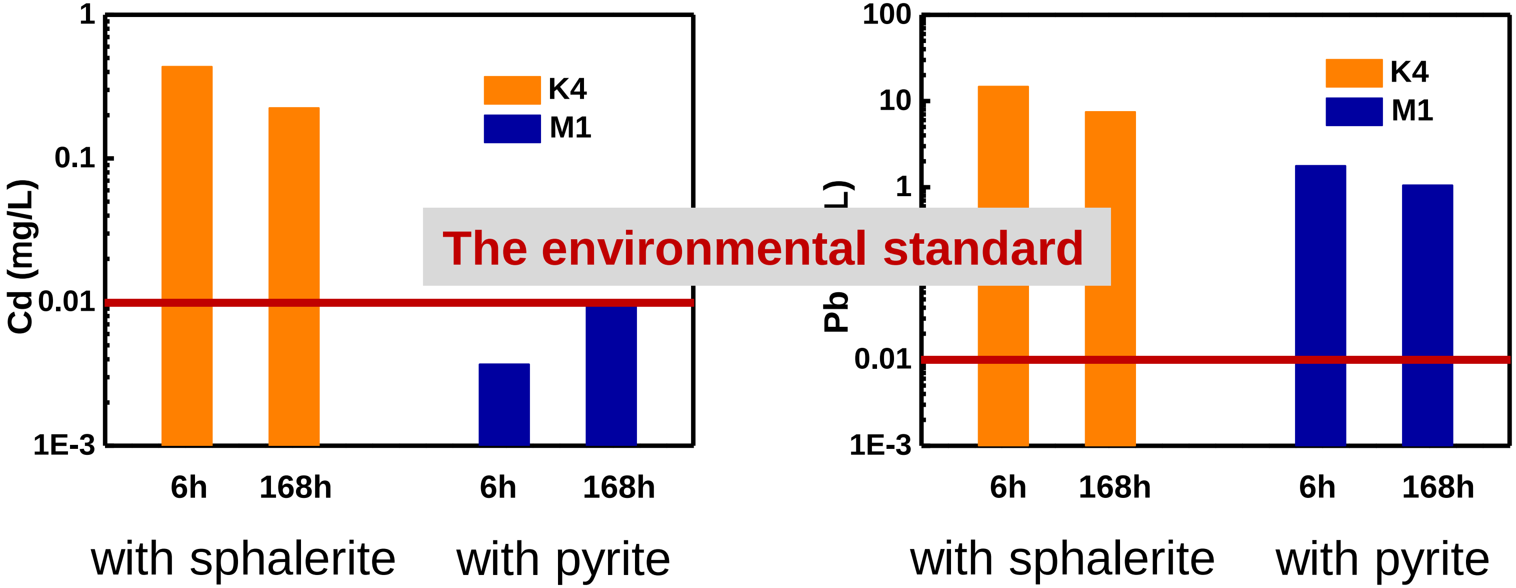
Results -Leaching behavior of As, Cd and Pb-



with sphalerite with pyrite with sphalerite with pyrite

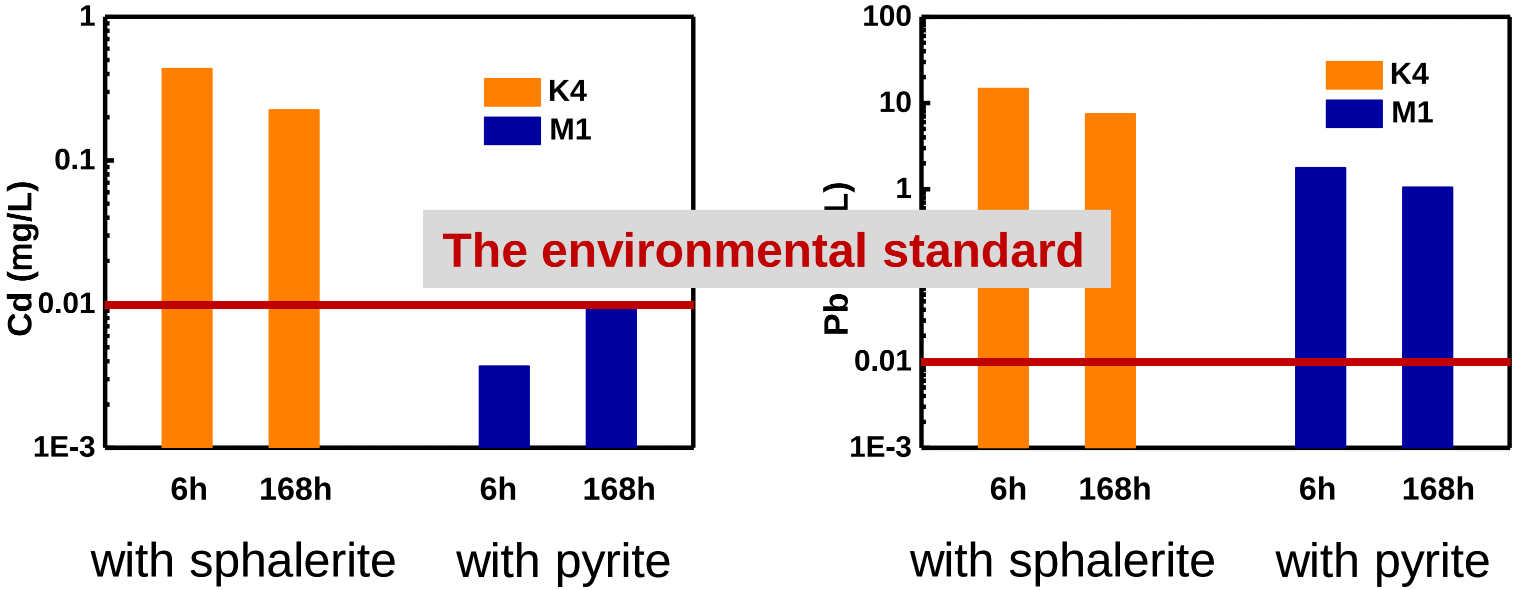
The concentrations of Cd leached from M1 were lower than the environmental standard of Japan (0.01 mg/L).
However, those from K4 were greater than this value.

Results -Leaching behavior of As, Cd and Pb-



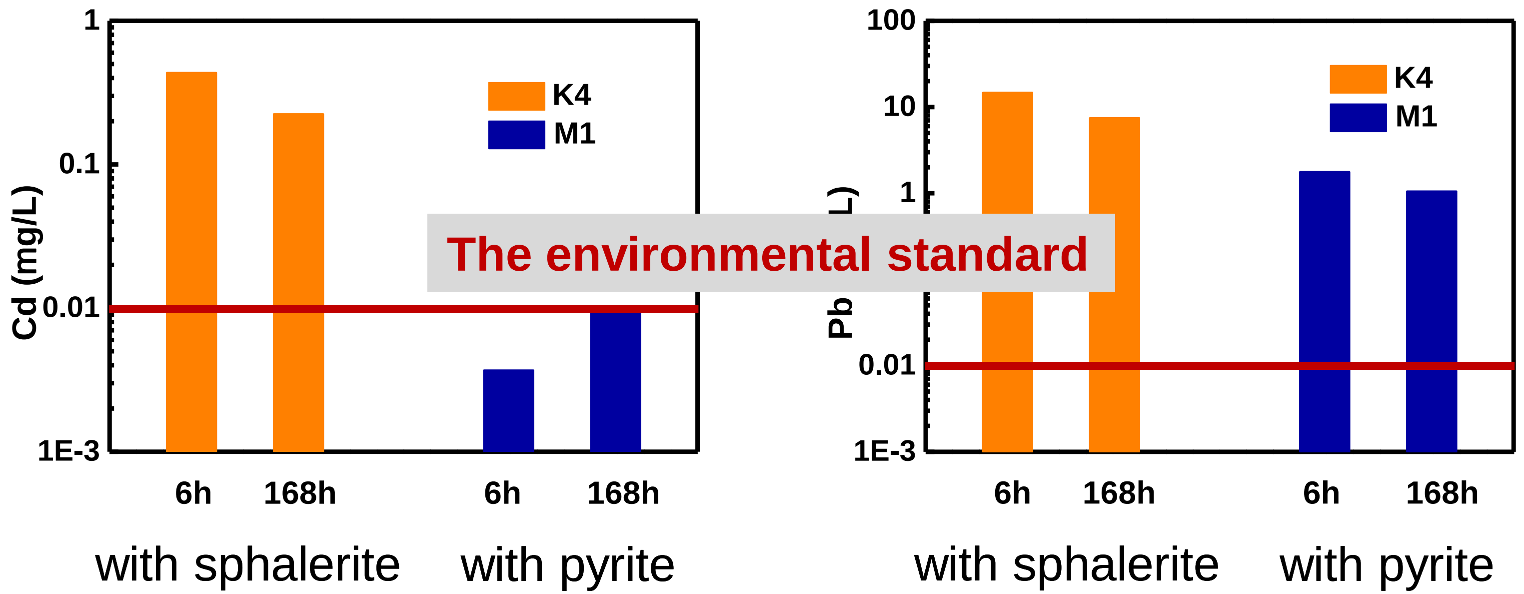
Although the concentrations of Pb leached from both K4 and M1 exceeded the environmental standard of Japan (0.01 mg/L), the concentrations of Pb leached from K4 were much higher than those from M1.

Results -Leaching behavior of As, Cd and Pb-



The leaching of Cd and Pb is associated with the sphalerite more than pyrite.

Results -Leaching behavior of As, Cd and Pb-



The concentrations of Cd and Pb in the leachate did not change dramatically with time, reaching apparent equilibrium after just 6 h.

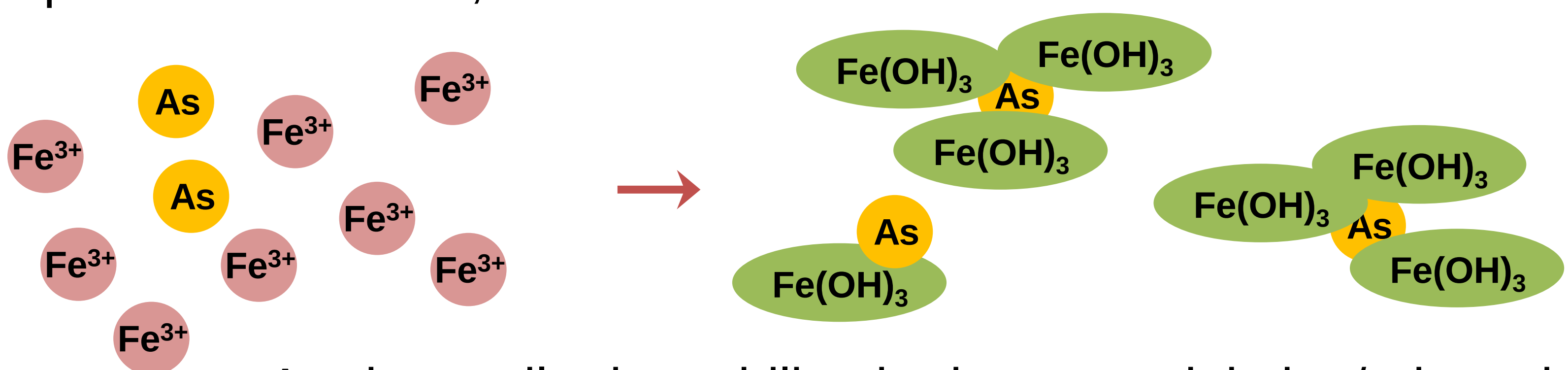
Results -Leaching behavior of As, Cd and Pb-

Although some samples contained considerable amounts of As, its leaching concentration was very low.

sample	pH	As contents (mg/kg)	As concentration (μg/L)
K4	6.06	1,580	ND
M1	3.94	32.0	ND

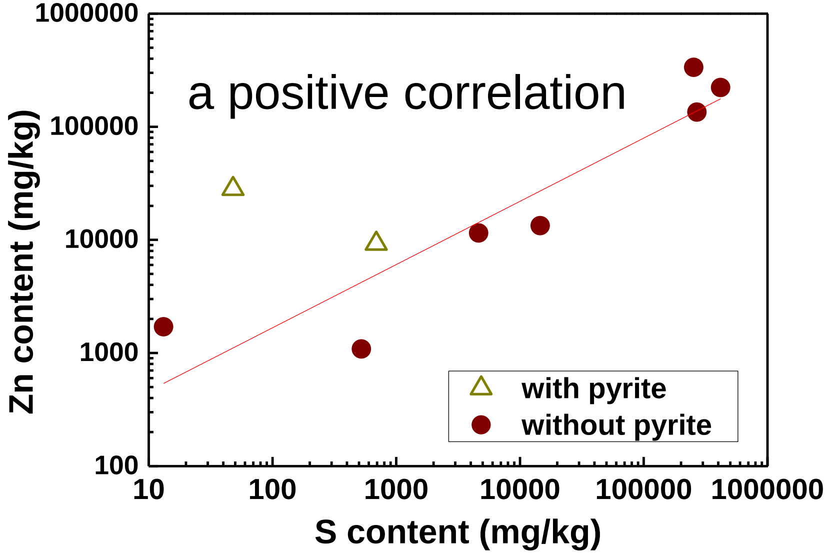
Average of As: 1 – 10 mg/kg

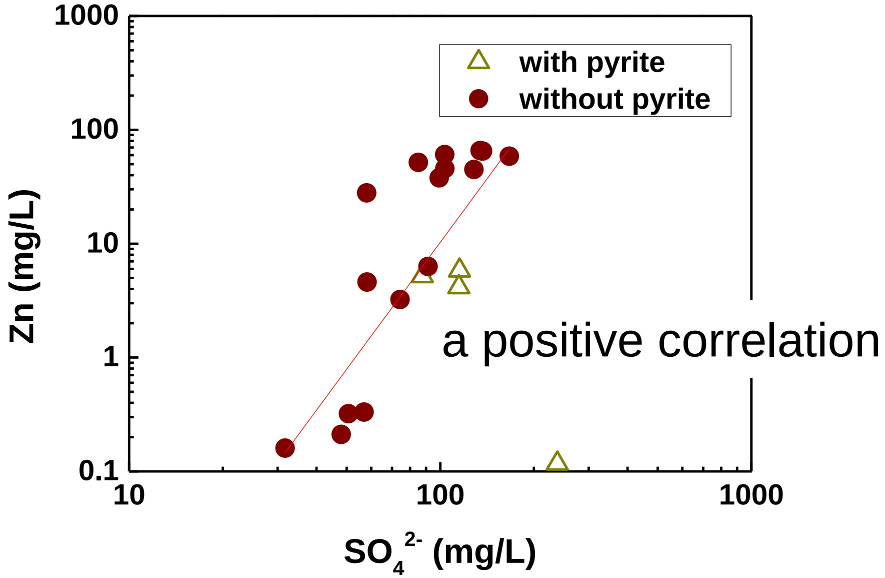
When pH is above 3 or 4,



As is easily immobilized via coprecipitaion/adsorption with/onto ferric hydroxide ($Fe(OH)_3$).

Discussion



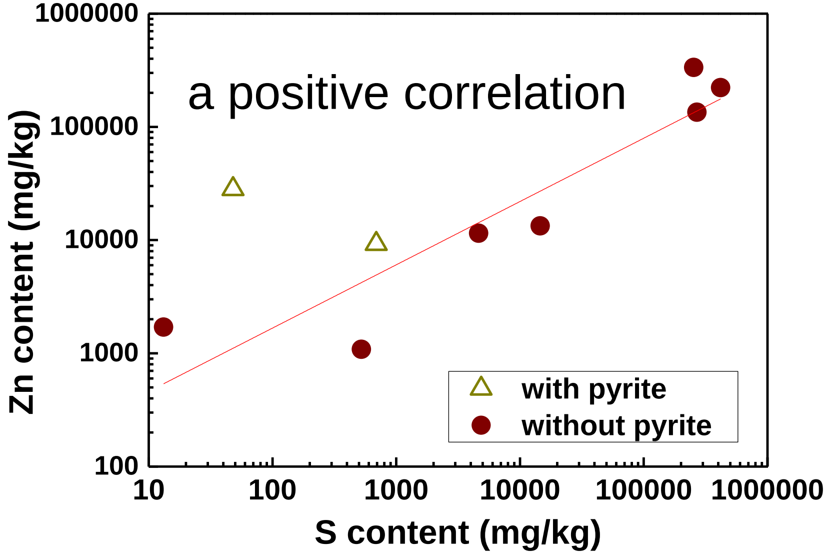


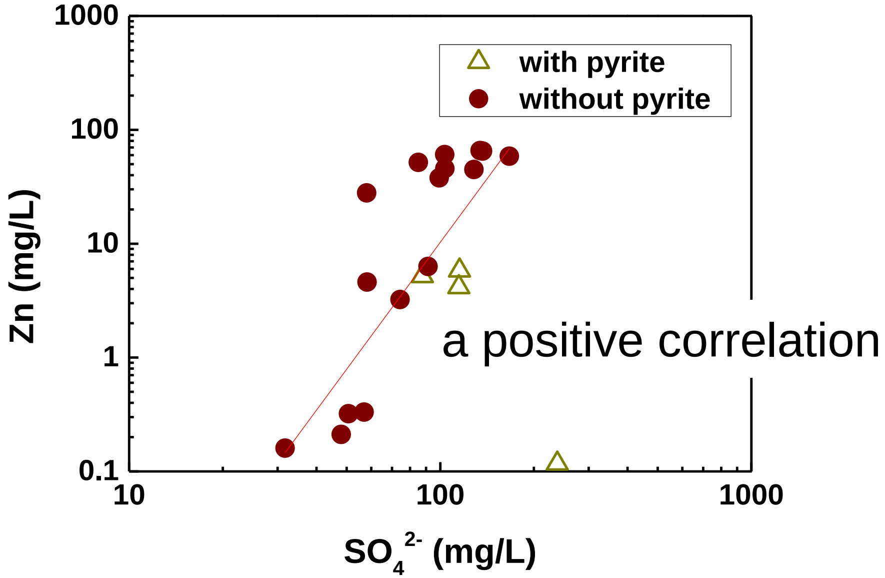
$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$

$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

Most of Zn and S exist as sphalerite.

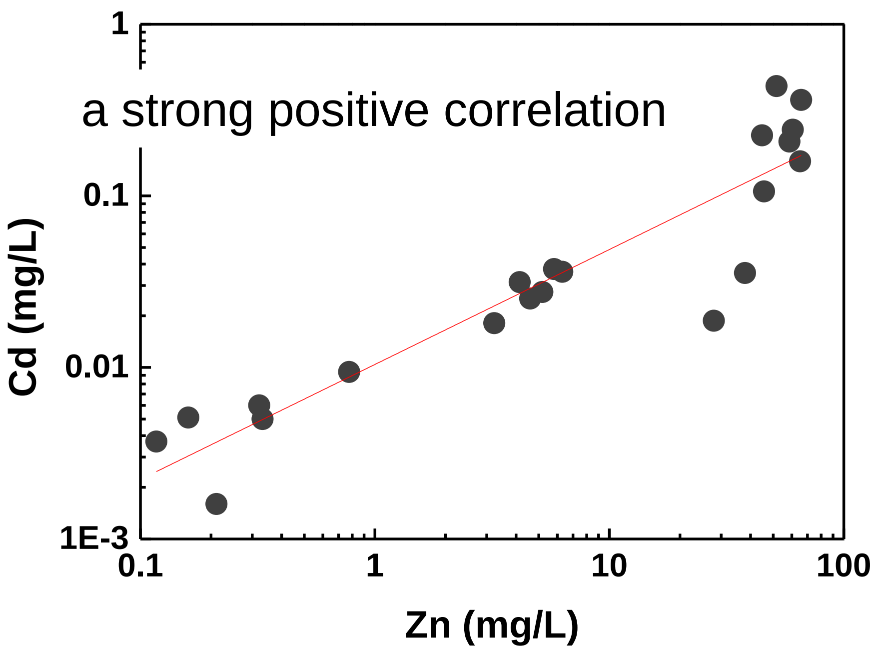
Discussion

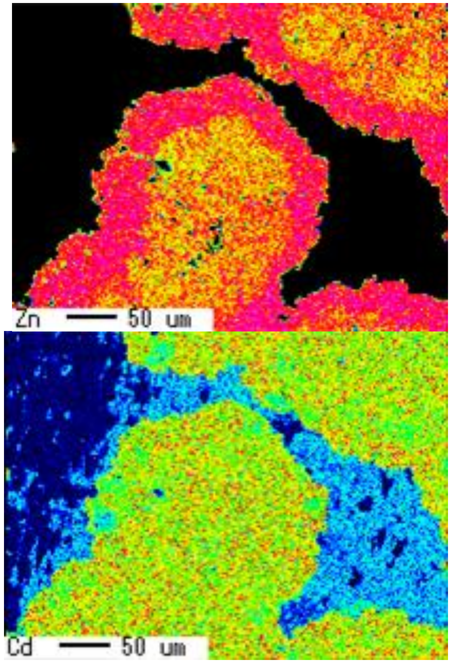




The oxidation of sphalerite is the primary source of Zn and SO_4^{2-} in most of the rock samples.

Discussion





The processes responsible for Cd and Zn release are similar.

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The main release mechanism of Cd is the oxidation of sphalerite.

Conclusions

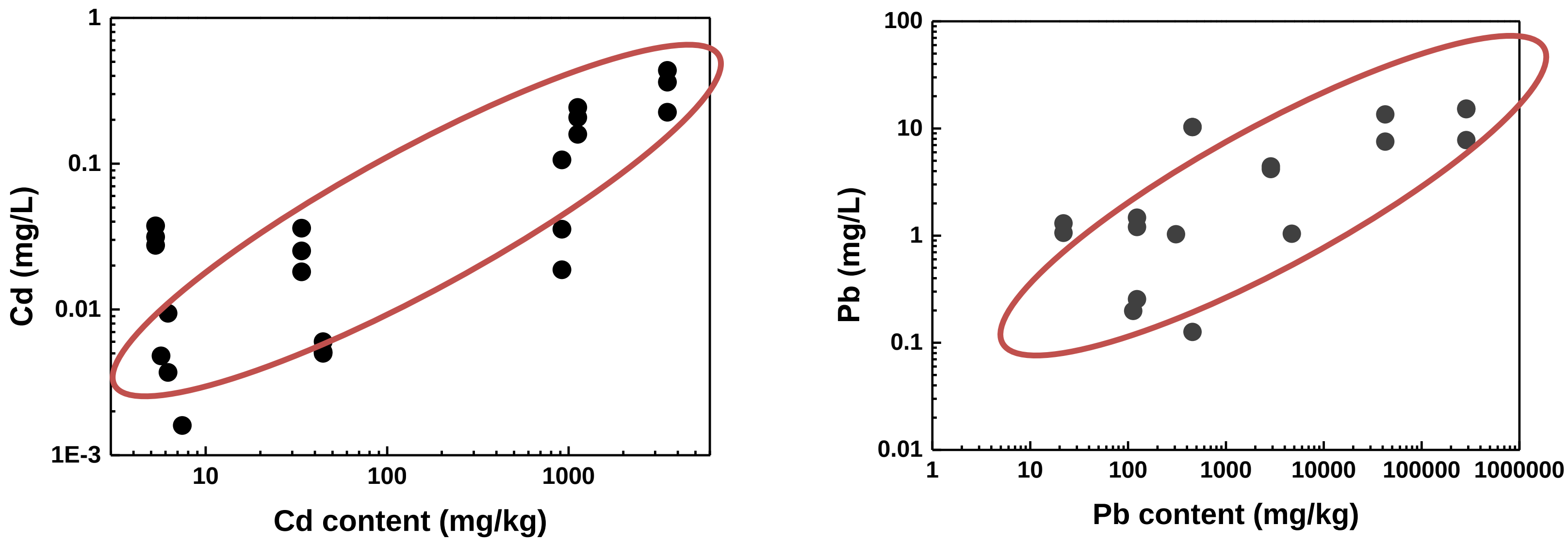
- Mineralized rock samples collected near tunnel construction sites contained sulfide minerals such as sphalerite, galena and pyrite.

- Significant leaching of Zn, Cd and Pb was observed from mineralized rock samples.

- The leaching of heavy metals was caused by the oxidation of sulfide minerals, especially sphalerite.

Thank you for your kind attention!

Discussion



The total amounts of Pb and Cd leached from the rocks strongly depended on their initial contents of these elements.

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We can estimate the approximate leaching concentration of Pb and Cd from their initial contents in the solid-phase.

XRF

	S (mg/kg)	As (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
K1	335,000	1.00	287,000	1120	254,000
K2	9,250	7.20	124	5.30	690
K3	135,000	438	456	919	269,000
K4	222,000	1,580	42,600	3,510	418,000
K5	11,500	16.8	2,890	33.8	4,640
O1	13,400	32.0	4720	44.4	14,600
T1	1,090	5.14	309	5.68	523
M1	28,200	32.0	22.0	6.20	48.0
M2	1,710	4.82	113	7.43	13.0

XRD

Sulfide minerals

	Qtz	Sph	Gal	Ang	Sus	Cer	Brt	Pyr	Msc	Rdc	Hdb
K1		+++	+	+	++		+				
K2	+++							-	+		
K3	+	+++					++				
K4		+++	+			+	++				
K5	+++										
O1	++								+++		
T1	+++										+
M1	+++							-			
M2	+++										

+++: high; ++: medium; +: miner; -: trace; Qtz: quartz; Sph:Sphalerite; Gal:Galena: Ang;Anglesite; Sus:Susannite; Cer:Cerussite; Brt:Barite; Pyr:Pyrite; Msc:Muscovite; Rdc:Rhodochrosite; Hdb:Hedenbergite

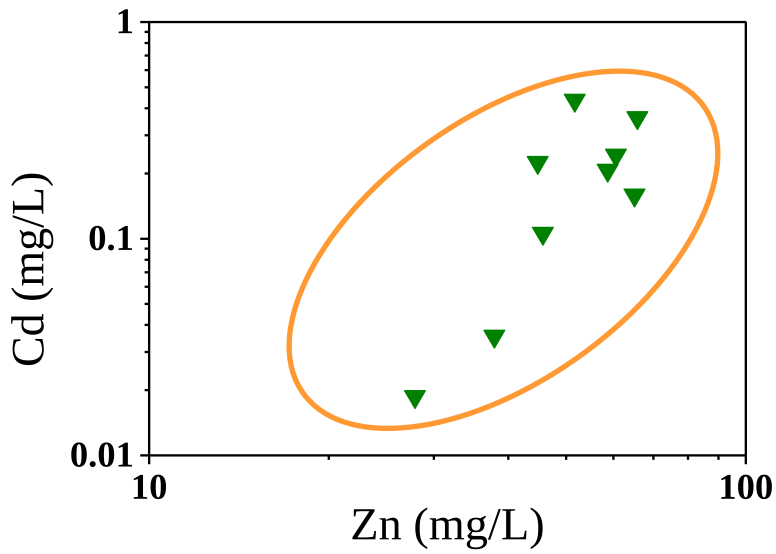
EPMA ~Single point quantitative analysis

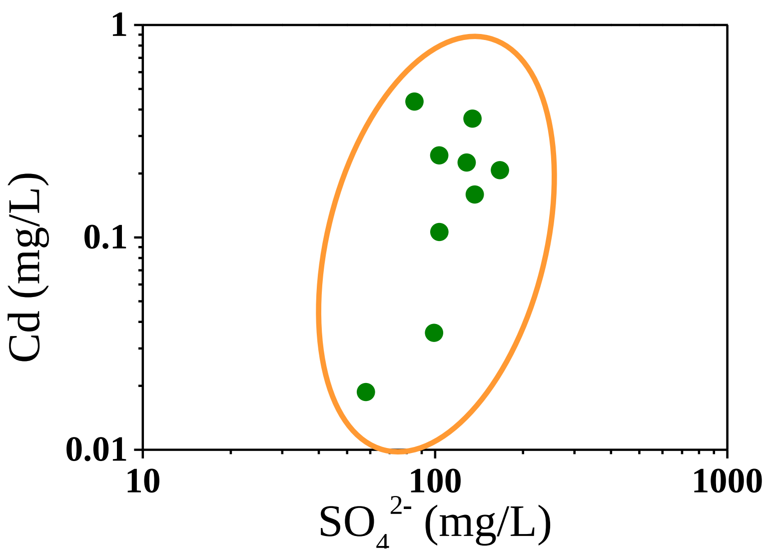
	ZnS(pure)	ZnS(center)	tennentite	chalcopyrite	galena
S (wt%)	32.4	31.0	28.0	33.7	8.41
Pb (wt%)	0.311	3.02	1.09	0	73.9
Cd (wt%)	0.382	0.488	0.199	0.02	0.128
Sb (wt%)	0	0.084	0.829	0	0
As (wt%)	0	0.826	17.3	0	0
Fe (wt%)	0.041	0.994	0.578	27.8	0.056
Cu (wt%)	0.201	3.22	40.3	31.4	0.413
Zn (wt%)	58.1	51.8	7.88	1.03	0.604
Total (wt%)	91.4	91.5	96.1	93.9	83.5

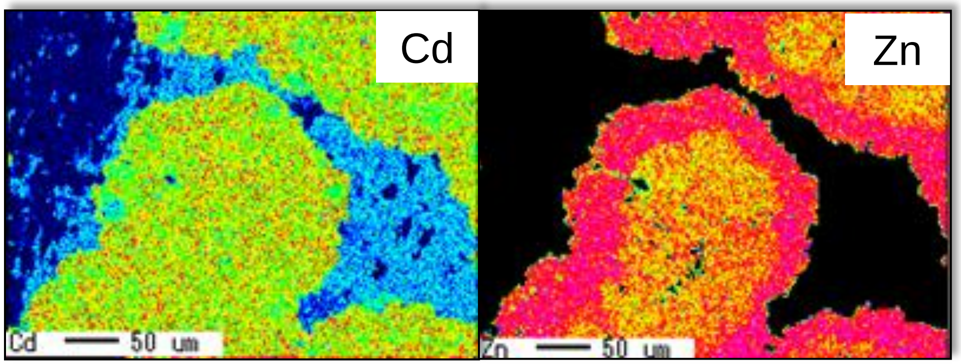
Batch leaching experiment

	pH	As (μg/L)	Fe (mg/L)	Cd (mg/L)	Pb (mg/L)	Zn (mg/L)	SO_4^{2-} (mg/L)
K1	5.18	2.04	2.04	0.243	7.78	60.6	103
K2	4.15	1.98	9.75	0.0275	0.255	5.18	87.6
K3	6	2.32	ND	0.0187	0.126	27.9	58.0
K4	6.06	1.68	ND	0.436	7.53	51.7	85.1
K5	5.29	32.5	0.183	0.0252	4.42	4.60	58.2
O1	7.21	1.80	ND	0.0051	0.119	0.160	31.7
T1	7.62	ND	ND	ND	ND	ND	92.9
M1	3.94	ND	39.2	ND	1.06	1.47	208
M2	4.75	ND	1.98	ND	ND	0.00130	101

Relationship of sphalerite and Cd







Cd leaching is caused by the **weathering of sphalerite.**