A bench-scale process to remove Pb from firing range soils

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Abstract

A bench-scale process for the removal of Pb from army firing range soils has been developed. Owing to the high specific gravity of Pb (11 g/cm^3) and related Pb species, the conventional method for removing Pb from firing range soils entails the use of gravitational soil washing. Initial attempts to remove Pb from an indoor firing range soil by means of a spiral gravitational method were successful in concentrating the majority of metallic Pb. However, this method was not successful in reducing Pb concentrations to required regulatory levels for the bulk of the soil. The systematic study of Pb speciation in soils showed that the introduced metallic Pb particles of various sizes undergo multistage physico-chemical transformations producing a mixture of metallic Pb, Pb oxides, carbonates, hydroxo-chlorides, as well as ion-exchangeable, adsorbed and other Pb forms. Firing on the same soil over time seems to break the soil down into finer particles and compromise the protective surface layers that form onto fresh metallic lead particles. This results in the accumulation of Pb in the soils finer fractions. Quantitative phase analysis studies showed that the fine soil fractions contain considerable amounts of lead carbonates, which owing to their colloidal nature cannot be readily removed using gravitational methods. To overcome this, we have developed a bench-scale method based on dissolution of all common Pb containing phases, including metallic, oxides, carbonates, etc. Mixing the bulk soil with monobasic acid, effective separation of dissolved lead from the rest of the soil components was achieved, and then, the separated Pb was reprecipitated in the form of carbonates. According to the total digestion tests performed on the firing range soils treated by this method it was possible to reduce Pb concentrations below the required regulatory levels.

STUDY SITE LOCATION

FORT IRWIN
OVERALL PROJECT OBJECTIVES

- Life cycle management of small arms firing ranges
  - Research and evaluation of site specific ecological and environmental risks associated with the past and present use of military ranges
  - Maintenance and/or remediation of existing ranges
  - Optimization and/or modification of remediation alternatives
 - Identification of critical design aspects for new ranges

STUDY OBJECTIVES

➤ **Qualitative mineralogy of the soil –Optical and polarizing microscopy, XRD, SEM**

➤ **Quantitative mineralogy of the soil- Rietveld quantification**

➤ **Identification and quantification of the existing contaminants –physical states and chemical forms**

➤ **Soil washing from contaminated Pb (gravitational and chemical methods)**

ENVIRONMENTAL PARAMETERS

- ➤ Climate (arid/desert)
  - Low precipitation (4-6in. per year)
  - absence of vegetation (favors water runoff vs. infiltration)
- ➤ Soil characteristics (2 different areas)
  - a) Range 5   (active firing range)

    Berms of native sand

  - b) Goldstone (abandoned firing range)

    Berms of indigenous playa soil (ecologically sensitive area- endangered species habitat)
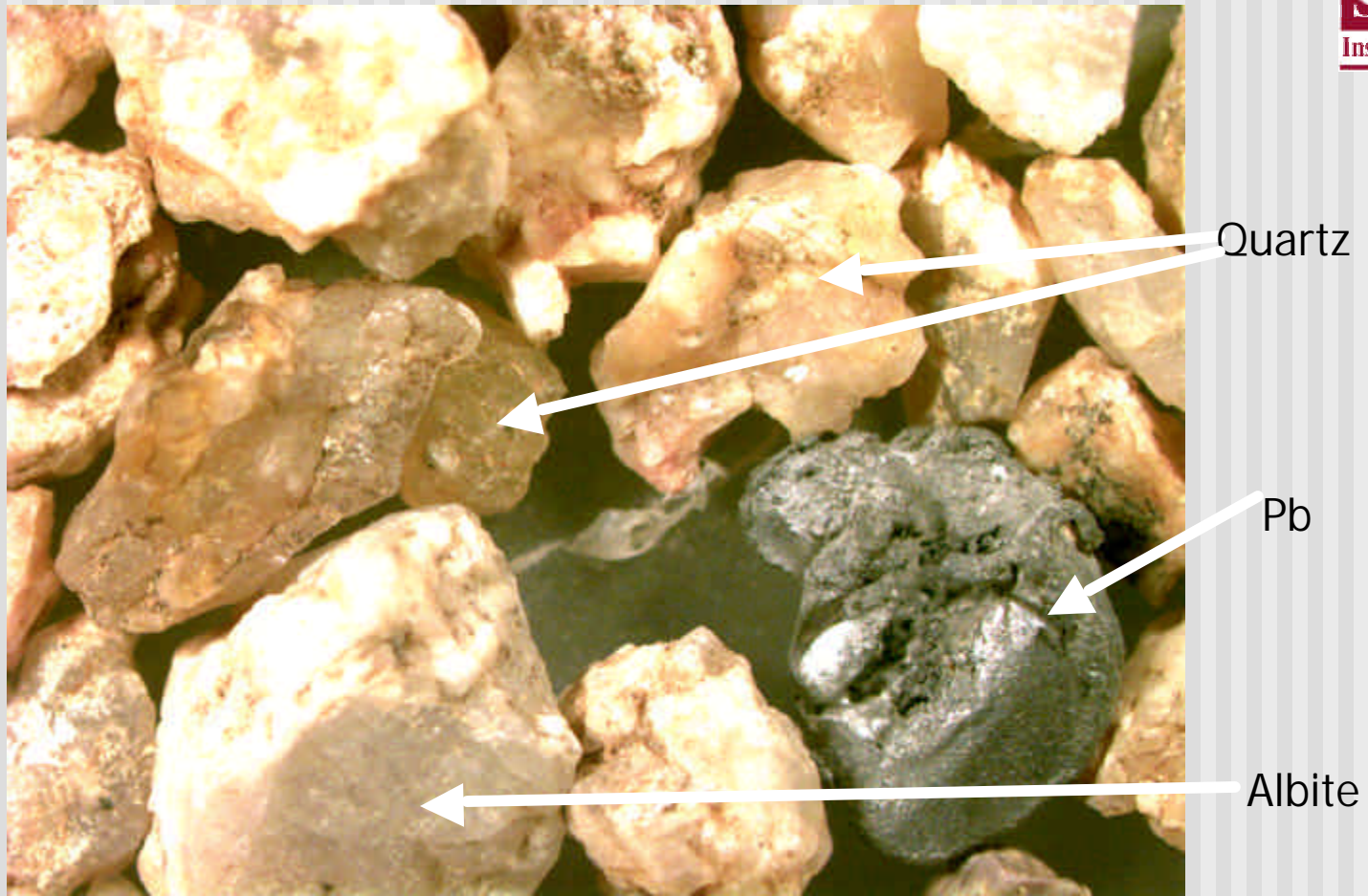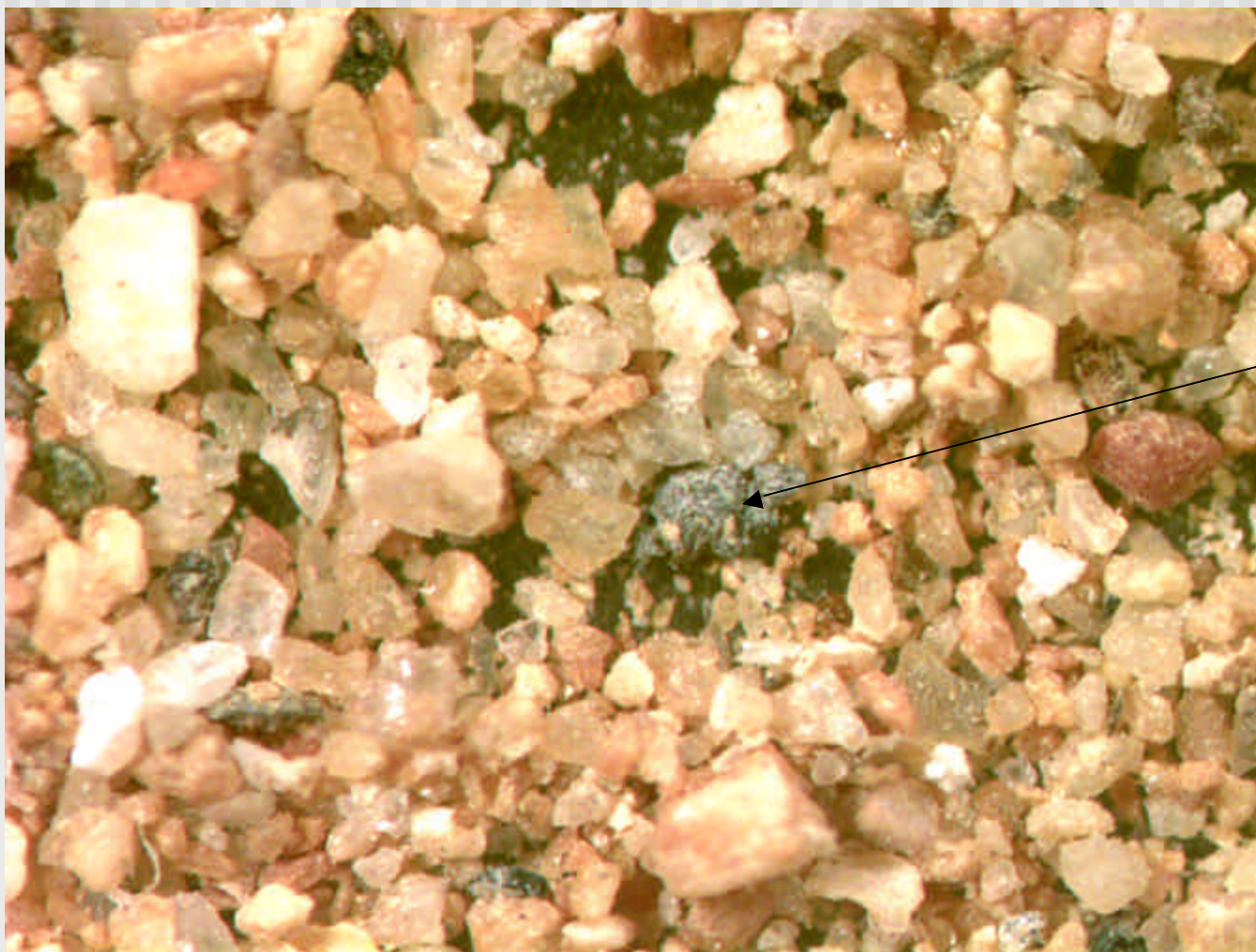
TYPICAL SAFR
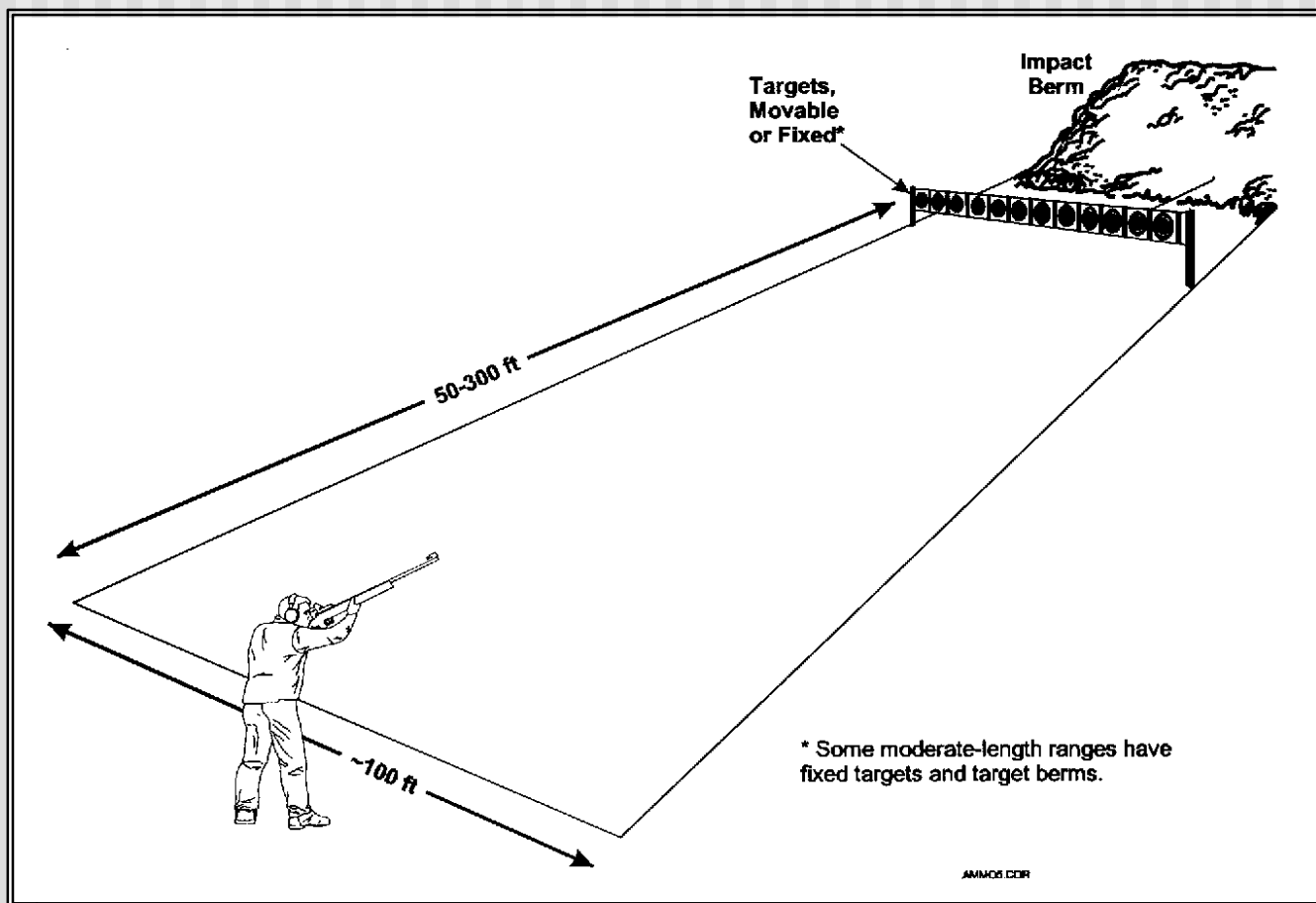
(USACE, 1998)

Pb contamination in SAFR

➤In recent years, there has been a concern for lead contamination from SAFR.

➤The type of arms SAFR are 50 caliber or less (pistols, rifles, shotguns; and machine-guns - military installations)

- RANGE 5 (primarily M-16)

  small diameter projectile-high velocity

  Jacketed bullets- Cu (89-95%), Pb (max.% 0.05), and Fe (max. 0.05) and Zn (5-11%) (Battelle, 1997)

- GOLDSTONE RANGE older facility (50 caliber and probably M1 munitions)

  steel bullets present

Quartz

Pb

Albite

Optical photo of R5S6 sample, showing relatively
fresh metallic Pb piece

Pb
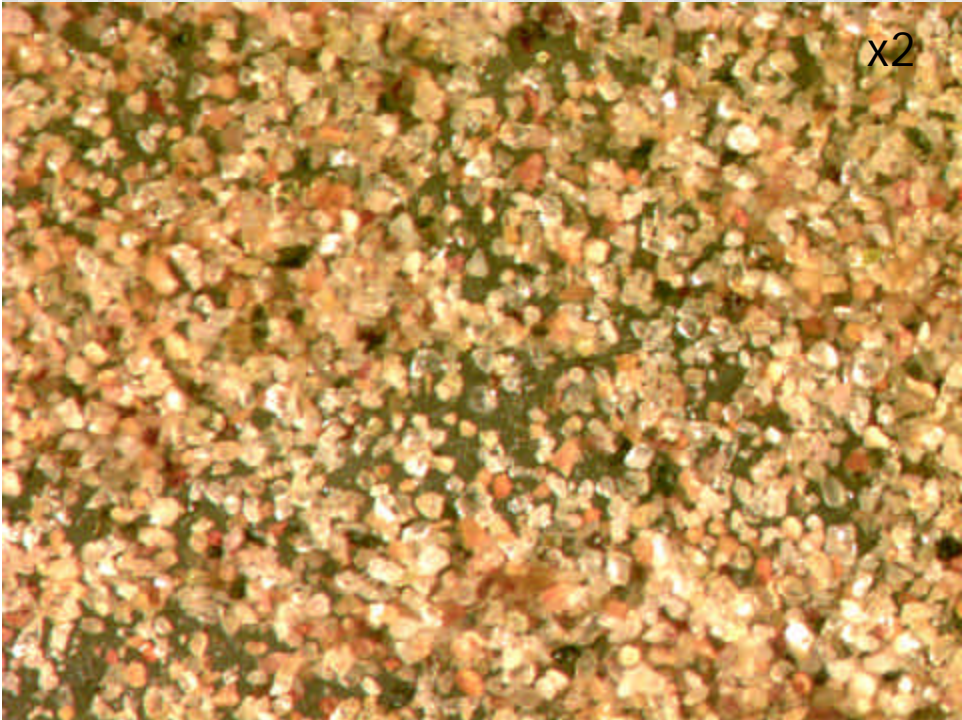
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Optical photo of R5S6 sample,
showing typical minerals assemblage,
containing mostly quartz and feldspar minerals
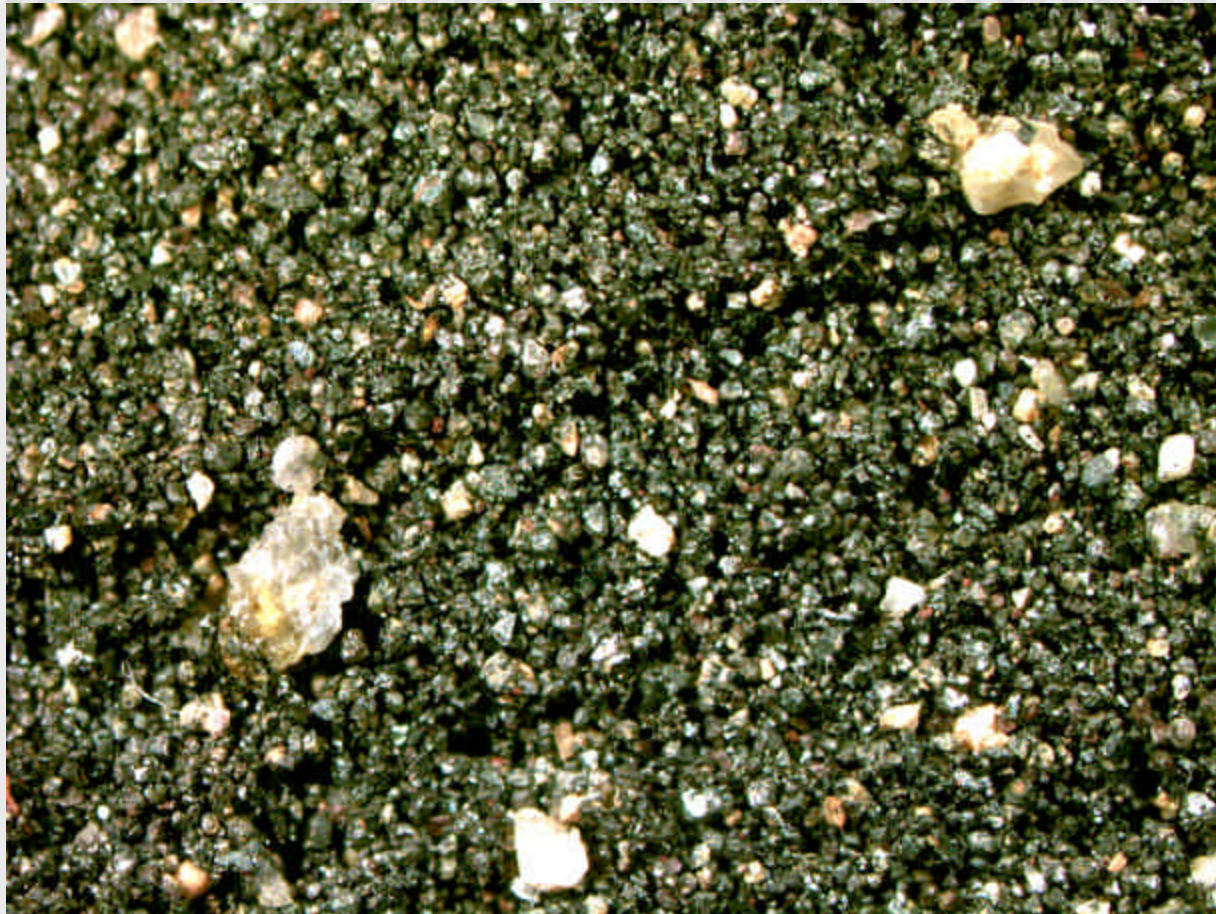
Optical photo of magnetic fraction of R5S6 sample
containing mostly Magnetite, Hematite

Goldstone soils

x2

x10

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Cerussite
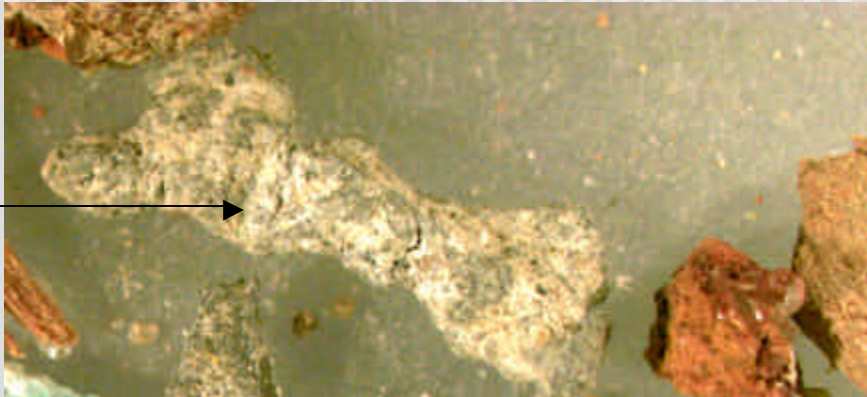
M-Montmorillionite-15A
I-Illite-2M$_1$
K-Kaolinite-1A
Q-Quartz
A-Albite
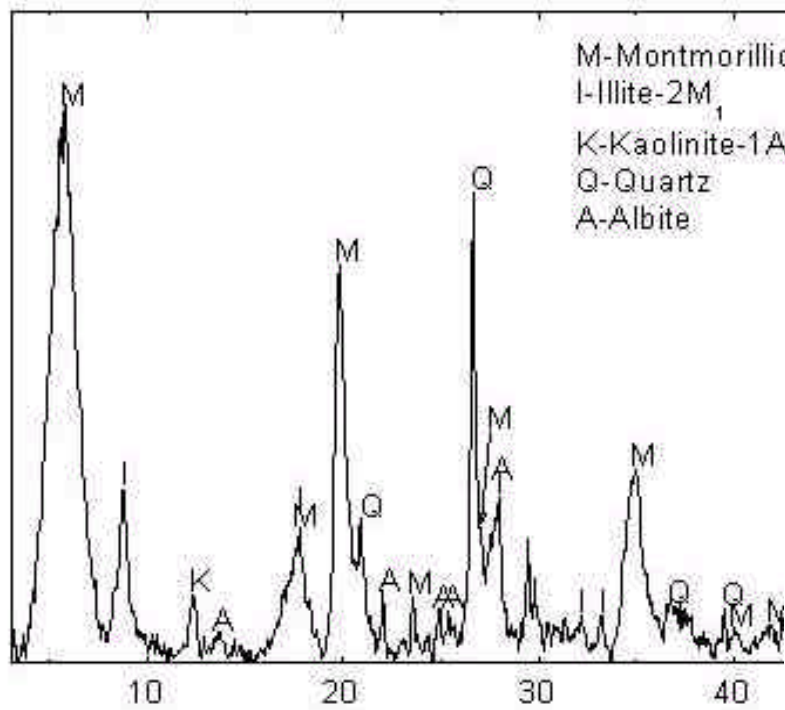
R5S2-400/24h-Down

R5S2-400/24h-UP

M-Montmorillionite-15A
Mu-Muscovite-Mica
K-Kaolinite-1A
Q-Quartz
A-Albite
O-Orthocalse

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Mu-Muscovite 2M2
Ad-Andalusite
Q-Quartz
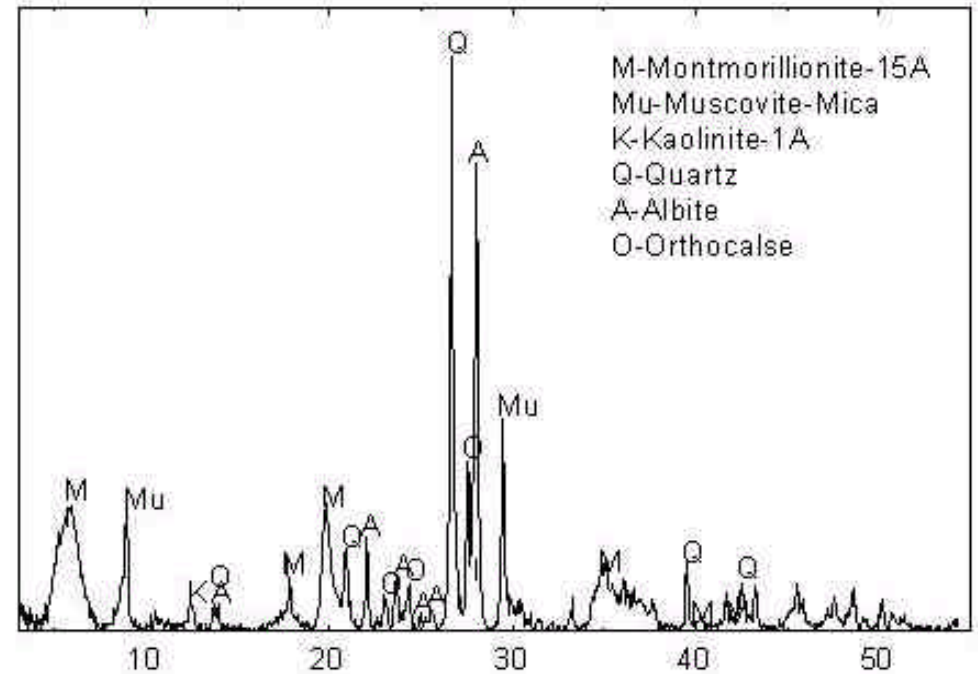
XRD pattern of magnetic particles found in sample R5S2-4+10

M-Magnetite Fe_3O_4
H-Hematite Fe_2O_3
Q-Quartz $SiO2$
FS-feldspar minerals
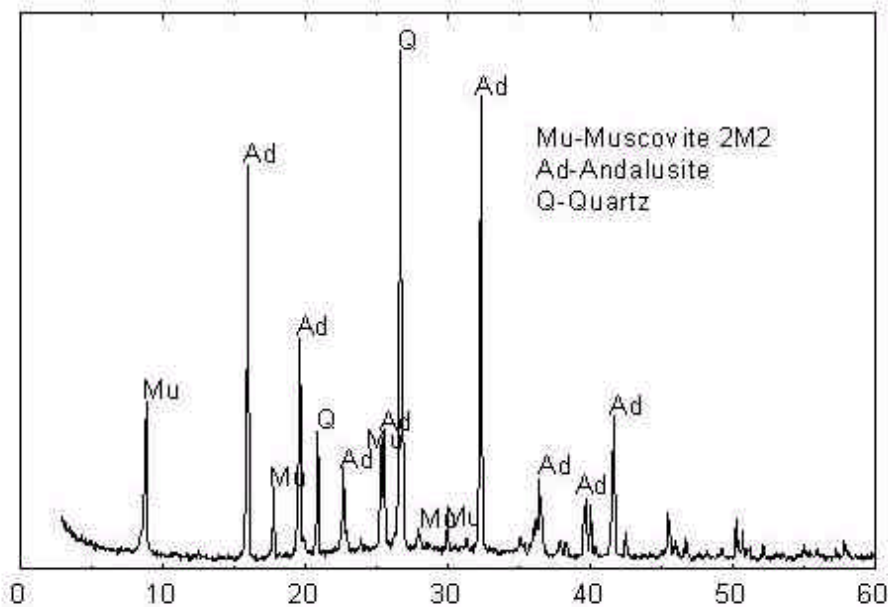
XRD pattern of black particle containing Only Muscovite, Andalusite and quartz found in sample R5S2-4+10

M-montmorillionite 15A
Mu-muscovite
I-Illite
K-kaolinite
FS-feldspar minerals
Cr-cristobalite
Ca-calcite
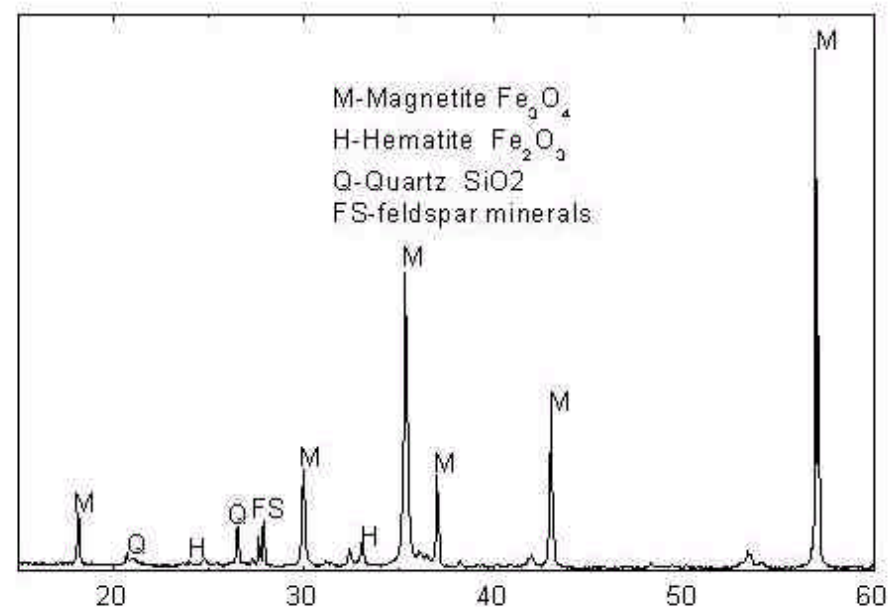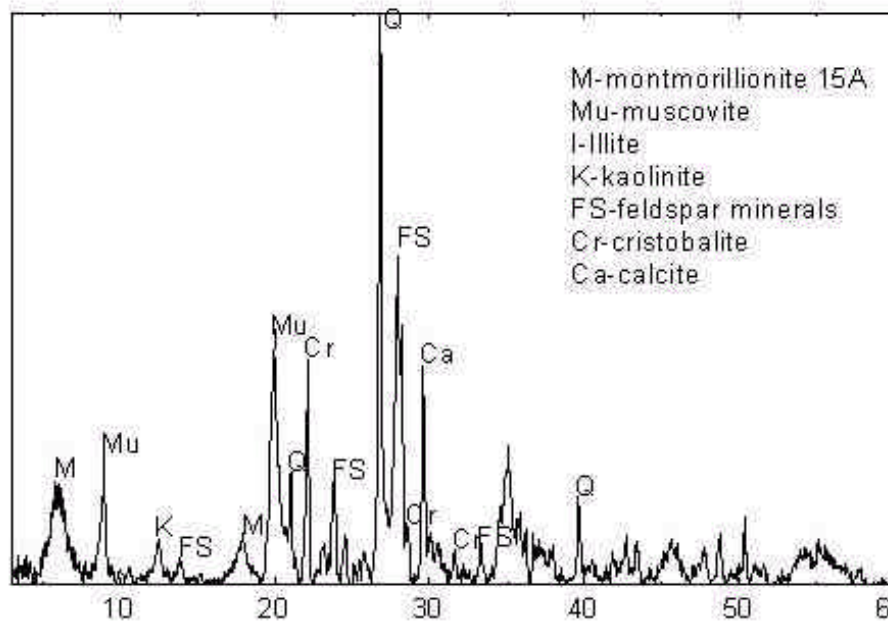
XRD pattern of sample
B7S1-400/24h-DOWN

XRD pattern of sample
B7S1-400/24h-UP

M-montmorillionite 15A
Mu-muscovite
I-Illite
K-kaolinite
FS-feldspar minerals
Cr-cristobalite
Ca-calcite
Gu-Gupsym $CaSO_4 2H_2O$

M-montmorillionite 15A
Mu-muscovite
K-kaolinite
FS-feldspar minerals
Cr-cristobalite
Ca-calcite
Gu-Gupsym $CaSO_4$ $2H_2O$
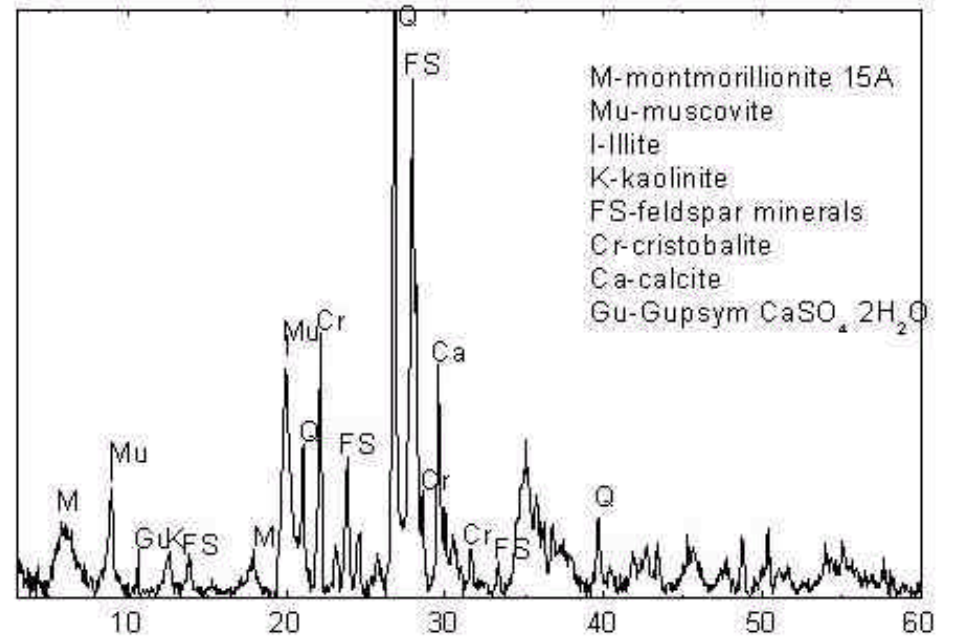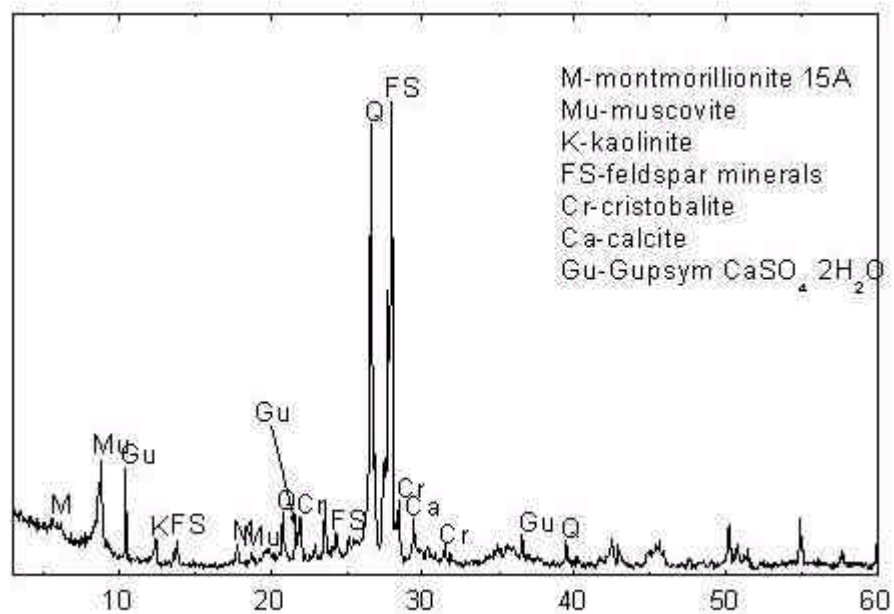
XRD pattern of sample B7S1-40+200

XRD pattern of sample B7S1-200+400

FS
M-montmorillionite 15A
Mu-muscovite
K-kaolinite
FS-feldspar minerals -Anorthite
Cr-cristobalite
Ca-calcite
Gu-Gupsym $CaSO_4$ $2H_2O$
LS-Leucosphenite $Na_4BaB_2Ti_2Si_{10}O_{30}$
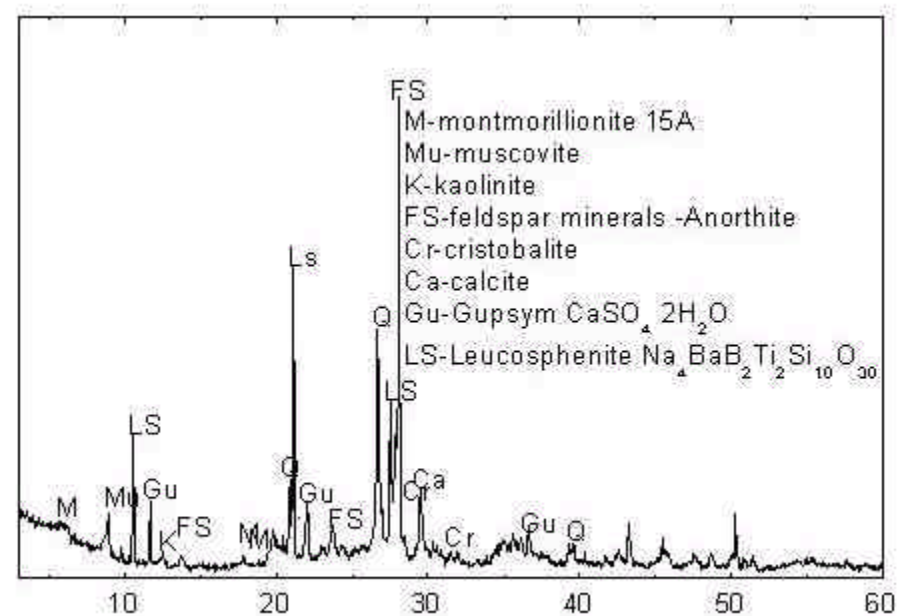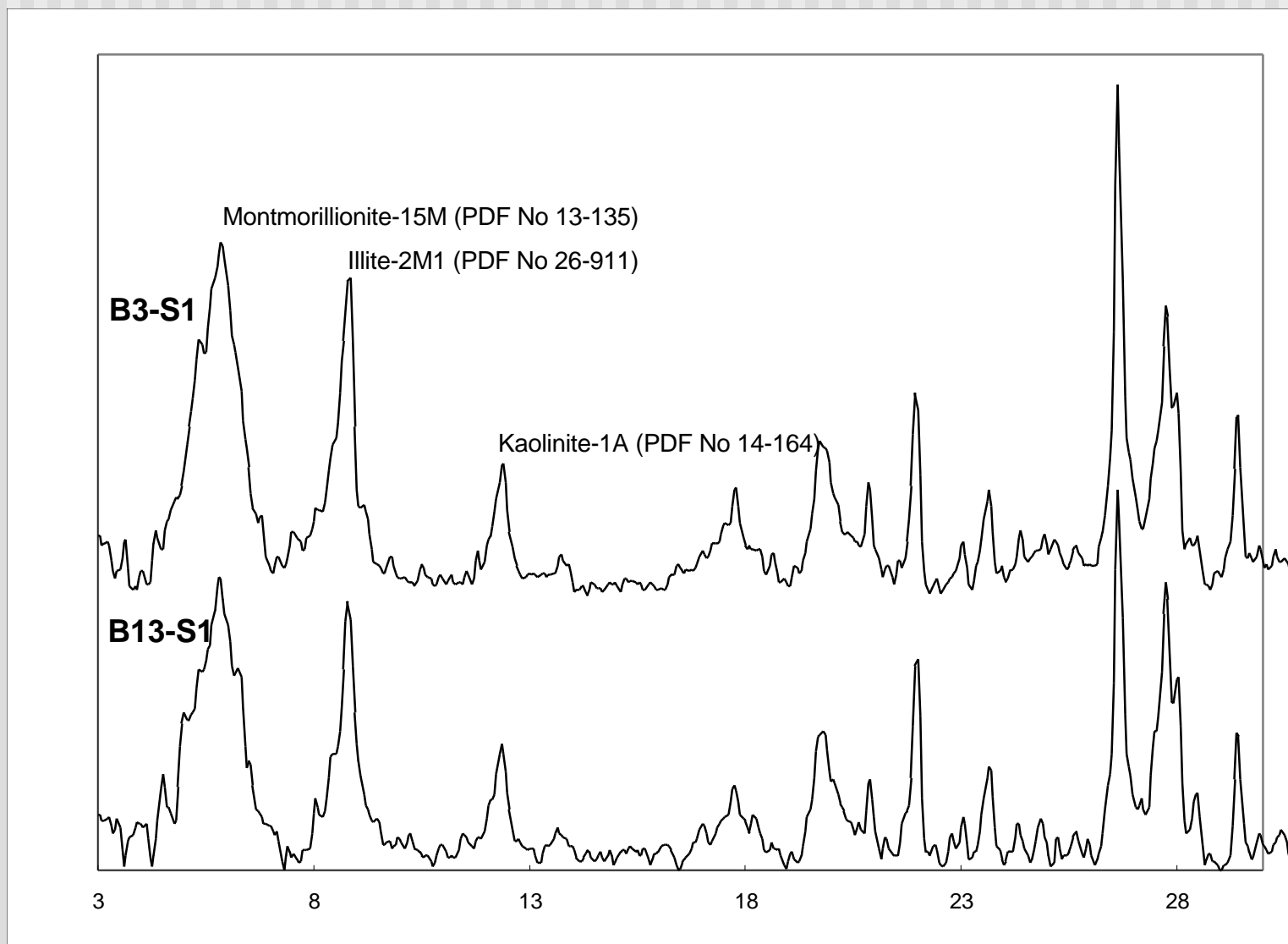
Clay minerals of Goldstone soils

Calculated cumulative diffraction patterns of Pb-SiO$_2$ mixtures (highest reflections are normalized to unity)
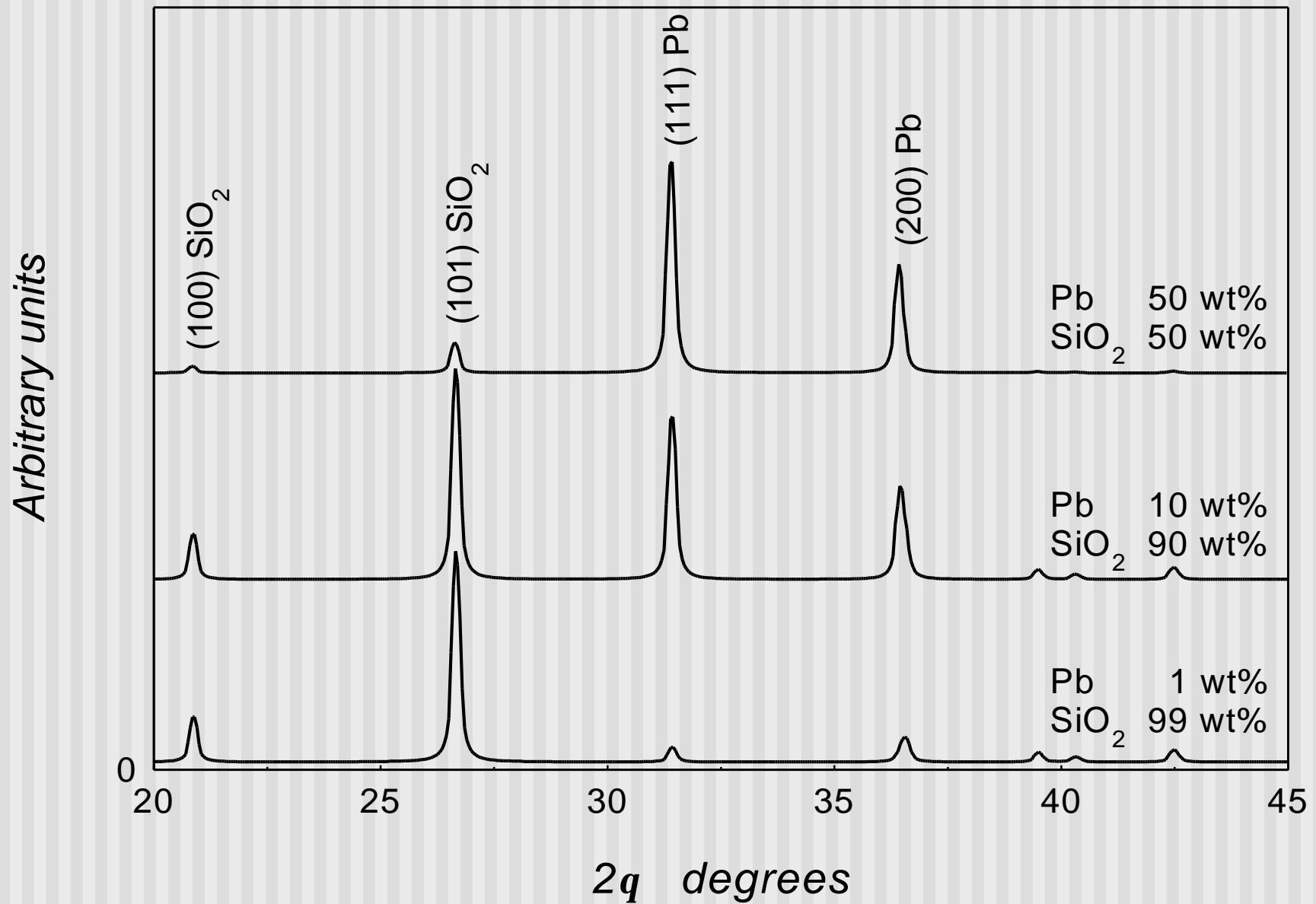
Theoretical calibration curve for metallic Pb concentration $I_{Pb(111)}/I_{SiO2(101)}$ for Bragg-Brentano geometry diffractometer

Mixture containing 12.6 wt% (3.19 vol%) of metallic lead will show intensity for (111) as high as (101) peak of Quartz.
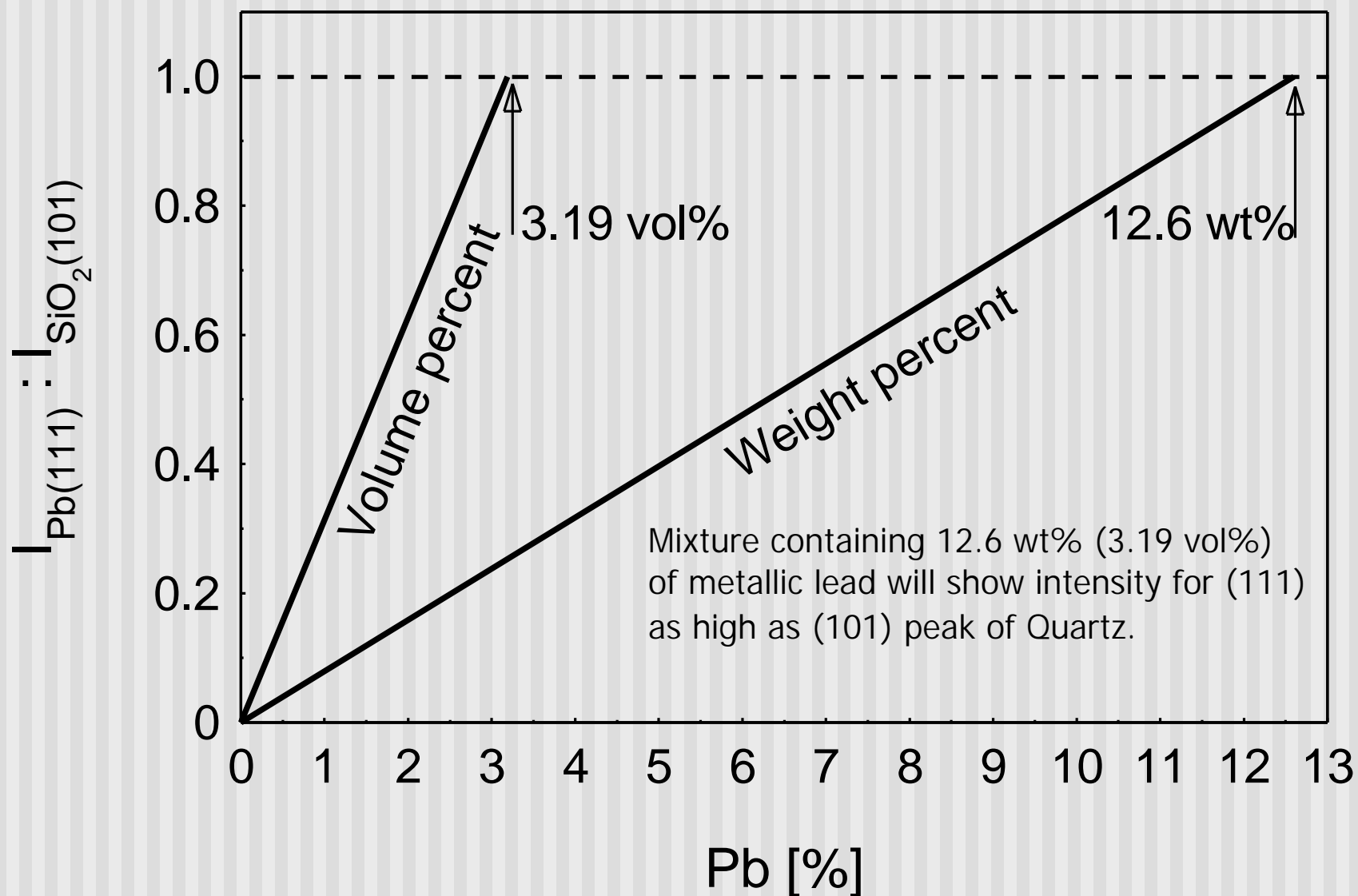
Grain size fractionation results for Fort Irwin Soil samples (wt%)

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Fractions	Range Five				Goldstone			
	R5S1		R5S6		B3S1		B7S1	
	A	B	A	B	A	B	A	B
Magnetic	1.48	1.59	1.05	1.10	1.63	1.47	0.12	0.09
-4+10	18.26	17.64	15.03	14.95	6.16	5.96	0.49	0.56
-10+40	45.75	46.41	41.03	40.69	13.14	12.89	0.58	0.68
-40+100	17.58	17.77	19.45	18.61	22.57	21.95	6.62	1.37
-100+200	5.04	6.67	8.02	8.36	17.30	16.58	4.13	5.41
-200+400	3.70	3.79	4.54	4.73	7.35	7.58	5.01	3.99
-400 Down	7.57	5.49	9.95	10.57	31.85	32.05	85.06	87.90
-400 Up	0.62	0.63	0.93	0.98	0.01	1.54	0.41	0.00

Mineralogical composition of Range Five soils

	Magnetic	4+10	10+40	40+100	100+200	200+400	400down	400 up	Totals
Muscovite	0.00	1.11	2.29	0.91	0.36	0.06	0.27	0.00	5.01
Quartz	0.00	8.44	18.16	8.97	1.33	0.79	1.76	0.04	39.49
Microcline	0.05	3.71	8.14	2.41	0.62	0.30	0.55	0.00	15.77
Albite (low)	0.00	4.98	17.11	5.15	2.42	1.15	2.17	0.05	33.03
Lead	0.03	0.02	0.05	0.02	0.00	0.01	0.01	0.00	0.13
Cerussite	0.00	0.00	0.02	0.02	0.00	0.00	0.08	0.00	0.12
Tremolite	0.00	0.00	0.00	0.00	0.32	0.19	0.48	0.00	0.99
Illite	0.00	0.00	0.00	0.00	0.00	0.74	0.46	0.09	1.29
Montnorillonite	0.00	0.00	0.00	0.00	0.00	0.38	1.63	0.38	2.40
Kaolin	0.00	0.00	0.00	0.00	0.00	0.08	0.24	0.05	0.38
Hematite	0.58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.58
Magnetite	0.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.81

Mineralogical composition of Goldstone soils

	Magnet	4+10	10+40	40+100	100+200	200+400	400down	-400 up	Totals
Muscovite	0.00	0.78	1.08	1.02	0.85	0.63	1.02	0.00	5.38
Quartz	0.00	0.60	1.62	7.09	3.65	1.03	2.74	0.00	16.73
Anorthite	0.20	1.54	4.00	9.06	4.15	1.69	1.62	0.00	22.26
Albite	0.11	2.75	4.69	4.32	8.03	3.82	5.73	0.00	29.45
Cristobalite	0.00	0.39	1.49	0.84	0.36	0.12	0.51	0.00	3.71
Lead	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cerussite	0.00	0.01	0.00	0.00	0.00	0.00	0.05	0.00	0.06
Laurionite	0.00	0.02	0.01	0.00	0.00	0.00	0.08	0.00	0.11
Cordierite	0.00	0.07	0.26	0.27	0.26	0.06	0.43	0.00	1.35
Illite	0.00	0.00	0.00	0.00	0.00	0.00	5.64	0.00	5.64
Montmorillonite	0.00	0.00	0.00	0.00	0.00	0.00	12.25	0.00	12.25
Kaolin	0.00	0.00	0.00	0.00	0.00	0.00	1.37	0.00	1.37
Calcite	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.41
Hematite	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54
Magnetite	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.78

Lead concentration vs particle size-fractions

- r5s6
- r5s1
- b3s1
- b7s1

Pb concentration [ppm]

Fractions: 4_10, 10_40, 40_100, 100_200, 200_400, _400down, _400up
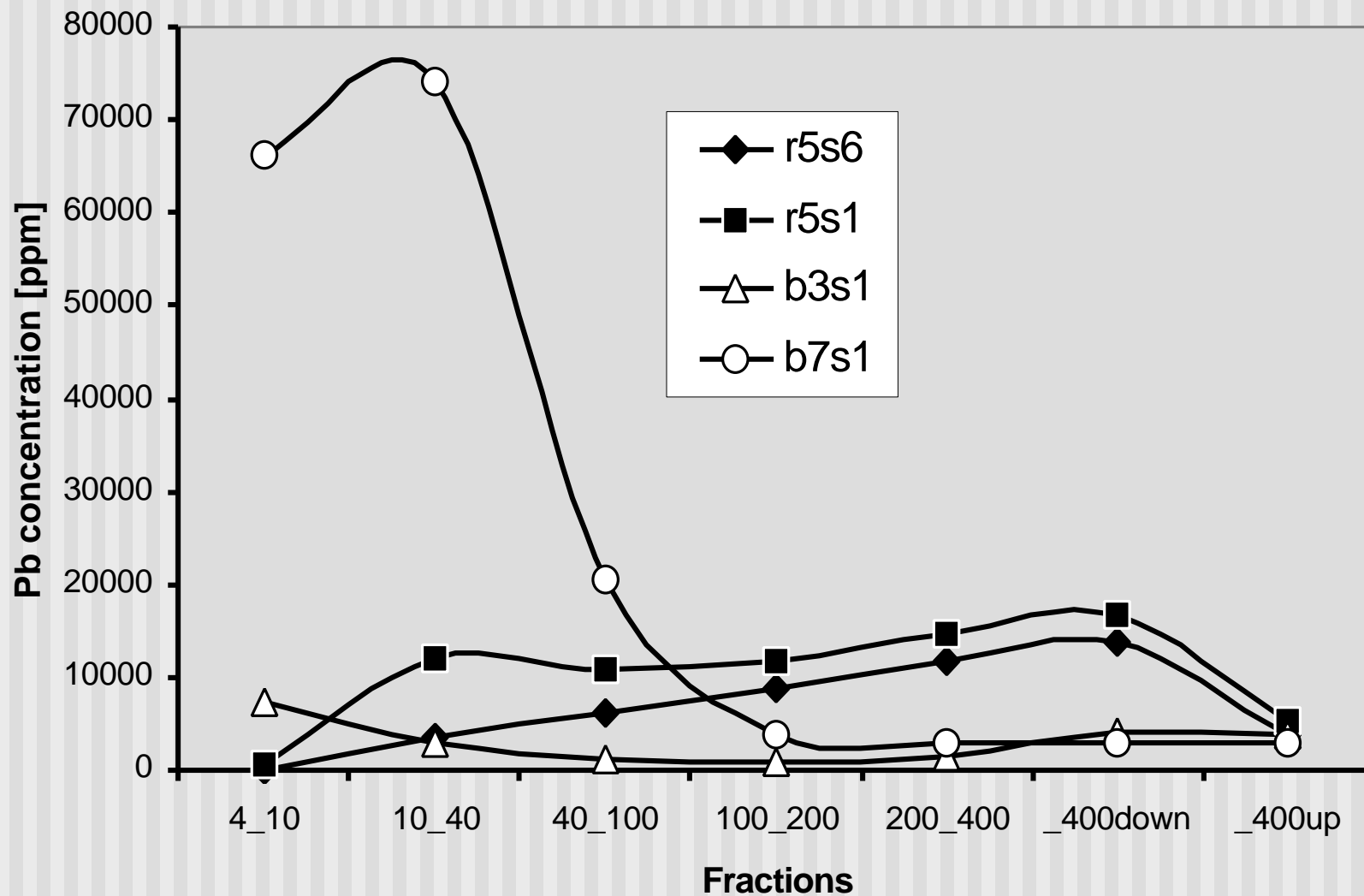
Normalized concentration of Pb vs particle size-fractions adjusted according to fraction's weight

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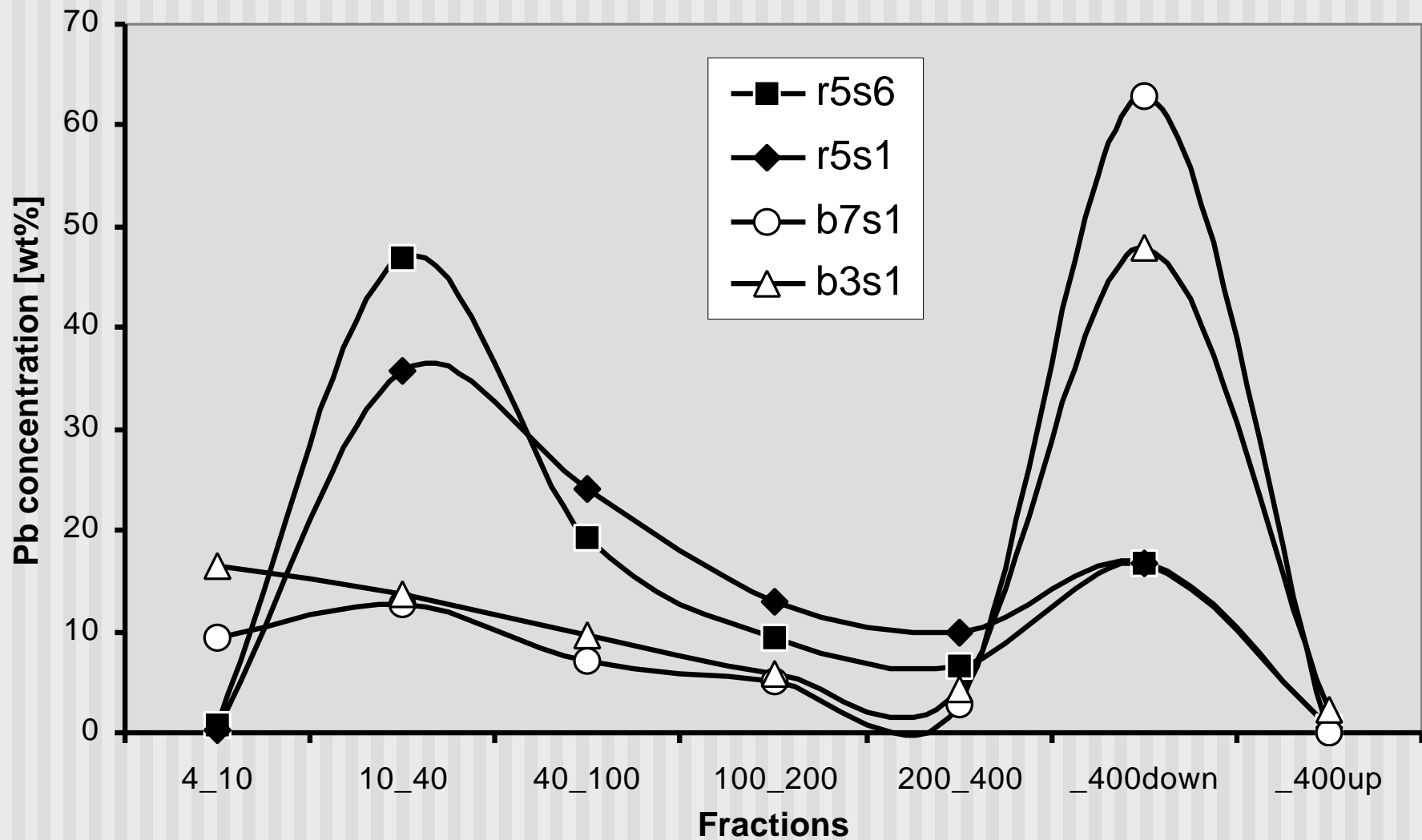
Rietveld plot of R5S1 –10+40 fraction

Observed background removed pattern

Calculated pattern

Difference pattern

Intensity [a.u.]

Two theta [^{o}]
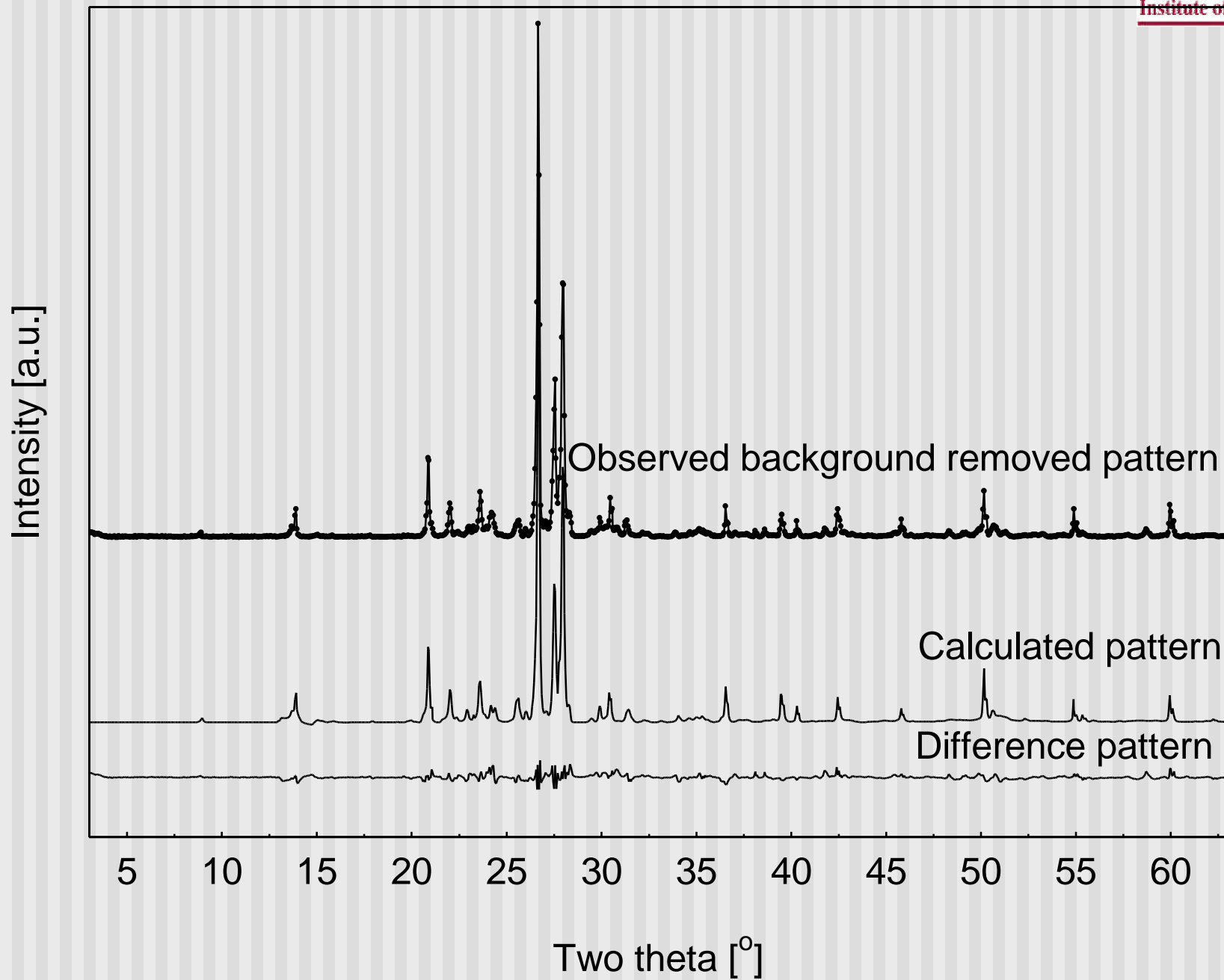
Rietveld plot of R5S1 –400up fraction
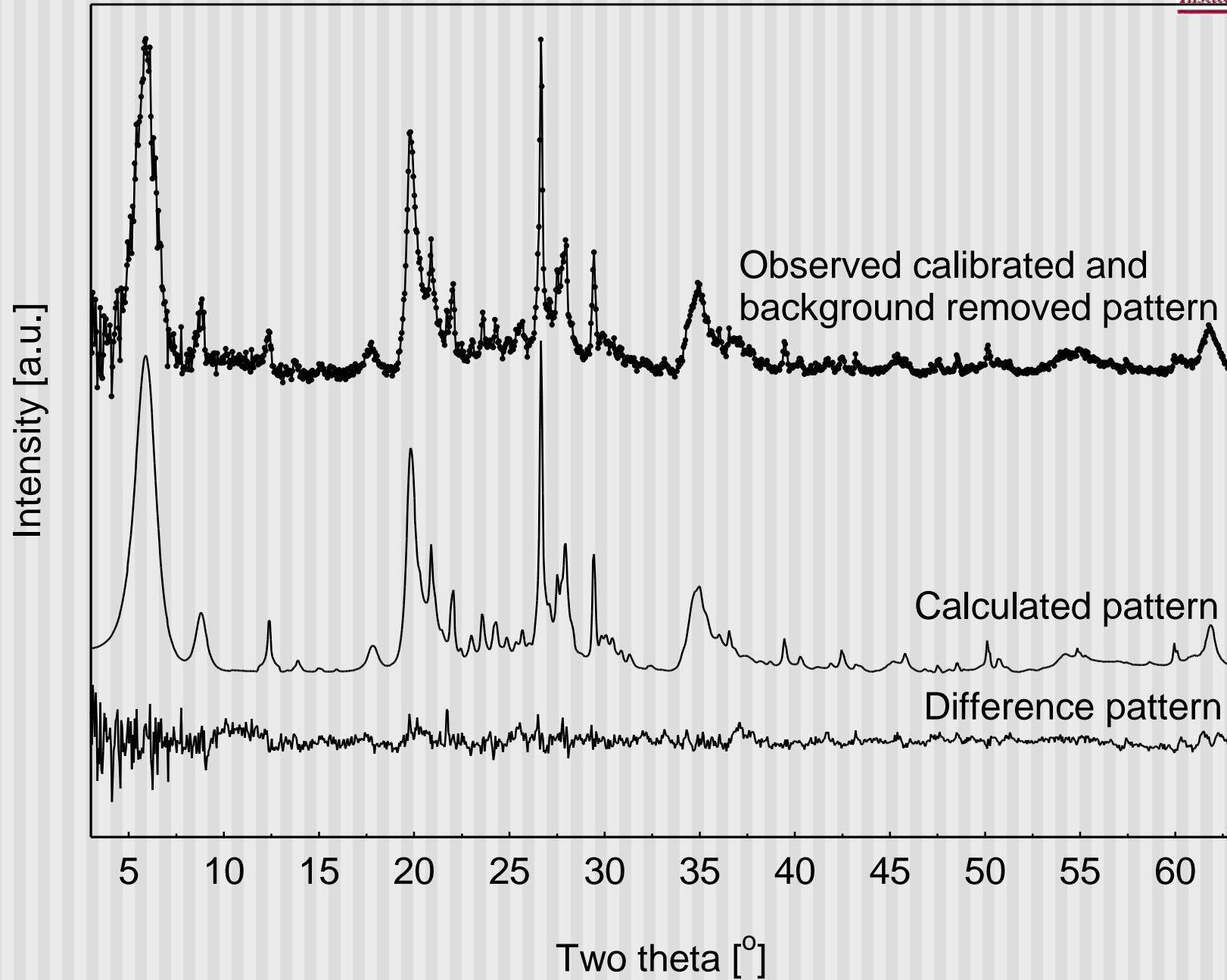
MATERIALS AND METHODS

➤ Geotechnical testing for Index properties of 7 samples from Range 5 and 5 samples from Goldstone

➤ Analytical testing of these samples plus those from one hand auger boring from Range 5

- Acid digestion (EPA method 3050B)
- Leachability test- TCLP (EPA method 1311)
- Sequential extraction (Tessier et al. 1979)

➤ Mineralogical testing

- SEM
- XRD

Soil and water chemistry

•High concentrations of dissolved organic matter (fluvic or humic acid) can increase lead concentrations due to its chelating abilities.

•Insoluble organic matter and clays can decrease lead concentrations by adsorption or formation of stable complexes).

•Lead concentrations can decrease or increase depending on the chemistry and its effect on the redox potential and metal speciation. Lower pH's (acid) increases lead concentrations, higher pH's (base) decrease the lead concentrations.

•Sandy soils are less likely to bind to lead and do not retain water

•Phosphate and sulfide Pb compounds are less soluble than carbonates or hydroxides

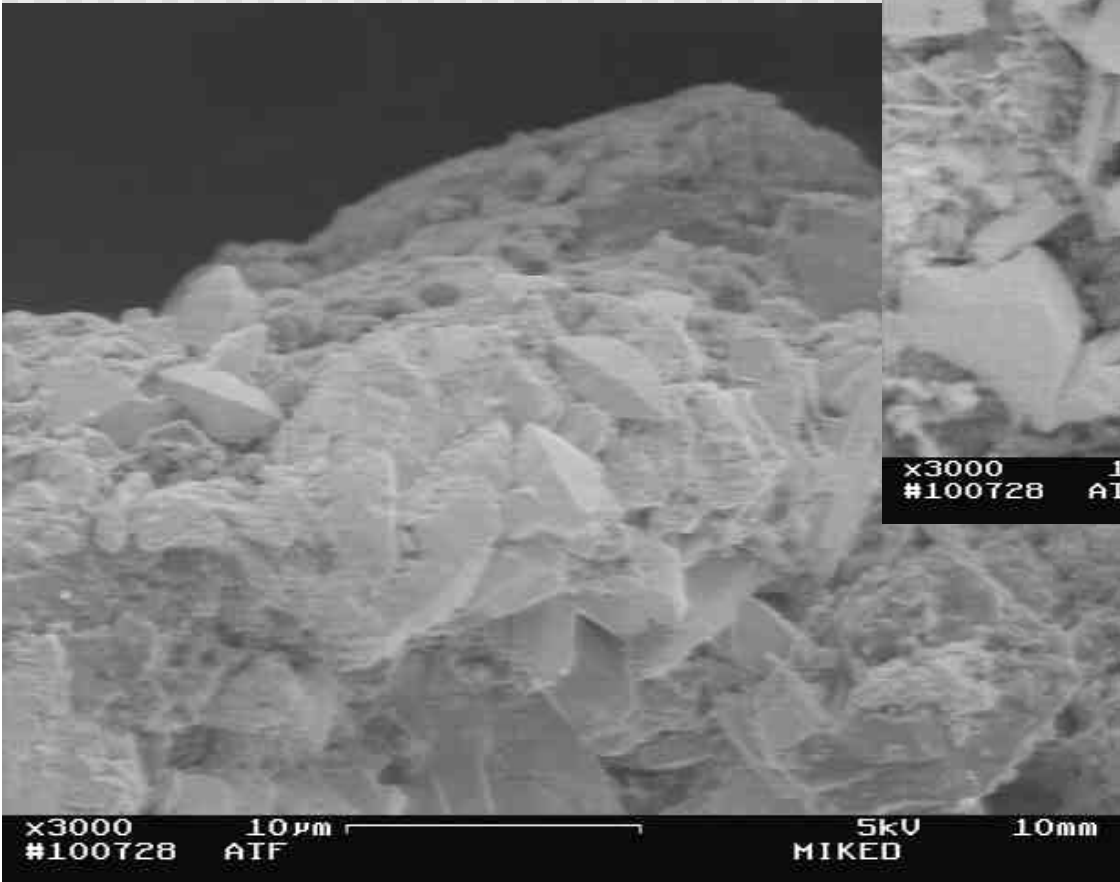# Pb Speciation in pE-ph Diagram
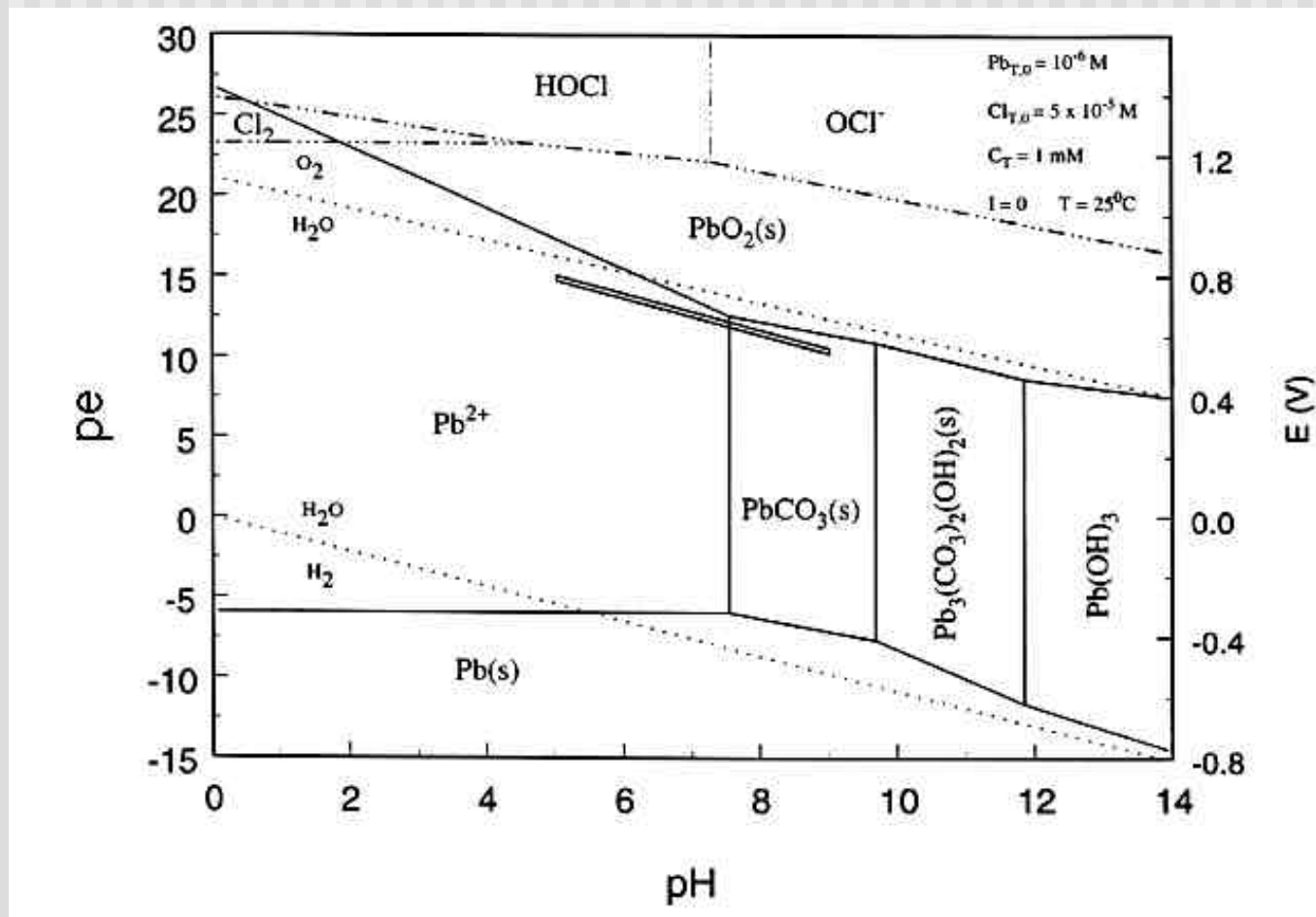
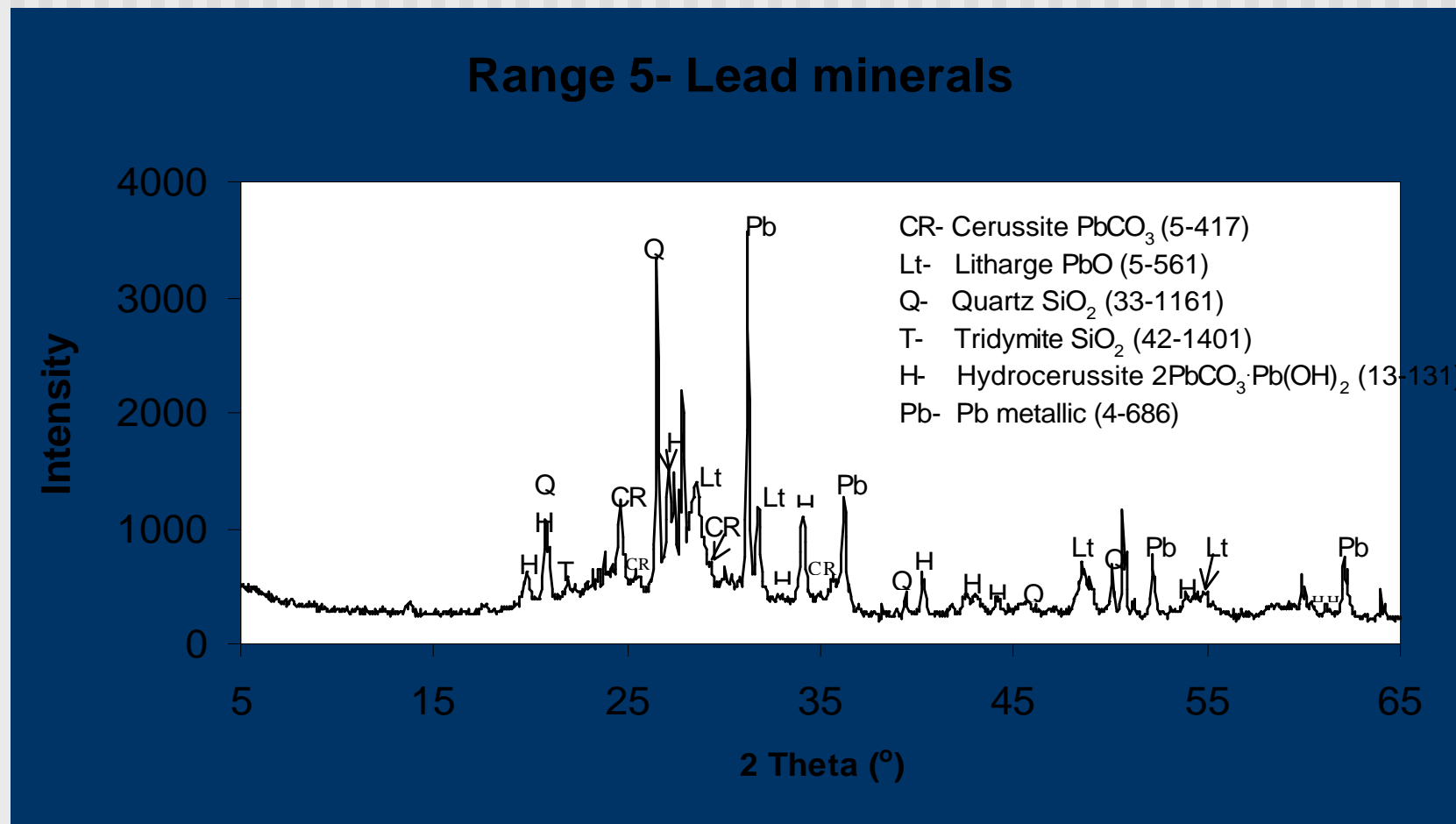# SEM of cerussite forming on lead particle
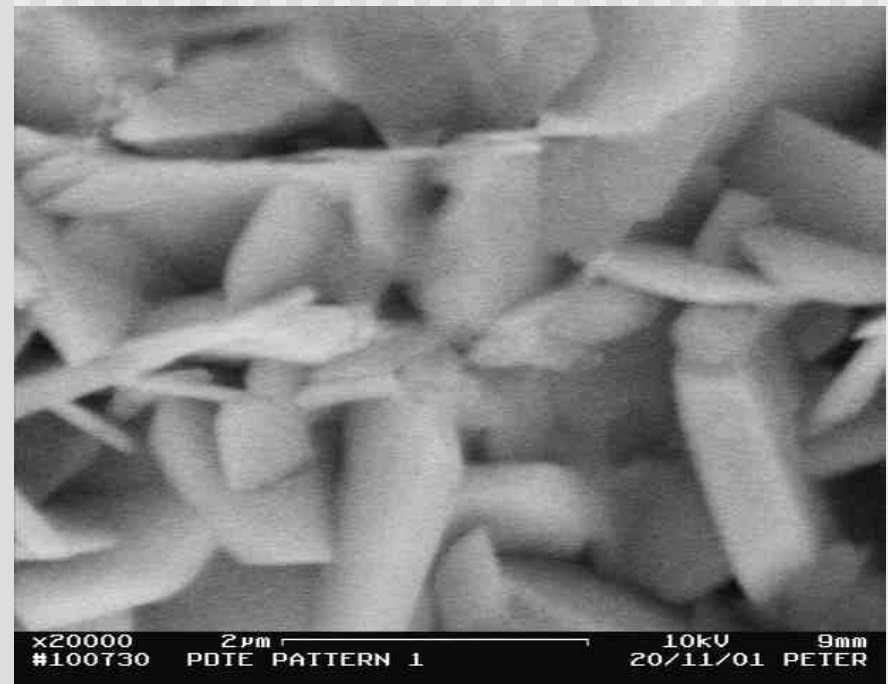
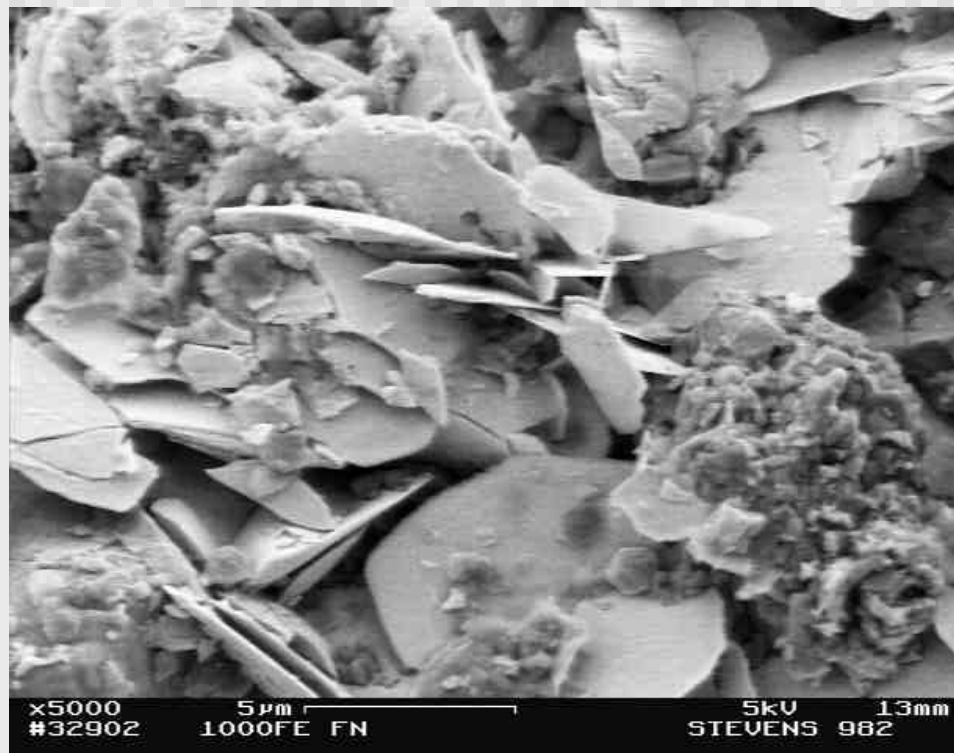Enlarged Lead particle reveals cerussite

SEM of well-developed crystals of cerussite on weathered surface of metallic lead particles

XRD of Pb core-shell particles

Range 5- Lead minerals

CR- Cerussite PbCO$_3$ (5-417)
Lt- Litharge PbO (5-561)
Q- Quartz SiO$_2$ (33-1161)
T- Tridymite SiO$_2$ (42-1401)
H- Hydrocerussite 2PbCO$_3$·Pb(OH)$_2$ (13-131)
Pb- Pb metallic (4-686)

SEM-GOLDSTONE
secondary minerals

x5000   5µm   5kV   13mm
#32902   1000FE FN   STEVENS 982

Laurionite PbClOH Crystals on Surface of Lead Particles

Goldstone XRD Pb core shell particles

Goldstone- Lead minerals

L- Laurionite PbClOH (31-680)
Pb- Pb metallic (4-686)
H- Hydrocerussite 2PbCO$_3$·Pb(OH)$_2$ (13-131)
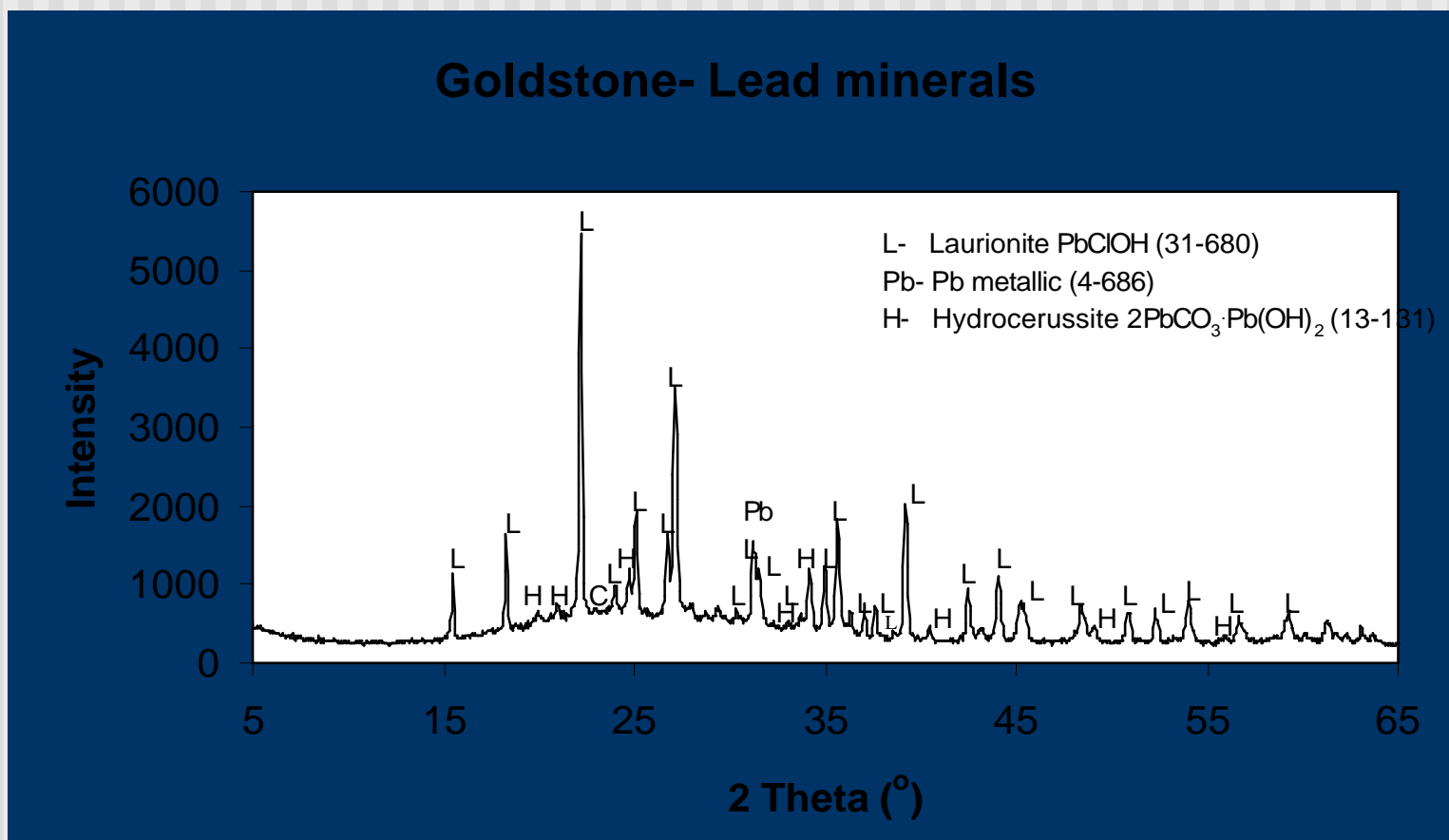
Spiral washing results

Feed	Solids Loading wt%	Flow Rate gpm	Pb Conc. mg/kg
Concentration = 25300 mg/kg			
-#10 + #50	5%	20	1175
		25	1078
		30	698
		35	584
		39.5	1885
Concentration = 10900 mg/kg			
-#50 +#200	5%	20	1121
		27.7	735
		30	533
		35	670
		40	1456

Soil washing scheme

Dissolve Pb and Pb compounds at low pH and precipitate at high pH

Soil

Add $H_2O + HNO_3$

Tumble

Soil: H_2O: HNO_3 =1:10:0.1-0.3

Filter or settle solid

Separate solid and liquid

Clean soil

Add NaOH

H_2O

Cerussite and Hydrocerussite
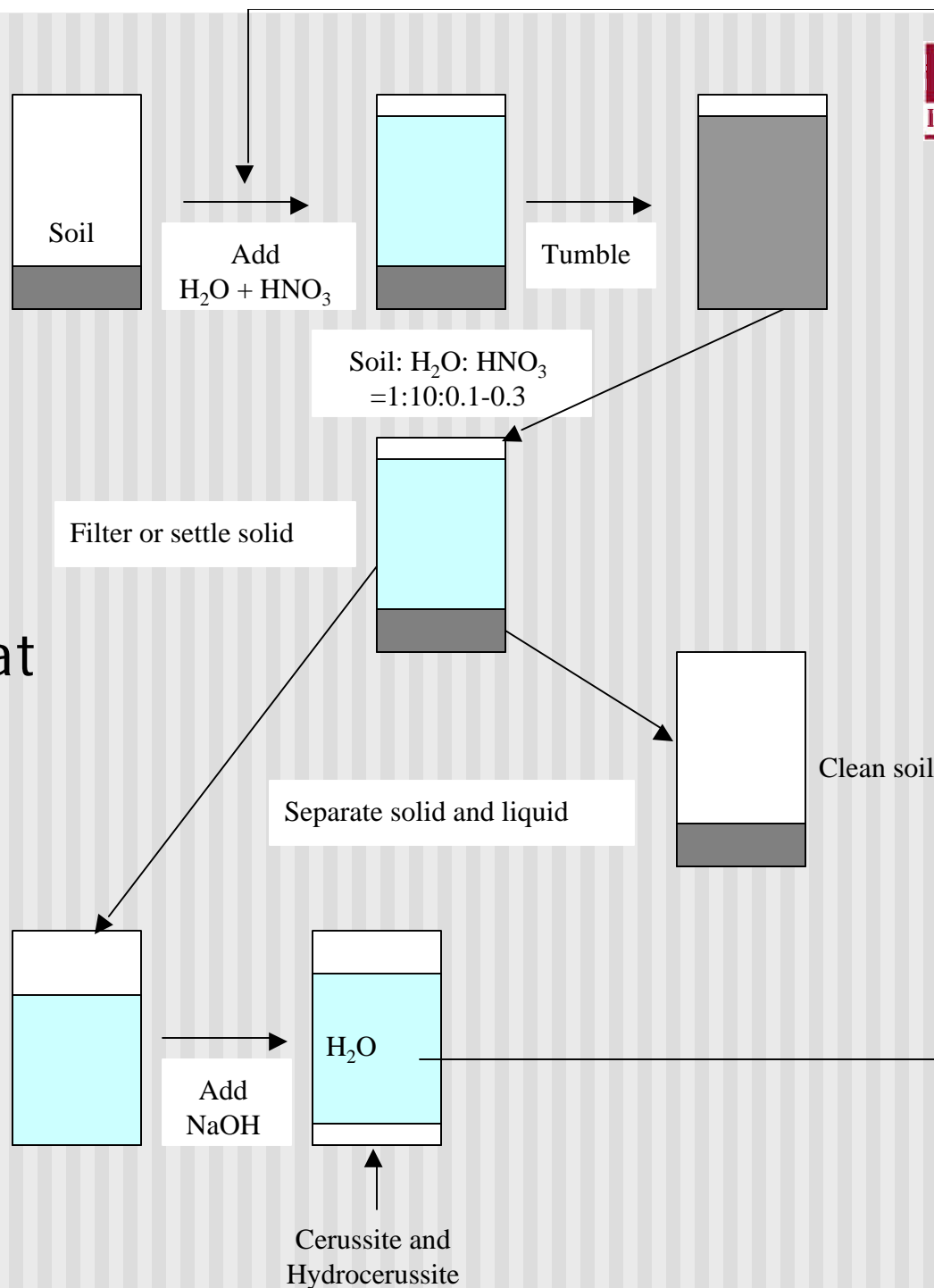
Basic reactions

Dissolution:

$$Pb + 2HNO_3 \rightarrow Pb^{2+}$$

$$PbO + 2HNO_3 \rightarrow Pb^{2+}$$

$$PbCO_3 + 2HNO_3 \rightarrow Pb^{2+}$$

$$Pb_2(CO_3)(OH)_2 + 2HNO_3 \rightarrow Pb^{2+}$$

$$PbCl(OH) + 2HNO_3 \rightarrow Pb^{2+}$$
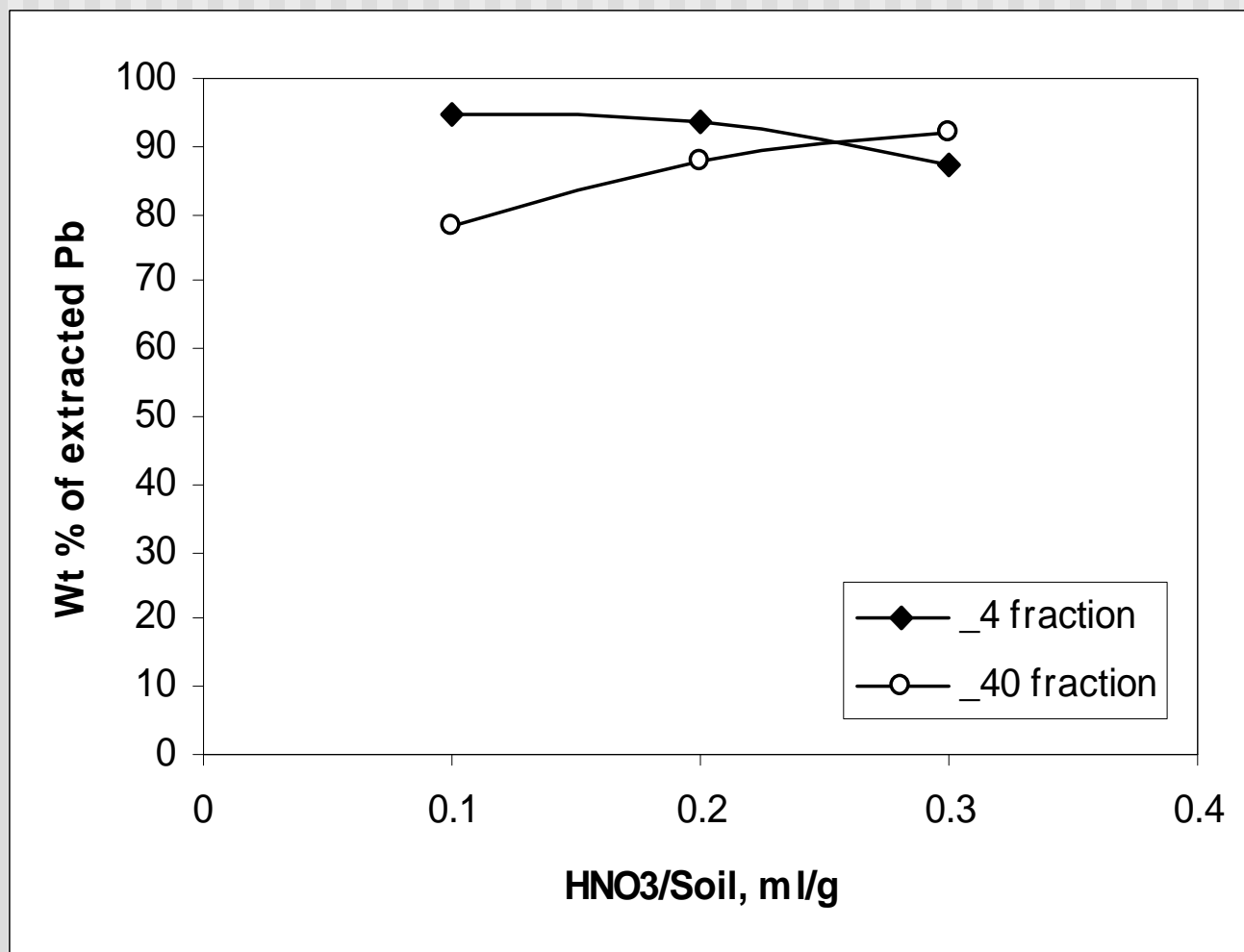
Precipitation

$$Pb_{2+} + 2NaOH \rightarrow Pb(OH)_2$$

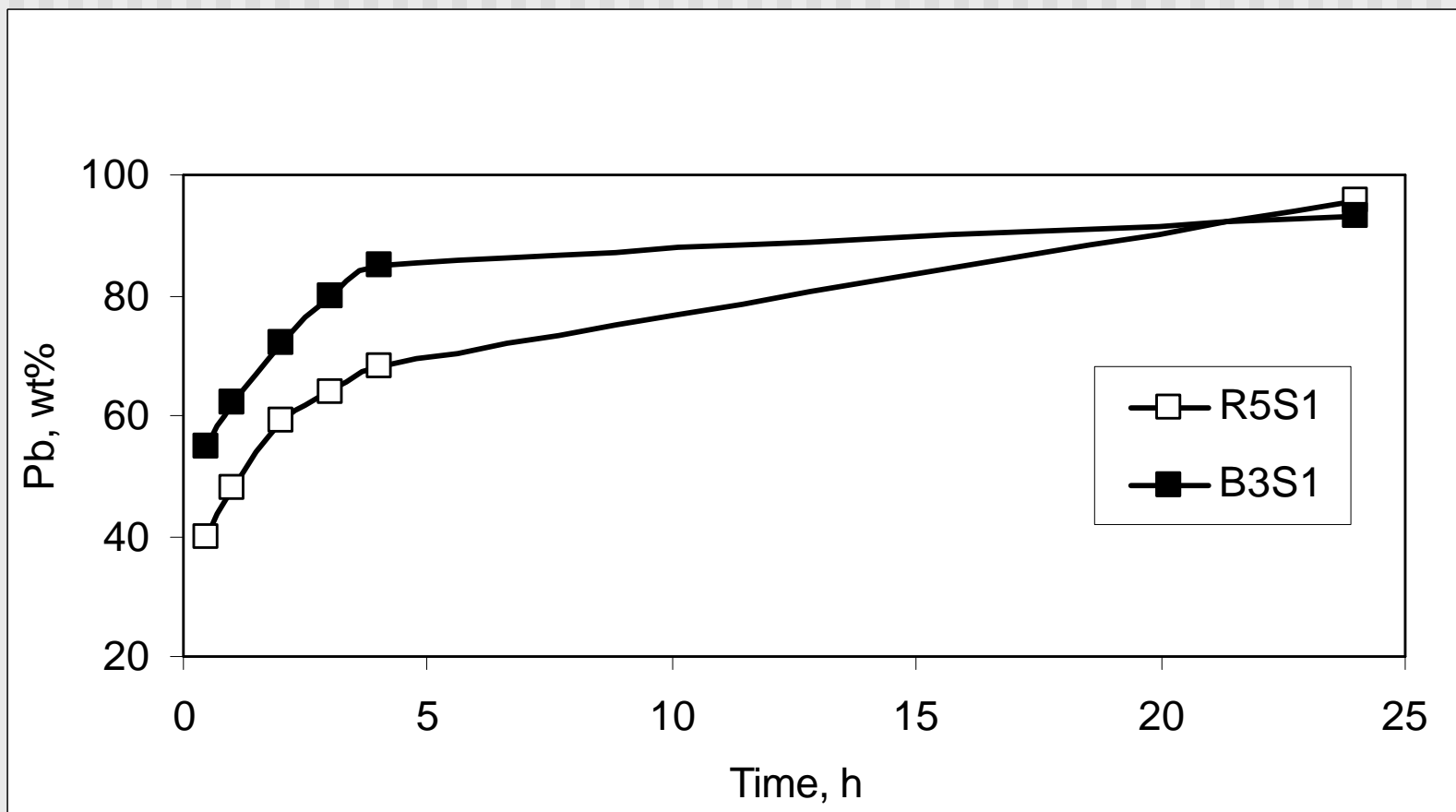$$Pb(OH)_2 + CO_2 = \text{cerussite and hydrocerussite}$$

Lead extraction from Range Five soils
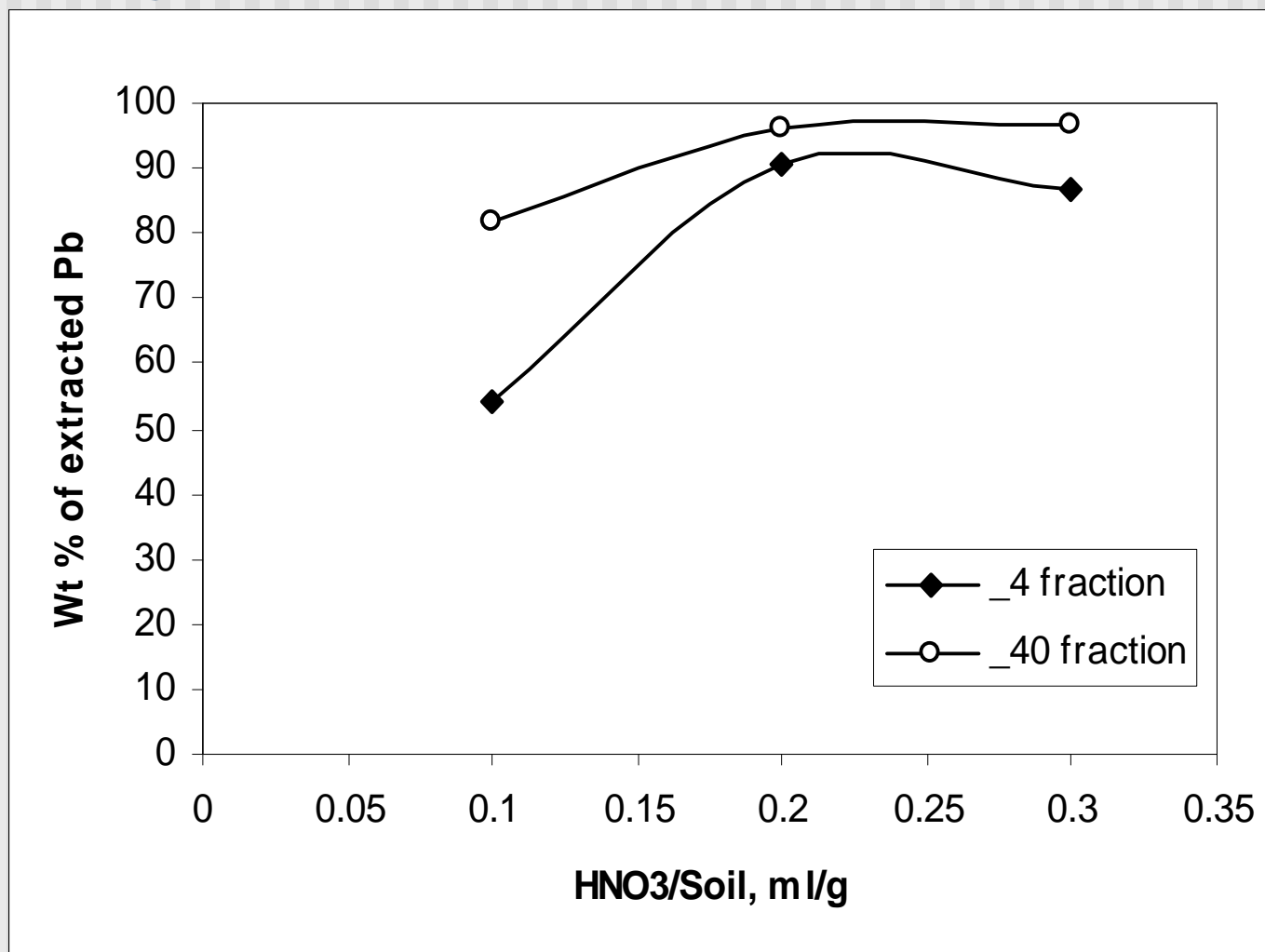
Lead extraction from Goldstone soils

Kinetics of lead dissolution

CONCLUSIONS

➤Limited contaminant migration due to:
- Low moisture content
- Arid environment, flush flooding events, rapid runoff, little water infiltration
- Formation of insoluble carbonate minerals

➤XRD-analysis shows that is Pb is present predominantly as:
  metallic Pb, cerussite and hydrocerussite in RANGE 5,
  metallic Pb, hydrocerussite, and laurionite in GOLDSTONE RANGE

➤Gravitational methods of soil washing are not effective for lowering Pb concentration to the regulatory levels (<600ppm)

➤Chemical washing of lead is an effective alternative to gravitational method