enviro**metal** technologies inc.

#11

REPORT ON RECENT ANALYSES OF GROUNDWATER SAMPLES AND REACTIVE ZONE CORES OBTAINED FROM THE PILOT-SCALE IRON WALL SHERBURNE, NEW YORK

Prepared for:

Stearns and Wheler
One Remington Park Drive
Cazenovia, New York 13035

Prepared by:

EnviroMetal Technologies Inc.
42 Arrow Road
Guelph, Ontario
N1K 1S6

ETI Reference: 31036.20

October 1997

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1.0 INTRODUCTION

This report presents the results of recent analyses on groundwater and core samples collected from a pilot-scale iron treatment system installed at an industrial facility in Sherburne, New York. This pilot-scale system was installed in May 1995 and monitored intensively for the next six months. ETI's interpretation of the 1995 data has been summarized in previous reports.

Groundwater velocity was measured and groundwater samples were collected from selected monitoring wells in June 1997, immediately prior to collection of a number of cores from the iron treatment zone. The cores were shipped to the University of Waterloo (U of W) for various analyses. A core was also supplied to General Electric's corporate Research and Development (GE CR&D) researchers for evaluation. The goal of this report is to document the performance of the system as of June 1997, after 2 years of operation.

This report addresses the following:

(i) interpretation of groundwater velocity measurements (Section 2);

(ii) analyses of groundwater samples in terms of observed rates of VOC degradation (Section 3);

(iii) results of carbonate analyses of core samples in terms of potential porosity loss (Section 4);

(iv) results of examinations of core samples by Raman spectroscopy, scanning electron microscopy, and dispersive x-ray spectroscopy, in terms of identification of precipitating mineral phases (Section 5);

(v) results of microbial analyses of core samples in terms of potential biofouling (Section 6); and

(vi) results of GE CR&D analyses (Section 7)

The implications of these results in the context of future long term operation of the system are discussed in the concluding section of the report. Data presented in our 19 June 1997 memorandum are incorporated into this report.

1.1 Sample Locations

Groundwater velocities were measured and samples were collected from the upgradient aquifer wells P3 and P8, upgradient gravel well MW-U2 iron wells MW-FE1 and FE2, downgradient gravel well MW-D2 and downgradient aquifer well MW-D5 along the center line of the installation (Figure 1). These samples were analyzed for VOCs and in the field for Eh and pH.

Three angle cores and two vertical cores were obtained from the iron zone. The cores were obtained with a drive point/piston sampler (Starr & Ingleton, 1992). Each core was 2 inches in diameter and about 40 inches in length. The three angle cores were taken at about 45° from horizontal and approximately parallel to flow (Figure 1 and 2). This allowed for sampling of the upgradient iron/pea gravel interface and the first few feet in the iron zone. The vertical cores were taken about 6 inches from the upgradient iron/pea gravel interface.

The coring tube did not appear to have any difficulty penetrating into the iron zone nor pea gravel zone or retrieving the core. If the iron zone was significantly cemented with precipitates or heavily oxidized, it would be expected that penetration into the subsurface zones would be more difficult. The upgradient interface where most of the precipitate would be expected to have formed, the iron material at the ends of the cores appeared to have little visual evidence of precipitate formation. Additionally, no bacterial "sliming" or odours were noticeable.

One angle core was examined in detail at the U of W, one at General Electric CR&D with the remaining cores being reserved for possible future evaluations. The complete angled core section was subdivided into 2 inch intervals and supplied to the respective laboratories for analyses. The U of W sample numbers shown in the Appendices were assigned to these core intervals and maintained through the various tasks:

U of W Sample Identifier	Location
2-3-A	0-2 inches from upgradient gravel iron interface along core
2-3-B	2-4 inches from upgradient gravel iron interface along core
2-3-C	4-6 inches from upgradient gravel iron interface along core
2-3-D	6-8 inches from upgradient gravel iron interface along core
2-3-E	8-10 inches from upgradient gravel iron interface along core
2-3-F	14-16 inches from upgradient gravel iron interface along core
2-3-G	18-20 inches from upgradient gravel iron interface along core
2-3-H	26-28 inches from upgradient gravel iron interface along core
2-3-A	6 inches from gravel-iron interface, core 2-5
2-6-A	6 inches from gravel-iron interface, core 2-6

2.0 GROUNDWATER VELOCITY MEASUREMENTS

Groundwater velocity was measured in the upgradient and downgradient aquifer and within the gate using a Model 40L Geoflo® meter. The meter provided both groundwater velocity and direction (Table 1). All well measurements were taken at approximately the mid point of the screened interval (39 in. from the well bottom). Although the meter was not calibrated specifically for pea gravel, the groundwater velocity was estimated using a calibration curve obtained for iron. From past experience with Geoflo® calibrations, these measurements would result in a slower velocity than using a pea gravel calibration curve. Flow direction obtained from the meter was independent of calibration, but can be affected by monitoring well effects/construction and local anomalies. From these results the following general observations were made:

- groundwater velocity in the iron gate appears faster than in the aquifer, ranging from 1.0 to 2.4 ft/day for the iron zone and 0.25 to 0.75 ft/day for the aquifer (Table 1). This was anticipated since the capture zone of a Funnel-and-Gate™ system is larger than the gate opening and therefore the groundwater velocity in the gate must increase accordingly.

- as expected, groundwater flow appears to be in a westerly direction. The easterly flow direction obtained for monitoring well MW-U2 was considered anomalous considering the consistent agreement in flow direction of the other four wells.

- the measurement obtained from monitoring well MW-FE1 of 1.0 ft/day in the west-northwest direction was consistent with measurements obtained on 30 September 1996 of 0.7 ft/day, north-northwest.

3.0 GROUNDWATER SAMPLE RESULTS

3.1 Eh and pH Field Results

Measurements of Eh and pH were conducted on monitoring wells along the center line through the gate and immediately upgradient and downgradient (Table 2). The Eh conditions upgradient indicate non-reducing (+400 mV) conditions, while reducing (-150mV) conditions within the iron gate and slightly reducing conditions (-68 to 86 mV) downgradient were observed. The pH values were neutral (7.0) in the upgradient aquifer and increased to values of 9.5 in the iron zone, and then decreased slightly in the downgradient aquifer. These values are consistent with those measured over the period June to December 1995. For comparison, we have included December 1995 values in Table 2.

Given the measured pH values, and assuming influent inorganic concentrations have not changed significantly over the two-year test period, precipitate formation in the iron zone would be expected to have occurred over the entire period. However, given the measured flow velocities, precipitates do not appear to have significantly effected the flow through the iron zone to date.

3.2 Organic Results

Organic samples were collected along the center line through the iron gate and in the upgradient and downgradient aquifer (Table 3). Concentrations directly upgradient of the gate were 198, 298 and 53 µg/L for trichloroethene (TCE), cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC), respectively. Trace amount of trans-1,2-dichlorothene (tDCE) and 1,1-dichloroethene (11DCE) were also detected. Within the iron treatment zone all compounds were non-detect with the exception of trace amounts (2.0 µg/L) of TCE. Within the downgradient pea gravel and aquifer, relatively low levels of TCE (1.5 µg/L), cDCE (15 µg/L) were observed. VC was not detected.

These results are consistent with those obtained during the SITE program evaluation in late 1995. The reactivity of the iron zone appears unchanged during the two years following installation.

4.0 RAMAN SPECTROSCOPY, SCANNING ELECTRON MICROSCOPY (SEM), AND ELECTRON DISPERSIVE X-RAY (EDX) RESULTS

Appendix A presents the results of examination of core samples by Raman spectroscopy, scanning electron microscopy (SEM), and electron dispersive x-ray (EDX) methods. Raman spectroscopy, and to a lesser extent EDX, confirmed the results of carbonate analyses. Iron from nearest the upgradient interface (sample A) showed the presence of significant calcite and aragonite when examined by Raman. Samples from sections of the core further downgradient showed small amounts of carbonate precipitates, but a variety of iron oxides and hydroxides were noted, including amorphous iron hydroxide and magnetite. Magnetite forms at the iron surface over time due to the conversion of iron hydroxides on the iron surface.

Calcite and aragonite appeared to be the predominant carbonate species observed; the presence of siderite was not indicated. Forms of "green rust" were observed on several iron samples throughout the core. Green rusts are complex iron hydroxides containing both Cl^-, SO_4^{2-} and carbonate (CO_3^{2-}). No crystalline iron sulphides were observed in any sample. Precipitate coatings on the iron surface were highly non-uniform.

5.0 DETERMINATION OF CARBONATE CONTENT AND ESTIMATED POROSITY LOSS

Determination of carbonate content in core samples involved the measurement of CO_2 gas evolved when the sample was treated with a strong acid. The procedure and results are provided in Appendix B. From Table 4 and Figure 3, sample results show the expected trend, with maximum carbonate content occurs in samples closest to the upgradient interface. About 5.6% carbonate reported as 5.6% $CaCO_3$ (5.6 g/100 g solid) was present in these samples. The initial porosity of this material has been assumed to be 0.4 based on previous laboratory estimates; however, based on the mass of iron placed in the gate during installation, the initial porosity could be as high as 0.59. The percent carbonate content can be converted to a corresponding porosity loss by using the molar volume of calcium carbonate (36.8 cm^3/mol). Using an iron field bulk density of 180 lb/ft^3 (2.88 g/cm^3), 5.6% $CaCO_3$ represents 0.0016 mol and therefore would occupy 0.059 cm^3 per cm^3 of material. As shown both in Table 4 and Figure 4, this represents a porosity loss of 10%, assuming an original porosity of 0.59, and a porosity loss of 15%, assuming an initial porosity of 0.4. Based on the field porosity at other sites, 10% is probably a closer approximation.

As noted in Section 4.0, no sulphide precipitates were observed in the core samples. Declines in aqueous sulphate concentration indicate that sulphide or sulphate containing minerals may have been formed. The molar volume of these minerals is smaller than that of carbonate, so the effect of sulphide or sulphate mineral formation on porosity loss would be less significant for a given mass of precipitate formed relative to carbonate mineral formation. From the results obtained in this study, it does not appear that sulphur containing mineral formation has appreciably affected porosity of the system.

If the initial porosity of the system was as low as 0.4, the core sample results indicate that the porosity now existing in the system might be in the order of 0.34 (i.e. 0.4 - 0.06 = 0.34). This should not have an appreciable effect on flow. It also appears that the system could operate for several more years before any "refurbishing" of the iron zone is required.

6.0 MICROBIAL ANALYSES

Two types of microbial analyses (Appendix C) were performed on the core samples, including standard microbial enumerations (plate counts), and determination of lipid biomass. The initial two tests were performed by the U of W and the third by Microbial Insights Inc. The lipid biomass result reported as a number of equivalent cells/gram dry weight, and enumeration results reported as colony forming units (CFUs) per gram (wet weight), are summarized in Table 5 and shown graphically in Figures 5 to 7. No microbial films were noted on the samples during their preparation for microscopic examination.

Both the enumerations and lipid biomass results show similar trends. Samples closest to the zone of redox near the upgradient interface show slightly higher populations than those samples taken from within the wall. There is no evidence of these microbial populations biofouling the reactive zone.

It is suspected that the results reflect transport of microbial populations into the zone from the upgradient aquifer. Microbial populations in the order of 10^6/gm are common in many aquifer and soil environments. Similar analyses performed on groundwater samples from the reactive wall after 6 months of operation showed microbial populations in the 10^3 to 10^4 cells/gm; the higher values here may reflect the common increase in biomass measurements in solid samples relative to groundwater samples.

7.0 RESULTS OF GENERAL ELECTRIC CR&D ANALYSES

As noted previously, one of the angle cores was supplied to researchers at General Electric CR&D for analyses. This group has been evaluating this technology for several years, and has cooperated with the U of W group previously. The results of their research, summarized in Appendix D, support the data presented herein. That is, most of the carbonate precipitate was confined to the first few inches of the core, and calcium carbonate was the predominant carbonate mineral identified.

8.0 SUMMARY

Based on the analyses presented in this report, the following conclusions are drawn regarding the performance of the pilot-scale iron treatment system at the Sherburne, NY site after 2 years of operation:

(i) the wall continues to degrade influent VOCs to below their MCLs, with no apparent decline in the rate of degradation;

(ii) inorganic geochemical changes, including increases in pH and declines in Eh, are still occurring to the same extent as observed in the first six months of operation;

(iii) carbonate precipitates have caused about a 10% loss of porosity in the upgradient few inches of the system. These carbonate precipitates are mainly calcite and aragonite, with only minor evidence of siderite. The remainder of the wall appears unaffected by carbonate precipitate formation; and

(iv) there is no evidence of significant microbial populations which have caused biofouling of the reactive material.

Based on these results, there is no reason to suspect that the wall would not continue to perform for several more years prior to rejuvenation/refurbishing, especially if the initial (installed) porosity was as high as 0.59. That is, the negative impacts of precipitate formation on hydraulic conductivity of the wall, relative to the aquifer, should not occur for some time.

9.0 REFERENCES

Starr R.C. and R.A. Ingleton 1992. A New Method for Collecting Core Samples without a Drilling Rig. Groundwater Monitoring Review, Winter 1992. pp 91-95.

Table 1: Groundwater Velocity and Direction, Pilot-Scale Funnel-and-Gate™ System, Sherburne, NY

Well Identification	Groundwater Velocity (ft/day)	Flow Direction (Relative to Magnetic North)
P3	0.76	South-Southwest
P8	0.40	South
MW-U2	>0.8[a]	East
MW-FE1	1.0	West-Northwest
MW-FE2	2.4 1.3	Northwest West-Southwest
MW-D2	>0.6[a]	West-Northwest
MW-D5	0.25	West-Southwest

[a] based on iron calibration curve. From previous calibrations, this results in a slower velocity estimate than by using calibration data for pea gravel.

Table 2: Field Parameter Measurements, Pilot-Scale Funnel-and-Gate™ System, Sherburne, NY

Well Identification	pH		Eh (mV)	
	June 1997	December 1995	June 1997	December 1995
P8	7.0	NA	440	NA
MW-U2	7.2	7.4	382	261
MW-FE2	9.5	9.5	-150	-459
MW-D2	8.5	8.6	-68	-156
MW-D5	7.4	7.4	86	-17

NA Not Analyzed

Table 3: VOC Concentrations at the Pilot-Scale Funnel-and-Gate™ System, Sherburne, NY

Well Identification	Organic Concentration (µg/L)				
	TCE	cDCE	tDCE	11DCE	VC
P8 (upgradient aquifer)	1280	1882	9.7	nd	26
MW-U2 (upgradient gravel)	198	298	2.2	1.4	53
MW-FE2 (iron)	2.0	nd	nd	nd	nd
MW-D2 (downgradient gravel)	1.5	15	nd	nd	nd
MW-D5 (downgradient aquifer)	11	30	nd	nd	1.4

Samples collected June 10, 1997

nd = non detect

MDL (µg/L): TCE 1.7
cDCE 7.8
tDCE 1.9
11DCE 3.2
VC 0.7

TABLE 4: Carbonate Content of Core Samples, Sherburne, NY

Sample Location (Core Number)	% $CaCO_3$	% Porosity Loss (n_o = 0.59)	% Porosity Loss (n_o = 0.4)
2-3-A	5.6	10	15
2-3-B	2.3	4.1	6.1
2-3-C	0.74	1.3	2.0
2-3-D	1.3	2.3	3.4
2-3-E	0.84	1.5	2.2
2-3-F	0.23	0.40	0.60
2-3-G	0.16	0.29	0.42
2-3-H	0.34	0.60	0.89
2-5-A	0.23	0.40	0.60
2-6-A	0.81	1.5	2.2
Fresh Iron	0.18	--	--

n_0 = original porosity, see text for explanation

Note:

1) See Figure 4 for graphical representations of results.

2) Fresh iron sample result may reflect carbon content of sample; no calcium carbonate exists on this sample.

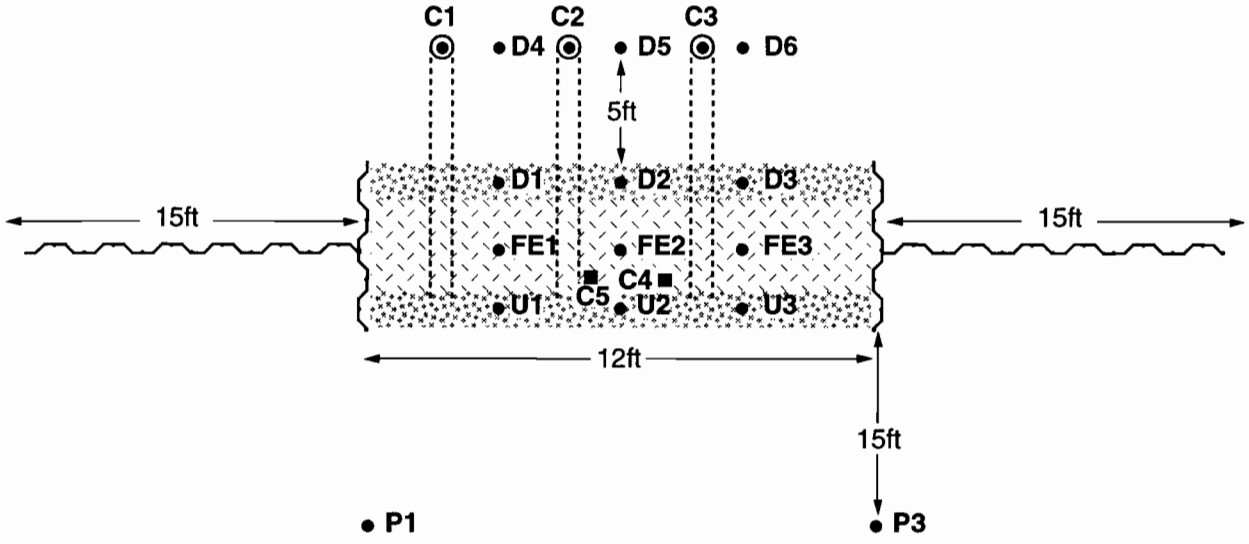
TABLE 5: Summary of Microbial Results, Sherburne, NY

Sample No. (Core Number)	Plate Counts		Lipid Biomass Equivalent Cells/gm dr (Lipid Biomass)
	CFUs/gm ww Aerobic (R2A) Agar	CFUs/gm ww Anaerobic Agar	
2-3-A	3.3×10^4	2.0×10^3 est	2.24×10^6
2-3-B	9.6×10^3	1.1×10^3	8.38×10^5
2-3-C	5.5×10^3	3.4×10^2	7.23×10^5
2-3-D	2.0×10^3 est	1.8×10^2 est	n.a.
2-3-E	1.1×10^3 est	1.5×10^2 est	1.22×10^6
2-3-F	5.0×10^2 est	53 est	n.a.
2-3-G	2.7×10^2 est	37 est	3.28×10^5
2-3-H	7.5×10^3	2.2×10^3	n.a.
2-5-A	5.1×10^4	1.3×10^3	n.a.
2-6-A	8.7×10^2 est	70 est	n.a.
Fresh Iron	33 est	<3	1.71×10^6

est = estimate

ww = wet weight

dr = dry weight



Angled Cores

Vertical Cores

Pea Gravel

Iron Filings

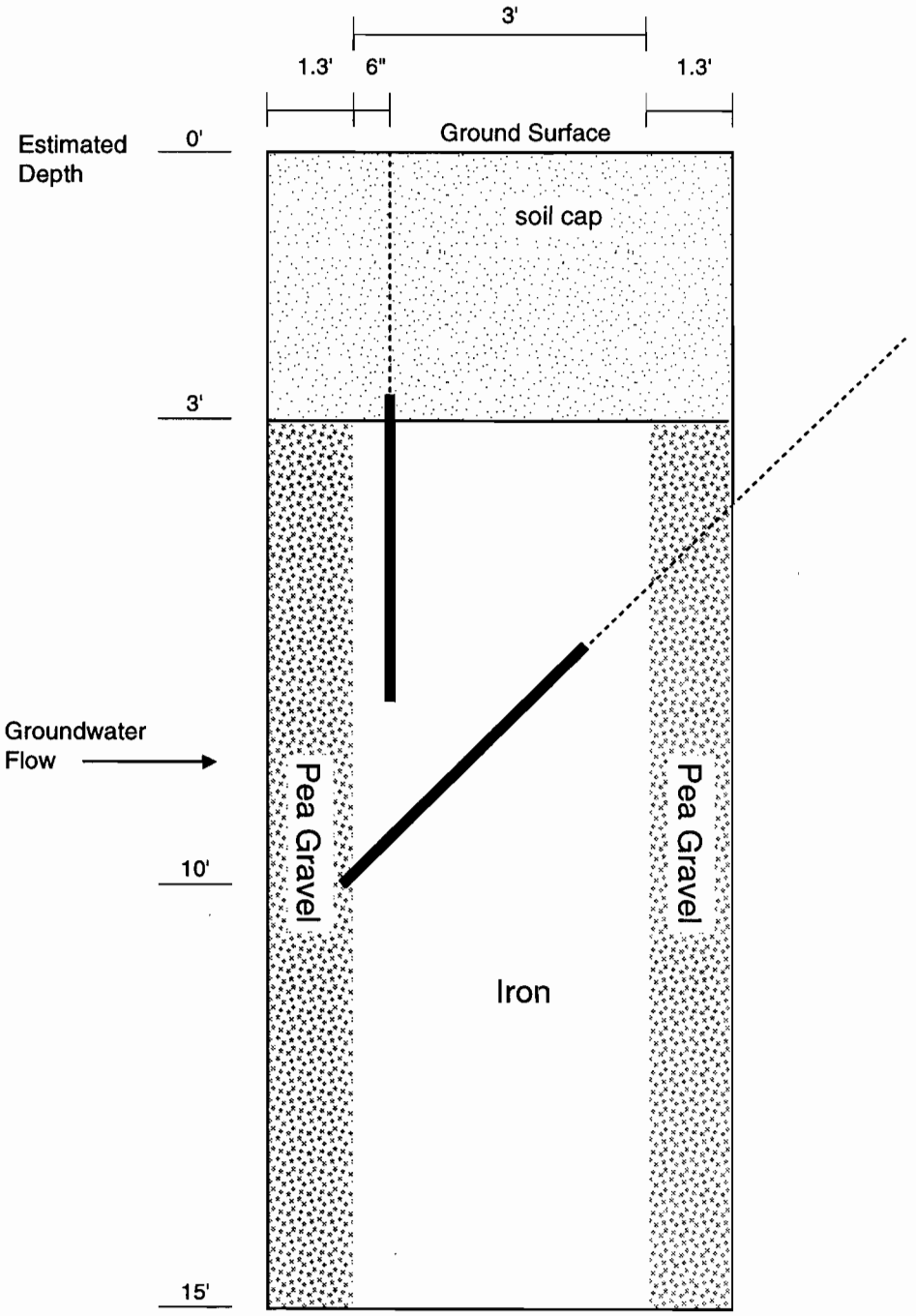
Monitoring Well

Sheet Piling

Direction of GW flow

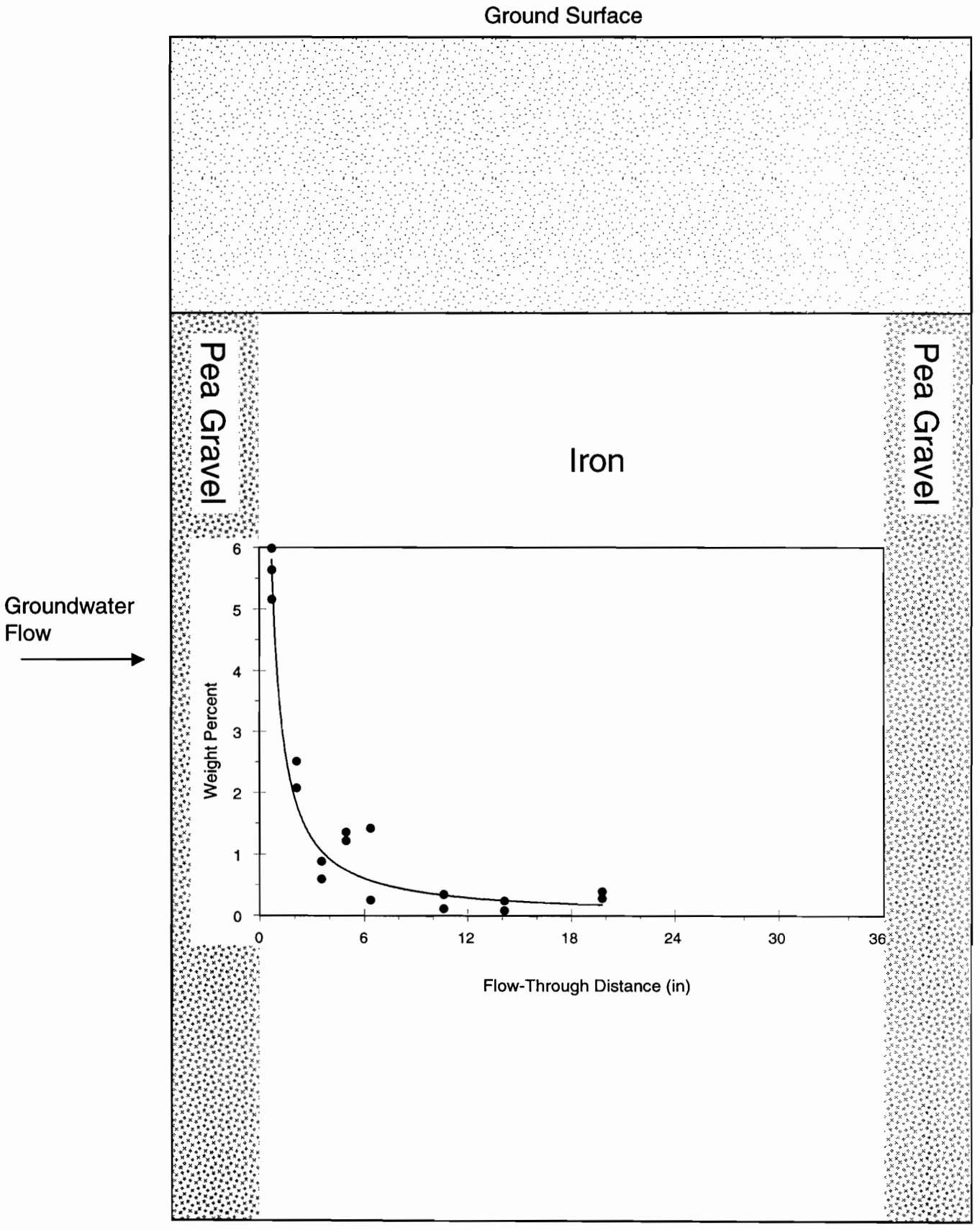
Plan View of Monitoring Well and Coring Locations
New York

environmetal technologies inc.	Figure 1	August 1997 Rev. 00



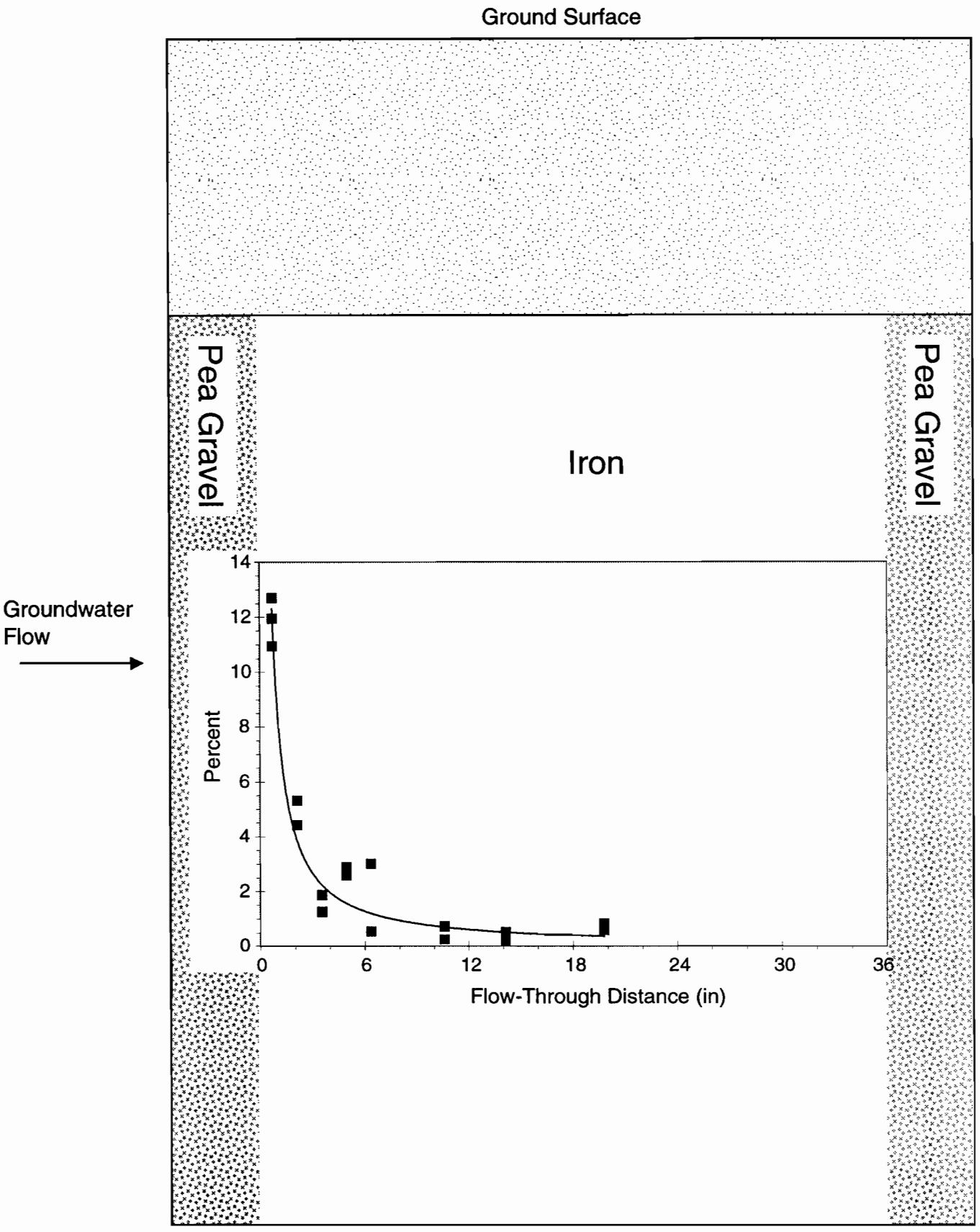
Section View of Core Sample Locations

enviro**metal** technologies inc.	Figure **2**	July 1997 Rev. 00



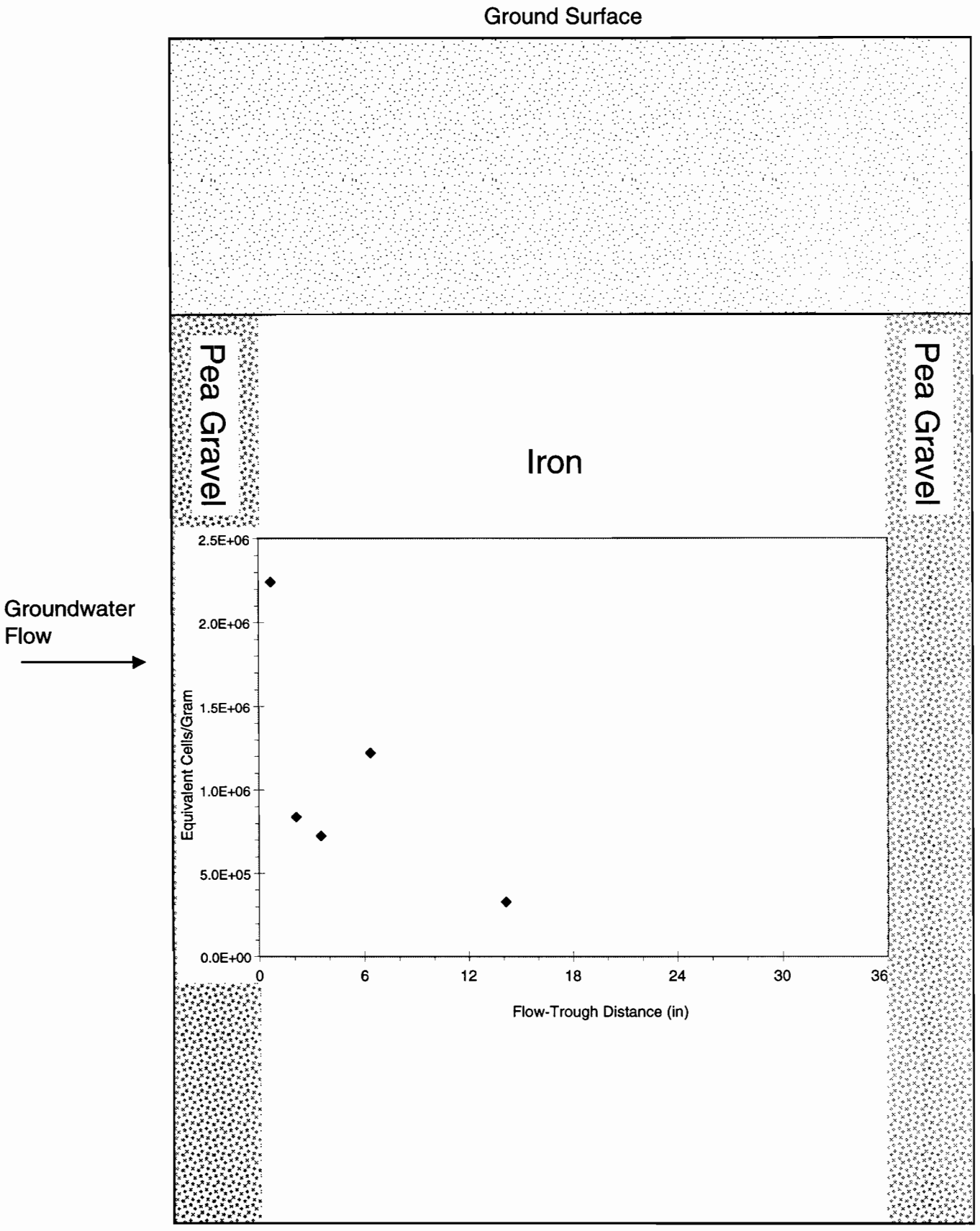
Calcium Carbonate Equivalent, Sherbyrne, NY

enviroMETAL technologies inc.	Figure 3	July 1997 Rev. 00



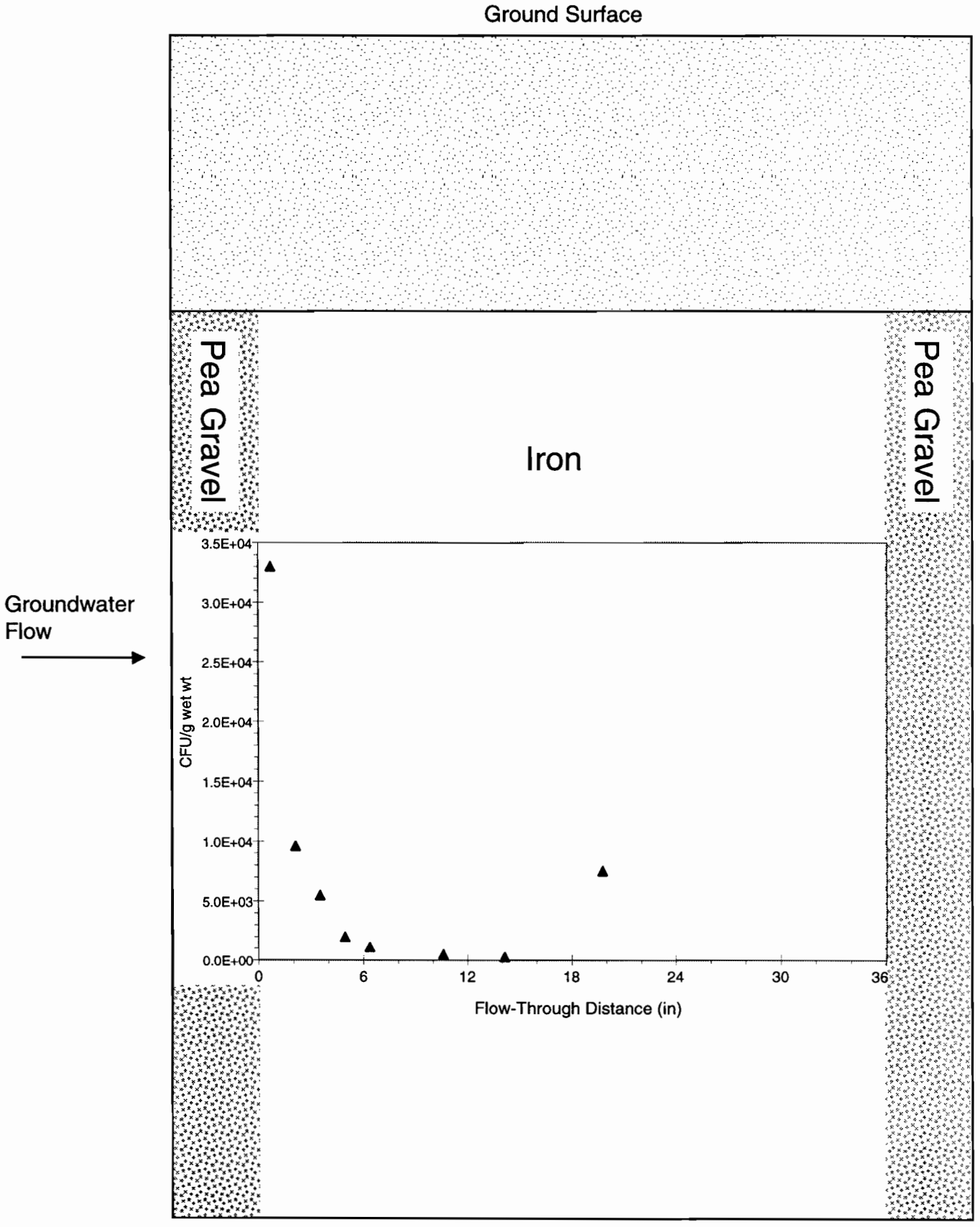
Estimated Porosity Loss, Sherburne, NY

enviroMETAL technologies inc.	Figure **4**	July 1997 Rev. 00



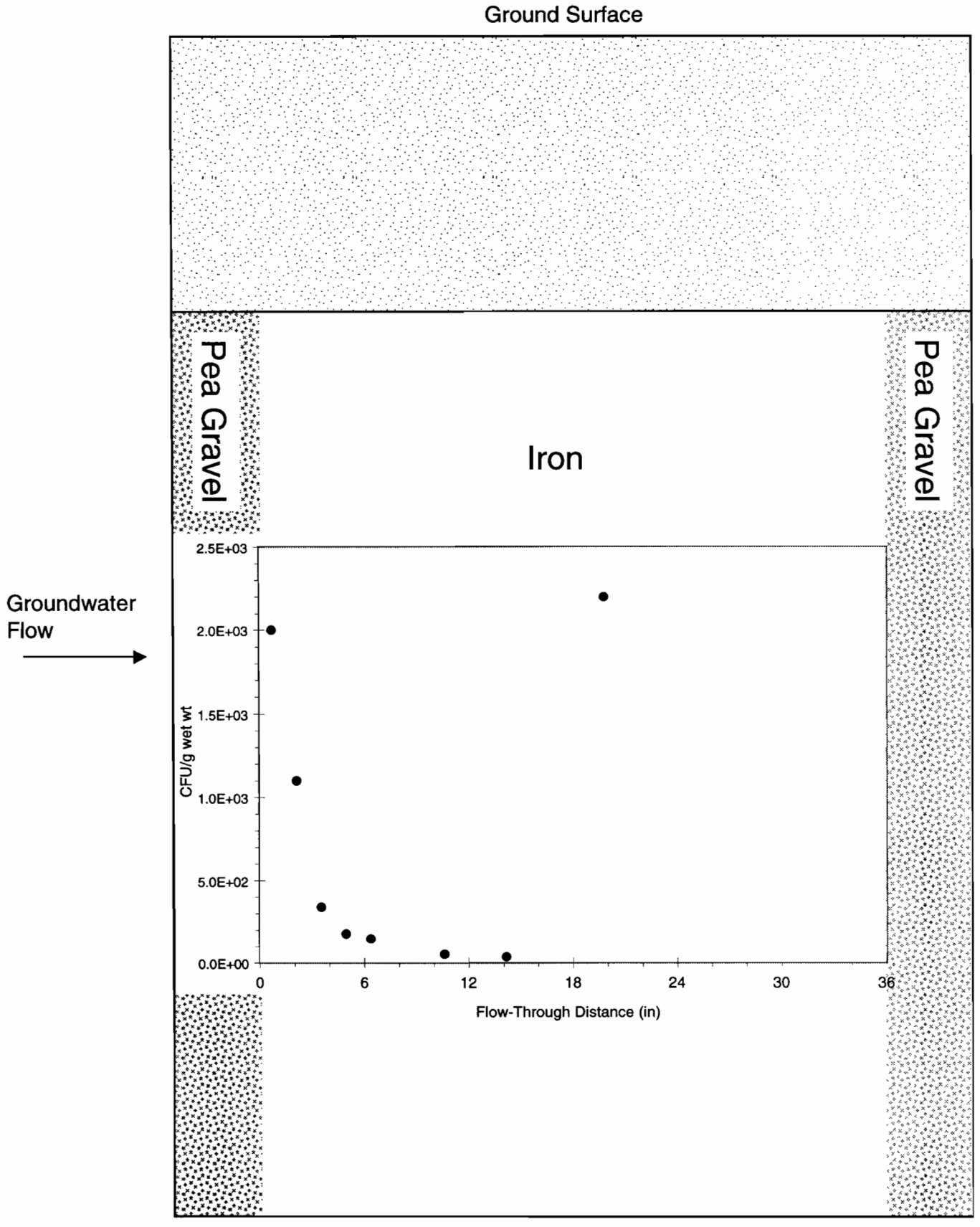
Lipid Biomass Results, Sherburne, NY

enviro**metal** technologies inc.	Figure **5**	July 1997 Rev. 00



Aerobic Culture Results, Sherburne, NY

enviro**metal** technologies inc.	Figure **6**	July 1997 Rev. 00



Anaerobic Culture Results, Sherburne, NY

enviro**metal** technologies inc.	Figure **7**	July 1997 Rev. 00

APPENDIX A

Raman Spectroscopy, Scanning Electron Microscopy, and Electron Dispersive X-Ray Spectroscopy Results

University of Waterloo

Waterloo, Ontario, Canada
N2L 3G1

Faculty of Science
Department of Earth Sciences
519/885-1211

Telex: 069-55259
Fax: 519/746-7484

Stephanie F. O'Hannesin, Project Director
Enviromental Technologies Inc.
42 Arrow Road
Guelph, Ontario N1K 1S6

September 18, 1997

Dear Stephanie,

Here you will find the requested report "Analysis of Iron Core Samples by Raman Microspectroscopy, Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy. Experimental Site Stearn & Wheler, NY". Note that in EDX analysis of "as received" Master Builder the varying carbon content in the samples indicates that we are dealing with highly carbonized unalloyed steel. This carbon is not related to the formation of carbonates. In the final version of previous report these "two carbons" were not properly distinguished.

Sincerely Yours,

Marek Odziemkowski

c/o
R.W. Gillham, Professor

ANALYSIS OF IRON CORE SAMPLES BY RAMAN MICROSPECTROSCOPY, SCANNING ELECTRON MICROSCOPY AND ELECTRON DISPERSIVE X-RAY SPECTROSCOPY. EXPERIMENTAL SITE 2 - STEARN AND WHELER, NY.

Prepared for Enviroметal Technologies Inc. by Dr. M.S. Odziemkowski

Department of Earth Sciences University of Waterloo, Waterloo, September 18, 1997.

Experimental Method

All samples were obtained in the sealed aluminum core tubes, in the cooler filled with the ice-packs. The core tubes were transferred into a Model 6550 programable anaerobic environmental chamber where tubes were open on both ends. Approximately 50 mm of the iron material on both ends was discarded as not representative due to a possible oxidation. The core material was then distributed into the glass bottles. Most of the iron material was transferred wet[1], to avoid drying and consequently surface modification, the bottles were immediately filled with the experimental site water and stored in anaerobic environmental chamber.

For Raman microspectroscopy a small amount of material (ca. 5-7g) was transferred from the bottle into previously designed spectroscopic cell (1), which was topped up with the site-water and sealed. In this manner the assembled spectroscopic cell was moved from the anaerobic environmental chamber to the Raman microscope, where Raman spectra were measured.

After Raman measurements the spectroscopic cell was disassembled in the anaerobic environmental chamber. The iron material was carefully washed three times with methanol and dried. This dried material from Raman studies was used for *ex-situ* scanning electron microscopic (SEM) and electron dispersive x-ray spectroscopic (EDX) analysis. This experimental methodology assure the repetition of *ex-situ* SEM and EDX measurements on the same material as taken for *in-situ* Raman studies, yet we can not guaranty that the *ex-situ* and *in-situ* measurements were carried out exactly on the same iron particles.

---

[1] The exception are sample 2-3-C, which were obtained dried.

SEM and EDX Instrumentation

Environmental Scanning Electron Microscope Model E-3 was used for SEM analysis. The electron gun was operating at 20 kV, cathode filament current was set to 1.37 A. The instrument is equipped with a Oxford Link EDX analyzer Model 6580 and silicon detector. In contrast to an older EDX analyzers it is supplied with a state of art a thin electron window ATW2. This thin window allows for qualitative elemental analysis of a light elements such as carbon.

Raman Instrumentation

In - situ Raman spectra were obtained with a Renishaw 1000 Raman microscope system. The instrument consist an Olympus microscope, a single spectrograph fitted with holographic notch filters for spectroscopy mode, and a Peltier-cooled CCD detector. The optical throughout of the instrument is high ($\geq$30%), as is the sensitivity. The detection of a very weak signal (1 photon/s) is possible. Excitation was achieved using the 632.8 nm line of a Melles Griot low-power HeNe laser. All Raman measurements were carried out using backscattering geometry. The long working-length objective lens used in the spectral studies has an objective magnification 50 (OLYMPUS IC50/MSPLAN 50, ∞/0 f = 180 , NA = 0.55). The laser was operated at it maximum power of 30 mW; this translates to ca. 5 mW at the sample surface. Such low light intensity is unlikely to alter the surface film composition, particularly for *in - situ* measurements. For well defined flat sample surface, this instrument allows to study a spot size of 2 μm with a confocal depth of field of 3 μm. For *ex-situ* study of "as received" Master Builder Iron and reference oxides an objective magnification 100 was employed. In this latter configuration the spatial resolution of Raman microscope is 1 micron.

Raman Spectra of Reference Iron Oxides and Selected Oxyhydroxides

Raman spectra of the reference oxides and α - FeOOH are presented in Fig.1. Very good correlation between our Raman results and available literature data is evident from Table 1. The high frequency bands above 800 cm^{-1} will not be discussed in this report for the reason given in the next section.

Raman Spectra of *As Received* Master Builder Iron

Raman spectra in the low frequency region of *as received* Master Builder Iron are shown in Fig.2a and 2b. The Raman spectrum shown in Fig.2b represented ca. 80% of the entire surface. It revealed the predicted phonon frequencies of magnetite at 300, 320, 538, and 665 cm^{-1} (8), two weak bands at 221 and 288 cm^{-1} are attributed to an outer layer of α - Fe_2O_3 (see Table 1). The mapping of the surface with the 1 μm laser beam revealed a strong surface heterogeneity. Randomly distributed the single maghemite phase (γ - Fe_2O_3) was observed, as indicated in the spectrum of Fig.2a. The intensity of α - Fe_2O_3 bands also varied indicating differences in the outer layer film thickness. The complete Raman spectrum of Master Builder iron is presented in Fig.3. Bands at 1331 and ca. 2654 cm^{-1} are attributed to the overtones of the strongest A_{1g} mode of magnetite. A broad band at 1591-1610 and weak one at 2912 cm^{-1} might be attributed to unidentified carbon species. Much more metallurgical and Raman measurements are required for the correct assignment of the two latter Raman peaks. Therefore in this report the high frequency bands above 800 cm^{-1} will not be discussed in details.

Table 1. Raman bands of selected iron oxides in 200 - 800 cm^{-1} region. The A_1 modes and other lines of a high intensity are underlined.

Species	Raman Band Position / cm^{-1} /									Reference
α - Fe_2O_3	<u>225</u>	245	<u>295</u>		<u>415</u>	500	615			(2)
α - Fe_2O_3	227	245	<u>293</u>	<u>298</u>	<u>414</u>	501	612			(3)
α - Fe_2O_3	<u>226</u>	245	<u>293</u>		<u>413</u>	500	612			(4)
α - Fe_2O_3	224 (vs)	244 (vw)	291 (s)		409 (m)	499 (vw)	609 (w)			this work
γ - Fe_2O_3	265	300	345		395	515	<u>645</u>	<u>670</u>	<u>715</u>	(2)
γ - Fe_2O_3			350			505		<u>660</u>	<u>710</u>	(5)
γ - Fe_2O_3	263		350		380	505	<u>650</u>		<u>740</u>	(6)
γ - Fe_2O_3	266 (vw)	290 (vw)	342 (s,sh)		380 (s,sh)	502 (s)	640 (s,sh)	668 (s,sh)	714 (s,sh)	this work
Fe_3O_4		300	320		420	560	<u>680</u>			(7)
Fe_3O_4		294	319		415	540	<u>669</u>			(8)
Fe_3O_4						540	<u>665</u>			(2)
Fe_3O_4			310 (vb)			540 (w)	669 (vs)			this work
α - FeOOH	245	300	<u>390</u>	420	480	550	685			(2)
α - FeOOH		<u>299</u>	<u>397</u>		479	550	685			(9)
α - FeOOH	250	300	<u>385</u>		470	560				(6)
α - FeOOH		298	<u>397</u>	414	474	550				(3)
α - FeOOH	245 (m)	298 (s)	388 (s)	412 (m,sh)	481 (m)	550 (w)	670 (vb)			this work

Intensity statements and abriviation:

vs - very strong
s - strong
m - medium
w - weak
vw - very weak
vb - very broad
sh - shoulder

SEM and EDX Analysis of *As Received* Master Builder Iron

Quantitative elemental analysis of as received Master Builder Iron, in similarity to Raman spectroscopy, revealed a strong chemical heterogeneity of the base material. For example C content in sample varied from 6.12 atomic % up to 47 atomic %. This reflects the varying carbon content in "as received" Master Builder Iron. More importantly the content of other alloying elements such as Cr varied from ca. 0 at. % up to 0.34 atomic percent. This latter observation clearly indicates the Master Builder Iron consists of a various unalloyed steels.

Green - Rust Compounds

Dissolution of iron or iron oxides in the aqueous solutions might lead to the formation of a thick unstable colloidal hydroxy salt layer called green rust (GR). The structure of GR is composed of Fe^{2+}, Fe^{3+}, hydroxy ions, and interlayer hydroxy or non-hydroxy ions, may consist of sulphates, halides, nitrates, carbonates. Very recently in Raman Laboratory at University of Waterloo many of these GR compounds were characterized (1,10). Raman spectrum of green rust is characterized by two relatively strong peak at 420-434 cm^{-1}, and 497-510 cm^{-1}, which correspond to Fe^{2+} - OH and Fe^{3+} - OH stretching vibrations, respectively. Their exact position and band intensity ratio is strongly influenced by the anion present in the structure of green rust. At the high concentration of anions in solution, sometimes it is possible to identified these anions in the green rust structure (1,10).

Salt-Type Precipitates

Due to increase of pH inside the iron-wall, a salt-type precipitate are likely to form. These precipitates might consist of; calcium carbonates (calcite, aragonite), iron carbonate (siderite) and dolomite group carbonate mineral, ankerite - $CaFeCO_3$. Identification of the individual members of the carbonate group of minerals can be difficult when they are present as mixtures or as impurities in other substances. For example conventional X-ray powder diffraction is a convenient analytical method for bulk samples and for mixtures containing significant quantities of each crystalline component, e.g., more than 2 wt. % (11). In many mineralogical investigations, laser Raman microspectroscopy is unique because it provides a complete analysis of both lattice and molecular vibrations from extremely small quantities of sample. For example, in contrast to EDX analysis which are often not informative due to their inability to differentiate between Fe in the surface precipitate (such as $FeCO_3$) and underlying Fe particle (12), Raman spectroscopy is highly specific towards any carbonate minerals. Therefore is excellent complementary technique to SEM and EDX elemental analysis.

Location of Raman active vibrational modes of selected carbonates is presented in Table 2.

Table 2. Raman bands of calcite, aragonite, siderite and ankerite in 100-1200 cm^{-1} region. The A_1 and other high intensity bands are underlined (from Ref.11).

Mineral Phase	Raman Band Position in / cm^{-1} /				
Calcite	154	**283**		714	**1087**
Aragonite	**150**	**205**		704	**1085**
Siderite	190	**296**	509	734	**1089**
Ankerite		**285**		723	**1091**

Conclusions

1. Salt-type inorganic precipitates consisted of calcite and aragonite, and were found predominately in sample **2-3-A** closest to the upgradient interface of the wall and pea gravel.
2. No experimental evidence was found for the formation of siderite - $FeCO_3$.
3. The formation of various "green rust" compounds was confirmed on many areas of the core samples.
4. Further experimental evidences were collected which indicate that the autoreduction of the outer thick Fe(III) surface film, followed by charge transfer through the non-protective film, is reaction necessary for the effective performance of the commercially-produced iron materials in the degradation of chlorinated solvents (13).

References

1. S. Simard, M. Odziemkowski, D.E. Irish, L. Brossard, and H. Ménard, accepted for publication to J. Electrochem. Soc., September 1997.
2. T. Ohtsuka, K. Kubo, and N. Sato, *Corrosion,* **42,** 476 (1986).
3. R.J. Thibeau, C.W. Brown, R.H. Heidersbach, *Applied Spectroscopy,* **32,** 532 (1978).
4. I.R. Beatties and T.R. Gilson, *J. Chem. Soc. A,* 980, (1970).
5. N. Boucherit and A. Hugot-Le Goff, and S. Joiret, *Corros. Sci.,* **32,** 497 (1991).
6. D. Thierry, D. Persson, C.Leygraf, N. Boucherit, and A. Hugot-Le Goff, *Corros. Sci.,* **32,** 273 (1991)
7. J.L. Verble, *Physical Review B,* **9,** 5236 (1974).
8. M. Odziemkowski, J.Flis and D.E. Irish, *Electrochim. Acta,* **39,** 2225 (1994).
9. G. Nauer, P. Strecha, N. Brinda-Konopik and G. Lipstay, *J. Therm. Anal.,* 813 (1985).
10. P.M.L. Bonin, M.S. Odziemkowski, and R.W. Gillham submitted for publication in *Corrosion Science*, September 1997.
11. R.G. Herman, C.E. Bogdan, A.J. Sommer, and D.R. Simpson, *Applied Spectroscopy,* **41,** 437 (1987).
12. M.S. Odziemkowski, T.T. Schuhmacher, R.W. Gillham, and E.J. Reardon, accepted for publication in *Corrosion Science*, July 1997.
13. M.S. Odziemkowski and R.W. Gillham, 213th ACS National Meeting, San Francisco, Ca. Extended Abstracts, Division of Environmental Chemistry, **37,** p.177 (1997).

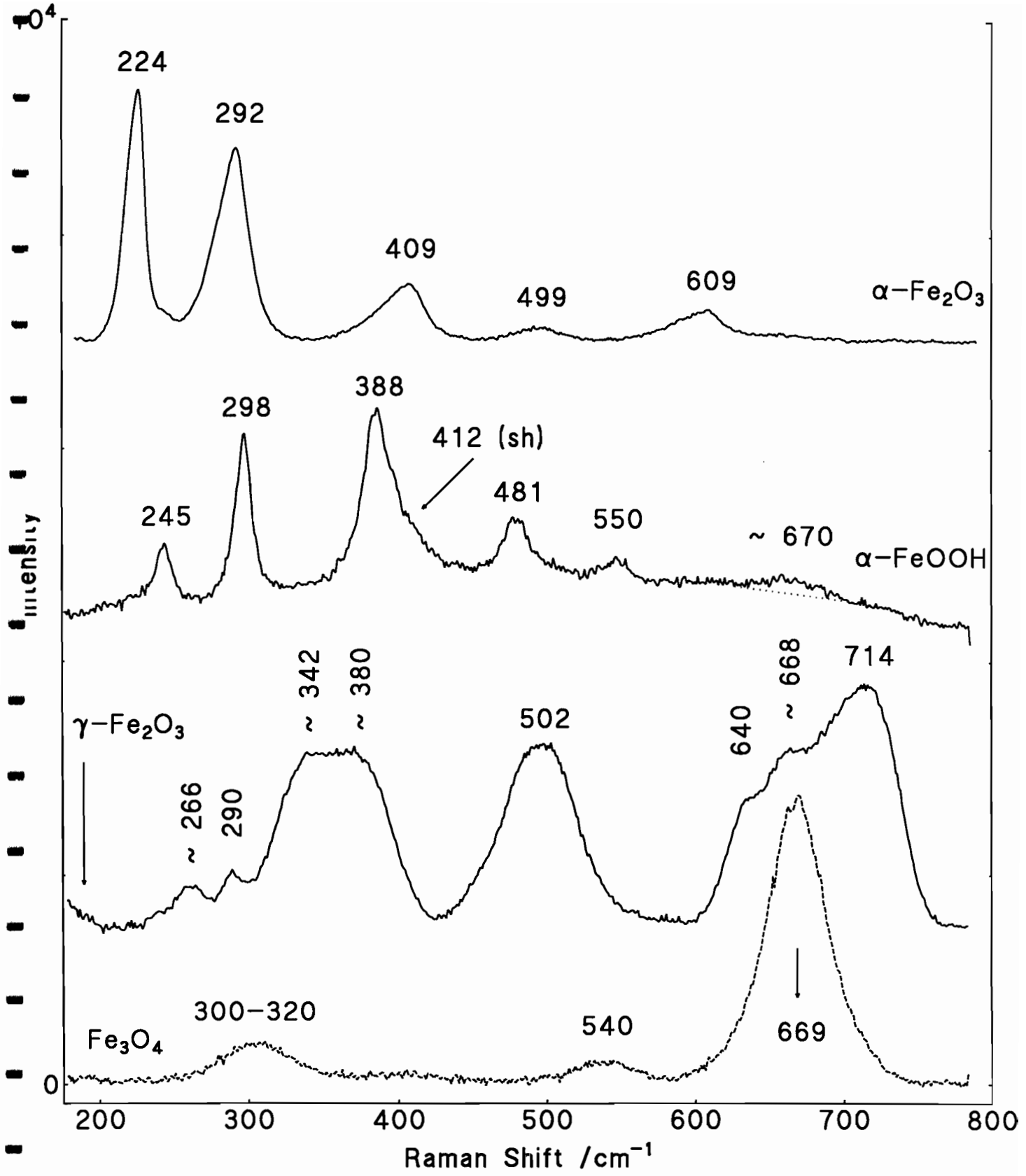

10^4
224
292
409
499
609
$\alpha-Fe_2O_3$
298
388
412 (sh)
245
481
550
~ 670
α-FeOOH
Intensity
~ 342
~ 380
714
~ 668
$\gamma-Fe_2O_3$
502
640
~ 266
290
300–320
Fe_3O_4
540
669
0
200
300
400
500
600
700
800
Raman Shift /cm^{-1}

Fig.1.

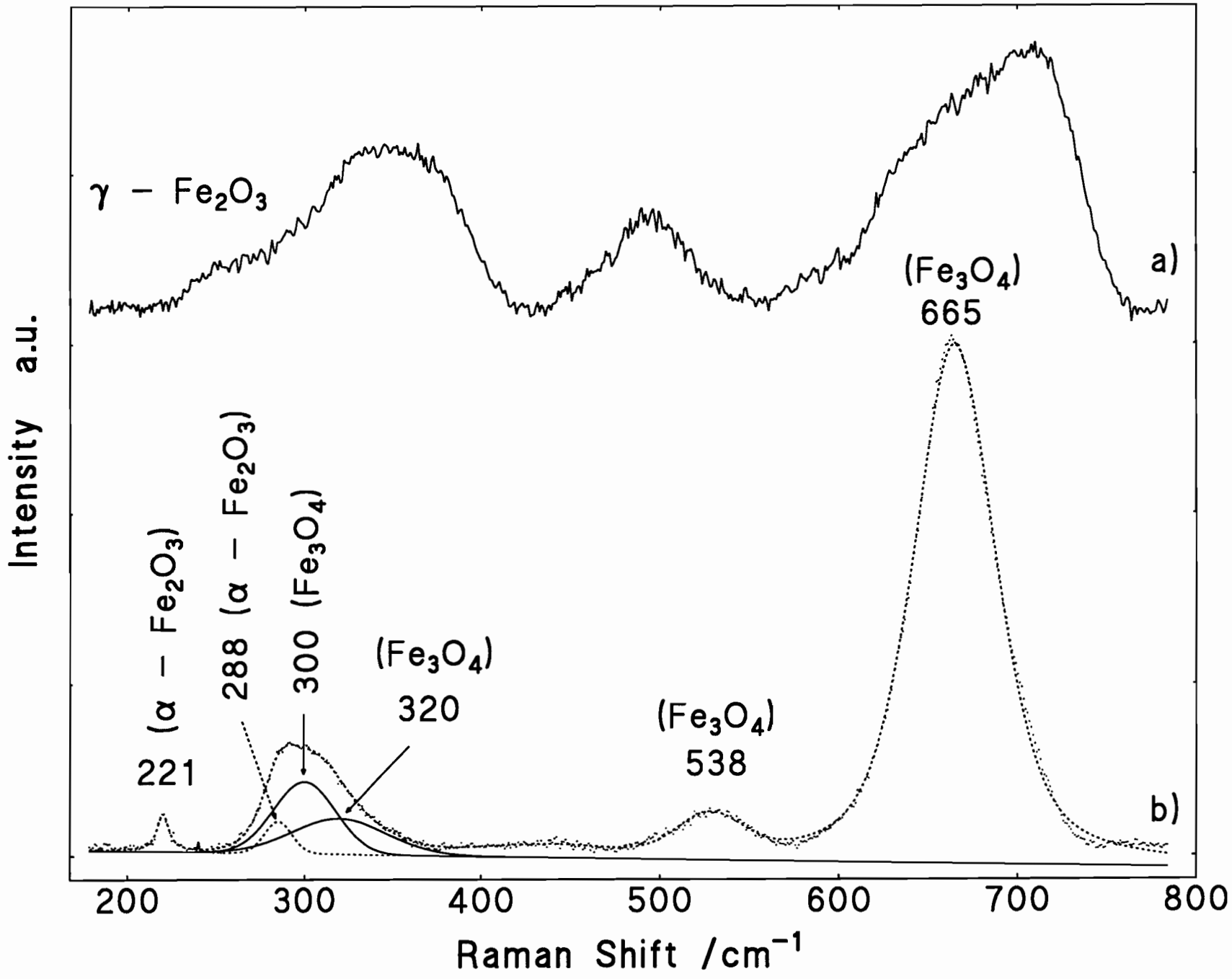

γ − Fe2O3
a)
(Fe3O4)
665
b)
(α − Fe2O3)
221
288 (α − Fe2O3)
300 (Fe3O4)
(Fe3O4)
320
(Fe3O4)
538
Intensity a.u.
200
300
400
500
600
700
800
Raman Shift /cm−1

Fig.2.

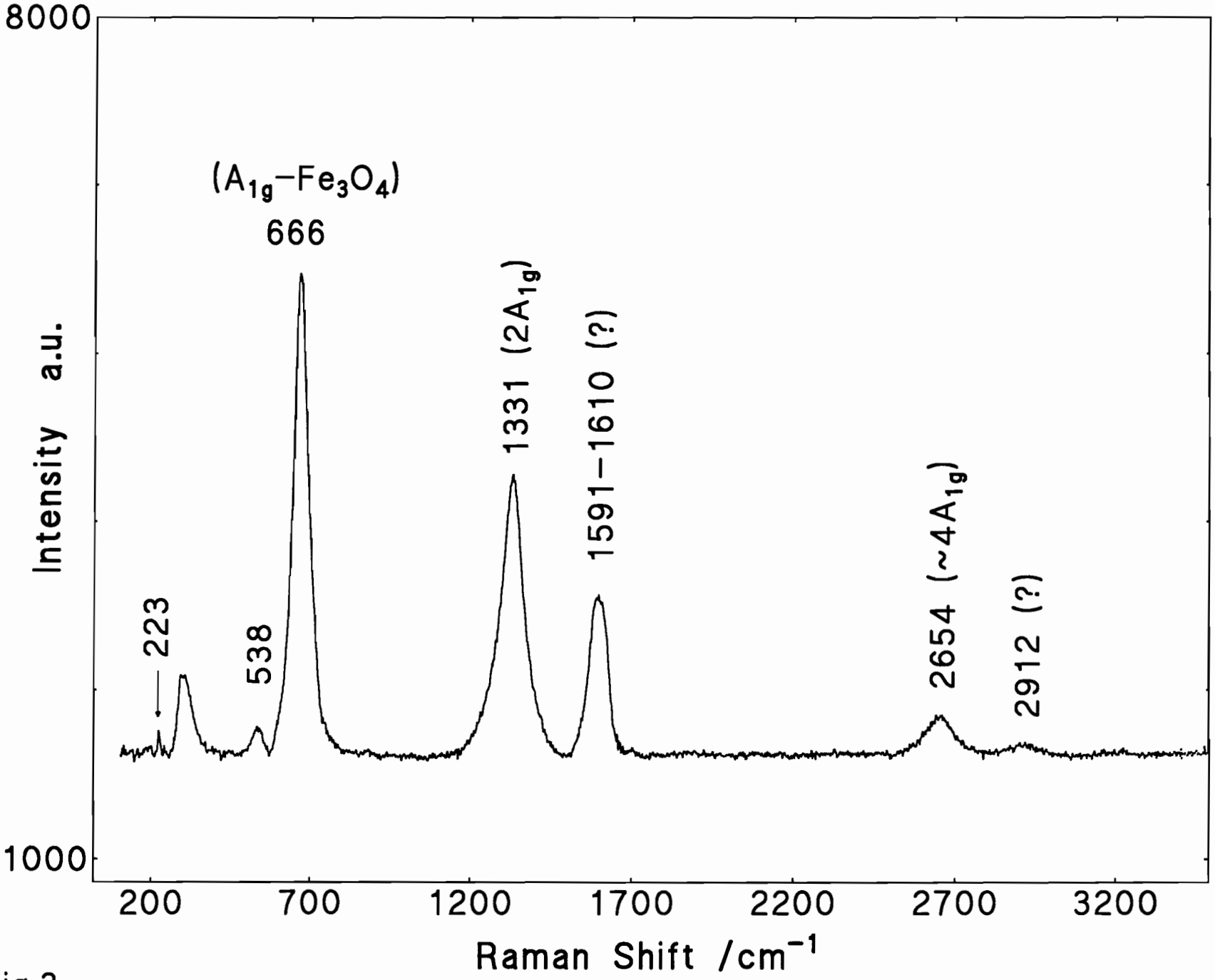

8000
1000
Intensity a.u.
(A1g–Fe3O4)
666
538
223
1331 (2A1g)
1591–1610 (?)
2654 (~4A1g)
2912 (?)
200
700
1200
1700
2200
2700
3200
Raman Shift /cm-1

Fig.3.

Summary of Raman Microscopic Analysis

LEGEND:

bold - indicates the strongest Raman bands

<u>underline</u> - indicates possible solution species

$GR(OH^-)$ - green rust containing OH^- anion

$GR(Cl^-)$ - green rust containing Cl^- anion

$GR(CO^{=}_3)$ - green rust containing $CO^{=}_3$ anion

$GR(SO^{=}_4)$ - green rust containing $SO^{=}_3$ anion or/and $FeSO_4$

Table 2-3-A. Raman characterization of the core sample N° **2-3-A**.

Fe Particle N°	Raman Band Position / cm^{-1} /										Surface Colour	Suggested Composition
1A				318	430	502	**667**		1054	**1068**	black-grey area	$CO^{=}_3$ solution species at interface, Fe_3O_4, GR($CO^{=}_3$)
2A	220	**252**	300	310	348	**379**	**528**	650	724	1070	yellow spot	α - Fe_2O_3 γ - FeOOH
3A	153	205			546	**668**	701	720	1069	**1085**	grey area	Fe_3O_4, aragonite $CO^{=}_3$ solution species
4A	150	202		386	549	**669**		724	**1068**	1084	shiny & pink area	$CO^{=}_3$ solution species Fe_3O_4, aragonite, FeOOH
5A	153	207	286	385		**670**	704		1069	**1084**	needle like crystal on black area	Fe_3O_4, aragonite $CO^{=}_3$ solution species possibly calcite & FeOOH
6A	152	204	240	384	480	684	703	724	**1068**	**1085**	milky area	mostly $CO^{=}_3$ solution species, aragonite, α-FeOOH, possibly Fe_3O_4

Table 2-3-A. Raman characterization of the core sample N° **2-3-A**, continuation.

Fe Particle N°	Raman Band Position / cm^{-1} /										Surface Colour	Suggested Composition
7A	220	**252**	309	348	**378**		523	650	1068	1085	orange brown area	mostly ***γ*** - FeOOH, residue of ***α*** - Fe_2O_3, $CO^{=}_3$ solution species at interface, a very small amount of solid carbonate ($CaCO_3$)

Table 2-3-B. Raman characterization of the core sample N° **2-3-B**.

Fe Particle N°	Raman Band Position / cm^{-1} /										Surface Colour	Suggested Composition
1A	226	293		414	431	503	613	669	1056	**1068**	green & metallic shiny area	$CO^{=}_3$ solution species, residue of ***α*** - Fe_2O_3, Fe_3O_4, GR($CO^{=}_3$)
2A	227		325		**430**	**499**		669	1056	1068	black area	Fe_3O_4 & GR($CO^{=}_3$), also possible GR($SO^{=}_4$) or/and GR(Cl^-)
3A	222		320		**433**	**501**		**670**		1069	blue spot	mostly Fe_3O_4 and GR(Cl^- or/and OH^-) $CO^{=}_3$ solution species
4A	206	299					**669**	705	1069	**1084**	milky spot	mostly Fe_3O_4 and calcite $CO^{=}_3$ solution species
5A	227	247	293	300	413		615	667			black area with shiny dots	Fe_3O_4 and ***α*** - Fe_2O_3
6A	219	**252**	310	349	379	528	651				yellow	mostly ***γ*** - FeOOH, residue of ***α*** - Fe_2O_3,

Table 2-3-C. Raman characterization of the core sample N° **2-3-C**. Sample 2-3-C was obtained dried.

Fe Particle N°	Raman Band Position / cm^{-1} /										Surface Colour	Suggested Composition
1A		312		412		547		**672**		1069	black area	only Fe_3O_4, $CO^{=}_3$ solution species
2A		**299**	**390**		476		557	**672**	684	1069	yellow-pink area	***α*** - FeOOH and Fe_3O_4
3A	247	**298**	**390**		478		556	670	686	1069	yellow area	mostly ***α*** - FeOOH, probably Fe_3O_4 $CO^{=}_3$ solution species
4A	133	194	242	384			671	683	724	1069	black - pink area	$CO^{=}_3$ solution species at interface ***α*** - FeOOH & Fe_3O_4 unknown species
5A	249	**299**		**392**			**669**	685		**1069**	yellow area	mostly of ***α*** - FeOOH $CO^{=}_3$ solution species small amount of Fe_3O_4

Note: a big amount of iron oxyhydroxide is the result of the surface oxidation of dried core sample. ***Raman data obtained from core sample 2-3-C are therefore not representative.***

Table 2-3-C. Raman characterization of the core sample N° **2-3-C**, continuation. Sample 2-3-C was obtained dried.

Fe Particle N°	Raman Band Position / cm^{-1} /										Surface Colour	Suggested Composition
6A	251	**298**		**389**	474	556	670	681	1065	1084	yellow -orange area	mostly ***α*** - FeOOH, small amount of Fe_3O_4, $CO^{=}_3$ solution species, solid carbonate ($CaCO_3$)
7A		252	**302**	**393**	477	556		682			yellow area	only ***α*** - FeOOH

Note: a big amount of iron oxyhydroxide is the result of the surface oxidation of dried core sample. ***Raman data obtained from core sample 2-3-C are therefore not representative.***

Table 2-3-E. Raman characterization of the core sample N° **2-3-E**.

Fe Particle N°	Raman Band Position / cm^{-1} /									Surface Colour	Suggested Composition
1A			300	320	425		540	**670**	1069	black area with shiny spots	only Fe_3O_4, $CO^{=}_3$ solution species
2A	228	**295**	300	416	**434**	**504**	615	**670**	**1071**	blue spot on black background	***α*** - Fe_2O_3, Fe_3O_4, GR (OH^-) $CO^{=}_3$ solution species
3A			303	320			645	**670**	1070	black area	only Fe_3O_4, $CO^{=}_3$ solution species
4A	221	**255**	314	352	**382**	435	508	531	655 & 670	yellow patch	***α,γ*** - Fe_2O_3 and ***γ*** - FeOOH Fe_3O_4
5A	230				**434**	**505**		672		blue spot	GR(OH^-), Fe_3O_4 possibly GR(Cl^-)
6A	230	320	**434**	**506**	548	**672**	853	927	1007	green patch on black area	GR ($SO^{=}_4$), and Fe_3O_4 possibly GR (Cl^-)
7A		320			545	**672**				shiny spots on black	only Fe_3O_4

Table 2-3-G. Raman characterization of the core sample N° **2-3-G**.

Fe Particle N°	Raman Band Position / cm^{-1} /									Surface Colour	Suggested Composition
1A			289	317	430	504	545	**669**		grey area with shiny spots	mostly Fe_3O_4 GR(OH^-), residue of Fe_2O_3
2A		283	300	320	434	502	543	**668**		bluish spot on black background	mostly Fe_3O_4 GR(OH^-), residue of Fe_2O_3
3A	228	284	293	320	412	547	615	**670**		grey area	mostly Fe_3O_4 residue of ***α*** - Fe_2O_3
4A			295	320			545	**671**		shiny spots on grey area	only Fe_3O_4

Note: due to instrument failure Raman measurements were not completed.

```
SEMQuant results. Listed at 13:32:05 on 02/07/97
Operator: James Wang
Client: none
Job: 17a
Spectrum label: 10a1mb

System resolution =  96 eV

Quantitative method: ZAF ( 2 iterations).
 Analysed all elements and normalised results.
Standards :
 C  K      Calcium carbonate for C 02/04/93
 O  K      Quartz - for Si 17/02/93
 Mg K      Magnesium oxide 14/02/93
 Si K      Quartz - for Si 14/02/93
 P  K      Gallium phosphide - for Ga and P
 S  K      Pyrite - for S 14/02/93
 Cl K      Potassium chloride - for Cl 16/0
 Ca K      Wollastonite - for Ca 14/02/93
 Cr K      Chromium metal 11/02/93
 Mn K      Manganese metal 11/02/93
 Fe K      Iron metal 11/02/93
 Ni K      Nickel metal 11/02/93
 Cu K      Copper metal 11/02/93
 Br L      Potassium bromide - for Br 14/02
```

Elmt	Element %	Atomic %
C K	1.63	6.97
O K	1.14	3.66
Mg K	-0.05*	-0.10*
Si K	0.14	0.25
P K	-0.04*	-0.06*
S K	0.03*	0.05*
Cl K	0.05*	0.07*
Ca K	0.13*	0.16*
Cr K	0.34	0.34
Mn K	0.12*	0.11*
Fe K	96.38	88.42
Ni K	0.17*	0.15*
Cu K	0.01*	0.01*
Br L	-0.07*	-0.04*
Total	100.00	100.00

```
* = <2 Sigma
```

EDX analysis of Master Builder reference material.

EDX Spectrum N°: **10A1MB**

Sample N°: **1-0-A**

Grain N°: **1MB**

SEMQuant results. Listed at 13:38:19 on 02/07/97
Operator: James Wang
Client: none
Job: 17a
Spectrum label: 10a2mb

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements and normalised results.
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Br	L	Potassium bromide - for Br 14/02

Elmt		Element %	Atomic %
C	K	16.47	47.41
O	K	0.71*	1.54*
Mg	K	-0.05*	-0.07*
Si	K	0.03*	0.04*
P	K	-0.05*	-0.05*
S	K	-0.10*	-0.11*
Cl	K	0.01*	0.01*
Ca	K	-0.16*	-0.13*
Cr	K	-0.12*	-0.08*
Mn	K	0.38*	0.24*
Fe	K	81.12	50.21
Ni	K	1.32	0.78
Cu	K	0.30*	0.17*
Br	L	0.12*	0.05*
Total		100.00	100.00

* = <2 Sigma

EDX analysis of Master Builder reference material.

EDX Spectrum N°: **10A2MB**

Sample N°: **1-0-A**

Grain N°: **2MB**

SEMQuant results. Listed at 13:49:24 on 02/07/97
Operator: James Wang
Client: none
Job: 17a
Spectrum label: 10a3mb

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements and normalised results.
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Br	L	Potassium bromide - for Br 14/02

Elmt	Element %	Atomic %
C K	1.44	6.12
O K	1.78	5.65
Mg K	-0.03*	-0.06*
Si K	0.05*	0.08*
P K	-0.03*	-0.05*
S K	0.02*	0.03*
Cl K	-0.01*	-0.02*
Ca K	0.08*	0.10*
Cr K	0.07*	0.06*
Mn K	0.16*	0.15*
Fe K	96.20	87.70
Ni K	0.14*	0.12*
Cu K	0.13*	0.11*
Br L	0.01*	0.01*
Total	100.00	100.00

* = <2 Sigma

EDX analysis of Master Builder reference material.

EDX Spectrum N°: **10A3MB**

Sample N°: **1-0-A**

Grain N°: **3MB**

SEMQuant results. Listed at 11:10:23 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-a1a

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.21	21.28
O K	0.03	2.22
Mg K	0.00*	-0.06*
Si K	0.00*	0.04*
P K	0.00*	0.06*
S K	0.01*	0.40*
Cl K	0.00*	0.06*
K K	0.02	0.61
Ca K	0.38	11.30
Cr K	0.00*	0.05*
Mn K	0.01*	0.14*
Fe K	2.97	63.24
Ni K	0.01*	0.19*
Cu K	0.00*	0.07*
Zn K	0.03*	0.49*
Br L	0.00*	-0.01*
Mo L	-0.02*	-0.21*
Cd L	0.01*	0.13*
Total	3.67	100.00

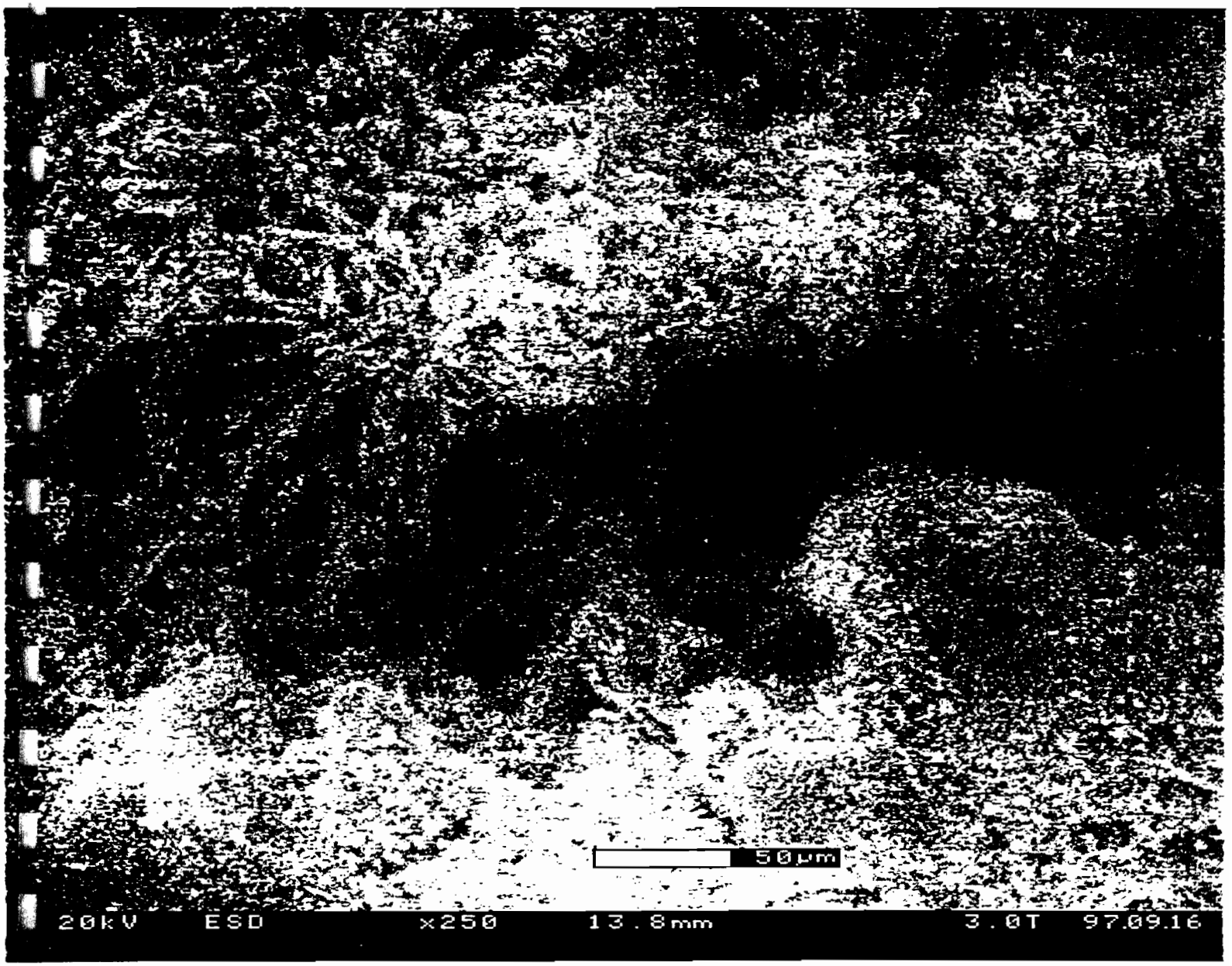
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-A1A**

Sample N°: **2-3-A**

Grain N°: **1AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-A**. Grain N°: **1AV**. Magnification 250.

SEMQuant results. Listed at 11:22:24 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-a2a

System resolution = 98 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt		Element %	Atomic %
C	K	0.22	24.48
O	K	0.05	4.48
Mg	K	0.00*	-0.05*
Si	K	0.00*	0.12*
P	K	0.00*	0.01*
S	K	0.01*	0.30*
Cl	K	0.00*	0.10*
K	K	0.01	0.40
Ca	K	0.28	9.28
Cr	K	0.00*	-0.02*
Mn	K	0.01*	0.23*
Fe	K	2.53	60.49
Ni	K	-0.01*	-0.14*
Cu	K	0.01*	0.19*
Zn	K	0.01*	0.19*
Br	L	0.00*	0.00*
Mo	L	-0.01*	-0.13*
Cd	L	0.01*	0.10*
Total		3.12	100.00

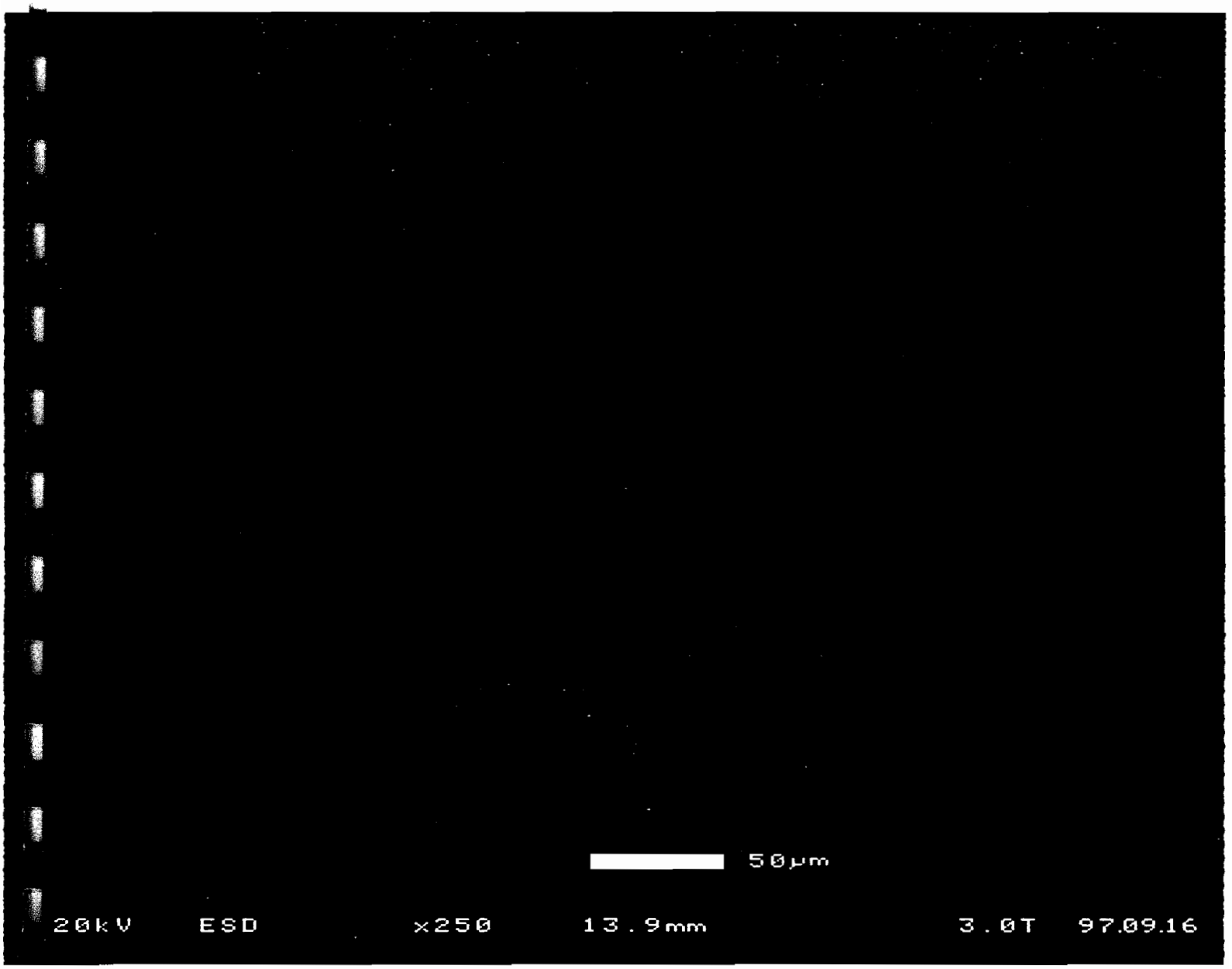
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-A2A**

Sample N°: **2-3-A**

Grain N°: **2AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-A**. Grain N°: **2AV**. Magnification 250.

SEMQuant results. Listed at 12:06:10 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-B1A

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt		Element %	Atomic %
C	K	0.23	17.72
O	K	0.01	0.86
Mg	K	0.00*	-0.02*
Si	K	0.00	0.11
P	K	0.00*	0.00*
S	K	0.00*	-0.01*
Cl	K	0.00*	-0.07*
K	K	0.01*	0.13*
Ca	K	0.01*	0.16*
Cr	K	0.01*	0.19*
Mn	K	-0.01*	-0.11*
Fe	K	4.88	81.14
Ni	K	-0.01*	-0.09*
Cu	K	0.00*	-0.05*
Zn	K	0.01*	0.11*
Br	L	0.00*	0.01*
Mo	L	0.00*	-0.05*
Cd	L	0.00*	-0.01*
Total		5.14	100.00

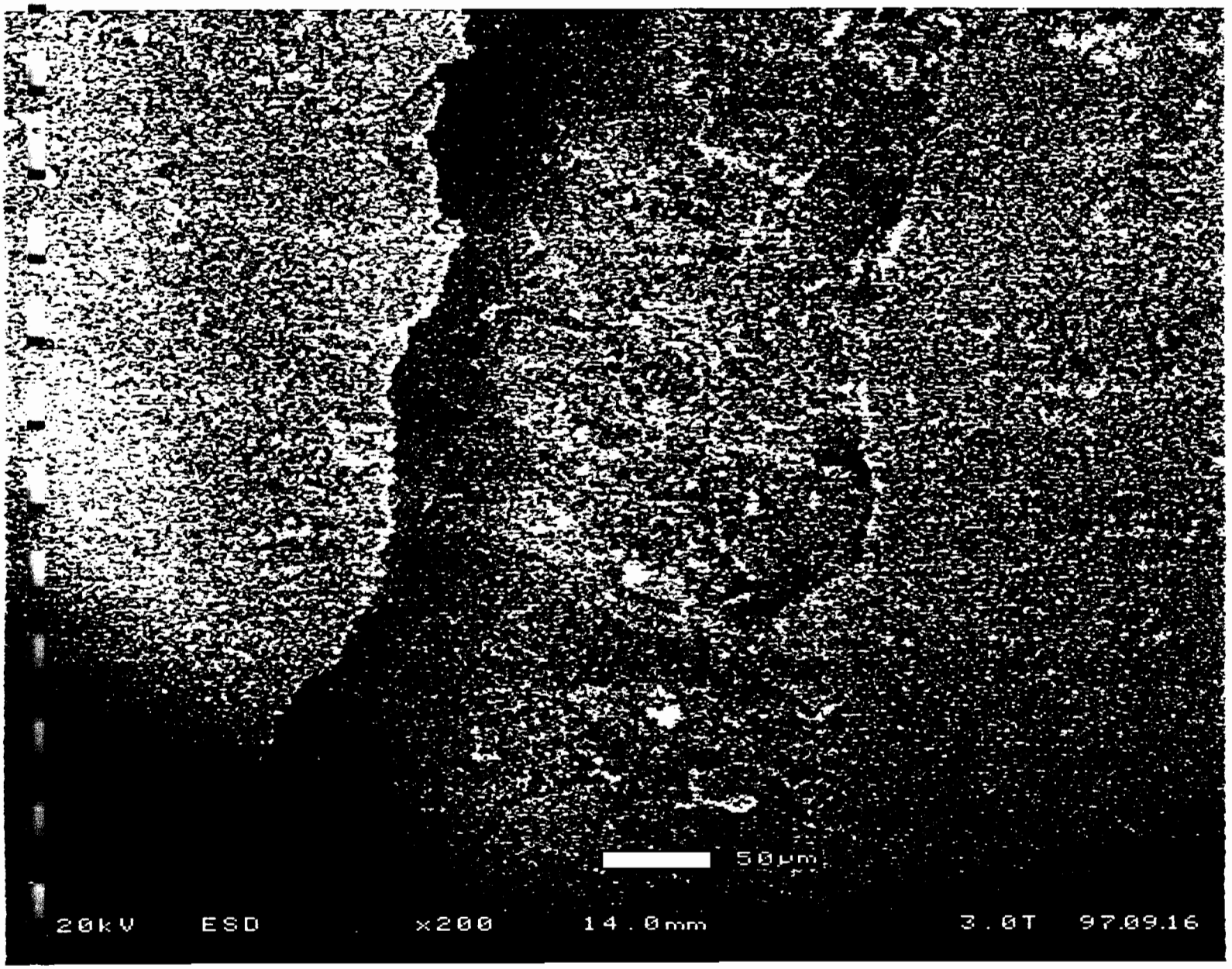
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-B1A**

Sample N°: **2-3-B**

Grain N°: **1AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-B**. Grain N°: **1AV**. Magnification 250.

SEMQuant results. Listed at 12:14:18 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-b2a

System resolution = 99 eV

Quantitative method: ZAF (1 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.11	10.93
O K	0.03	2.49
Mg K	0.00*	0.03*
Si K	0.00*	0.08*
P K	0.00*	-0.05*
S K	0.00*	-0.03*
Cl K	0.00*	0.14*
K K	0.00*	-0.02*
Ca K	0.02	0.55
Cr K	0.01*	0.29*
Mn K	-0.01*	-0.15*
Fe K	4.14	85.68
Ni K	0.02*	0.42*
Cu K	-0.03*	-0.53*
Zn K	0.00*	0.07*
Br L	0.00*	0.03*
Mo L	0.01*	0.09*
Cd L	0.00*	-0.02*
Total	4.32	100.00

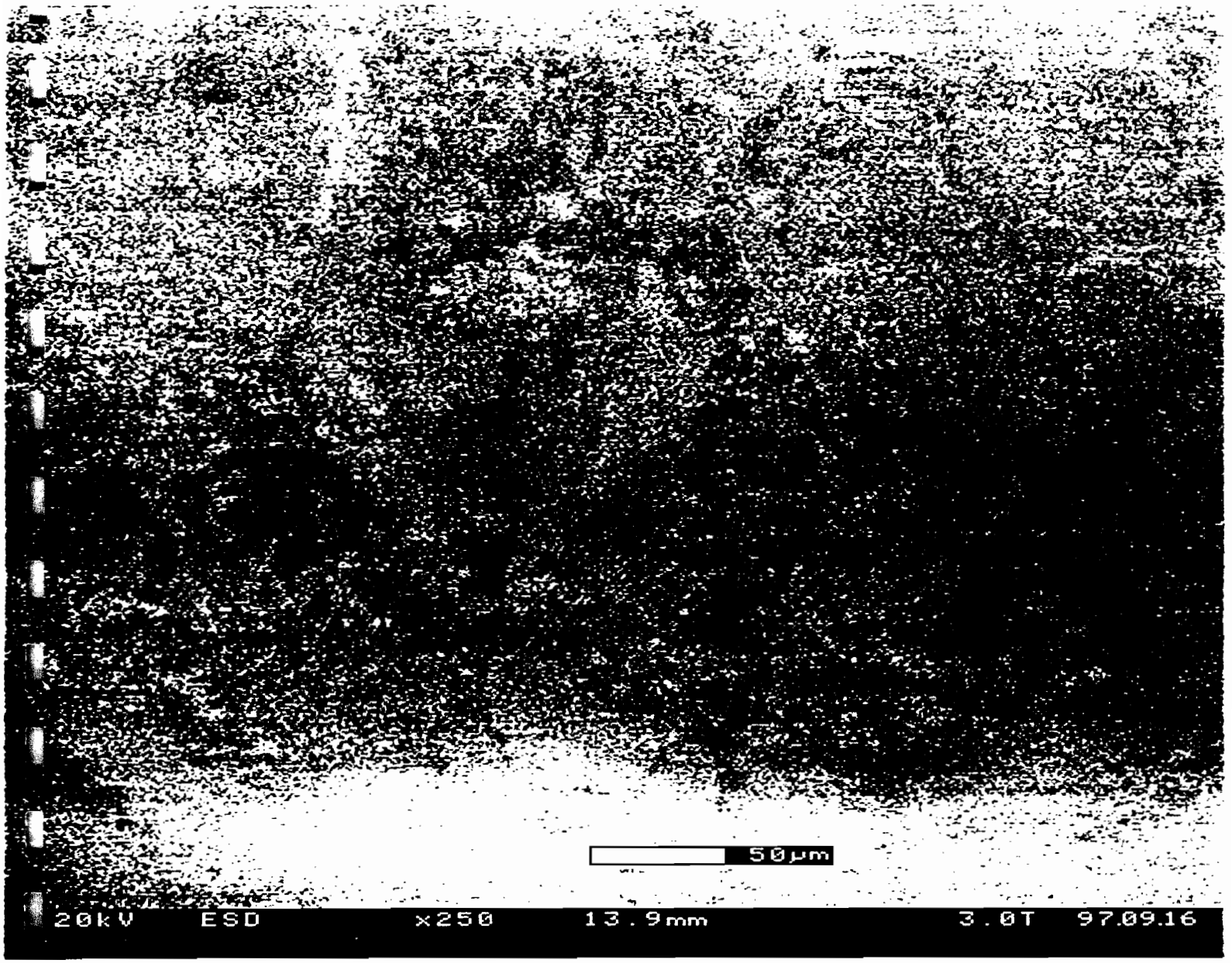
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-B2A**

Sample N°: **2-3-B**

Grain N°: **2AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-B**. Grain N°: **2AV**. Magnification 250.

SEMQuant results. Listed at 12:38:32 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-c1a

System resolution = 98 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.16	9.37
O K	0.06	2.75
Mg K	0.00*	-0.08*
Si K	0.00*	0.00*
P K	0.00*	0.01*
S K	0.01*	0.32*
Cl K	0.00*	-0.10*
K K	0.00*	0.01*
Ca K	0.02	0.36
Cr K	0.02	0.28
Mn K	-0.01*	-0.10*
Fe K	6.86	87.16
Ni K	0.02*	0.24*
Cu K	-0.02*	-0.23*
Zn K	0.02*	0.26*
Br L	0.00*	-0.03*
Mo L	-0.03*	-0.23*
Cd L	0.00*	0.00*
Total	7.11	100.00

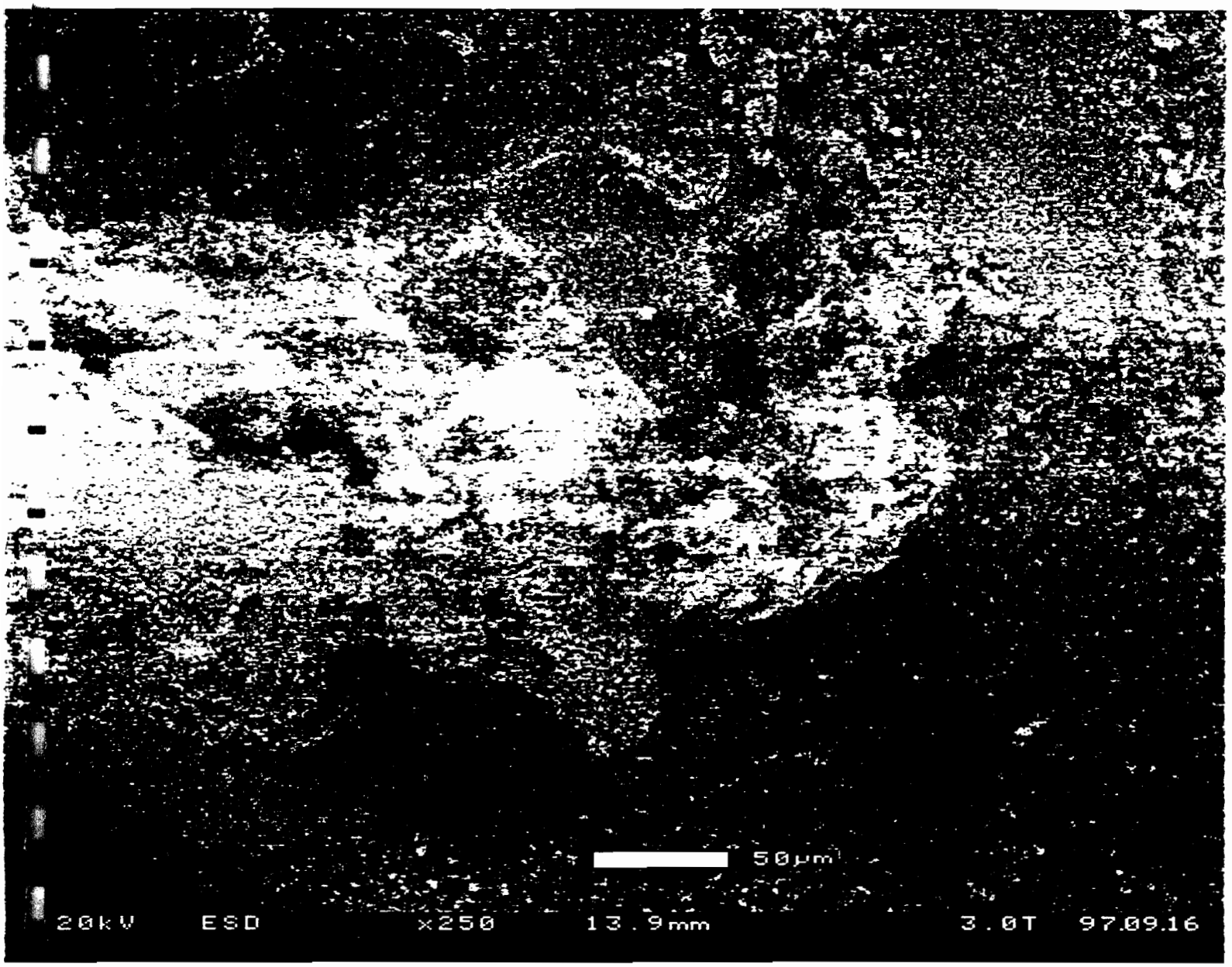
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-C1A**

Sample N°: **2-3-C**

Grain N°: **1AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-C**. Grain N°: **1AV**. Magnification 250.

SEMQuant results. Listed at 12:49:06 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-c2a

System resolution = 98 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.20	9.64
O K	0.09	3.18
Mg K	0.00*	0.00*
Si K	0.00*	0.04*
P K	0.00*	0.05*
S K	-0.01*	-0.12*
Cl K	0.01*	0.13*
K K	0.02	0.28
Ca K	0.52	7.46
Cr K	0.01*	0.10*
Mn K	-0.02*	-0.21*
Fe K	7.67	78.47
Ni K	0.03*	0.29*
Cu K	0.04*	0.32*
Zn K	0.03*	0.25*
Br L	0.00*	-0.03*
Mo L	0.01*	0.08*
Cd L	0.02*	0.08*
Total	8.61	100.00

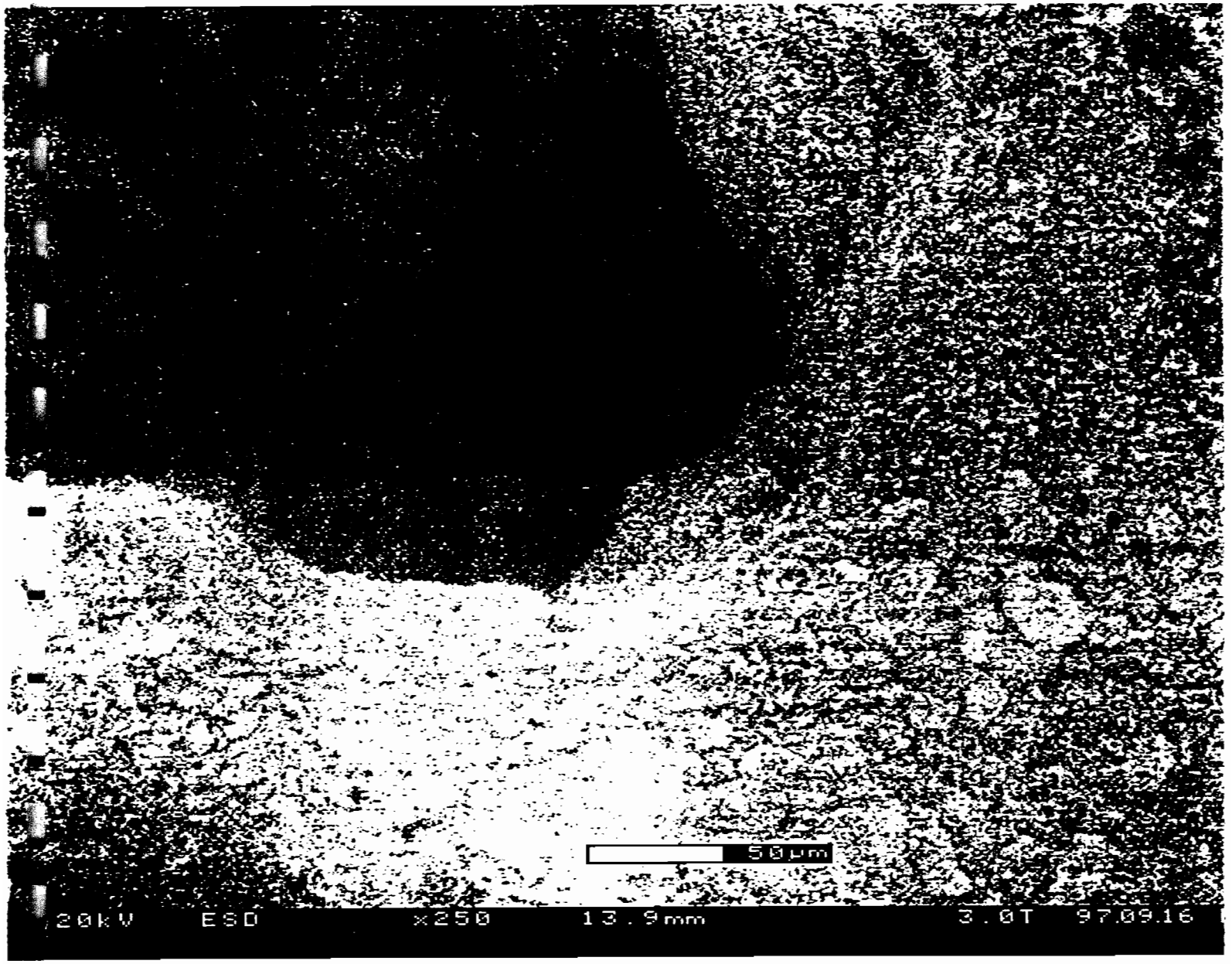
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-C2A**

Sample N°: **2-3-C**

Grain N°: **2AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-C**. Grain N°: **2AV**. Magnification 250.

SEMQuant results. Listed at 12:55:01 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-c3a

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.19	6.91
O K	0.13	3.62
Mg K	0.00*	0.01*
Si K	0.00	0.08
P K	0.00*	0.04*
S K	0.02*	0.26*
Cl K	0.00*	-0.02*
K K	0.02	0.25
Ca K	0.22	2.42
Cr K	0.02*	0.17*
Mn K	-0.02*	-0.13*
Fe K	10.78	86.53
Ni K	0.02*	0.14*
Cu K	0.00*	-0.03*
Zn K	-0.01*	-0.06*
Br L	0.00*	0.01*
Mo L	-0.04*	-0.18*
Cd L	-0.01*	-0.03*
Total	11.33	100.00

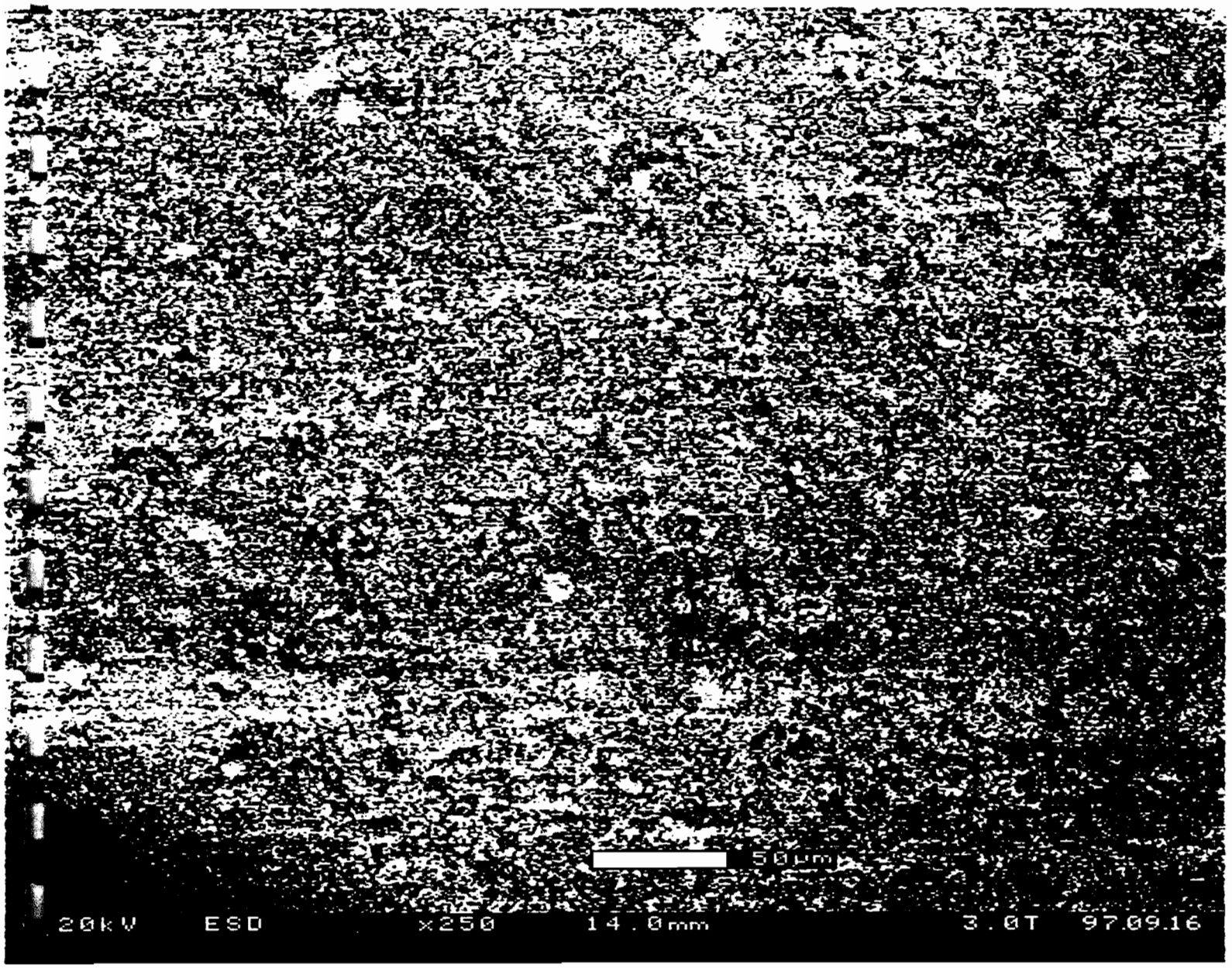
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-C3A**

Sample N°: **2-3-C**

Grain N°: **3AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-C**. Grain N°: **3AV**. Magnification 250.

SEMQuant results. Listed at 14:01:37 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-e1a

System resolution = 98 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.16	6.64
O K	0.05	1.68
Mg K	0.00*	0.00*
Si K	0.00*	0.03*
P K	0.00*	-0.02*
S K	0.01*	0.15*
Cl K	0.00*	-0.04*
K K	0.00*	0.02*
Ca K	0.02	0.29
Cr K	0.03	0.31
Mn K	0.04*	0.32*
Fe K	10.34	90.42
Ni K	0.02*	0.20*
Cu K	0.04*	0.30*
Zn K	-0.02*	-0.18*
Br L	0.00*	0.00*
Mo L	-0.03*	-0.13*
Cd L	0.01*	0.03*
Total	10.68	100.00

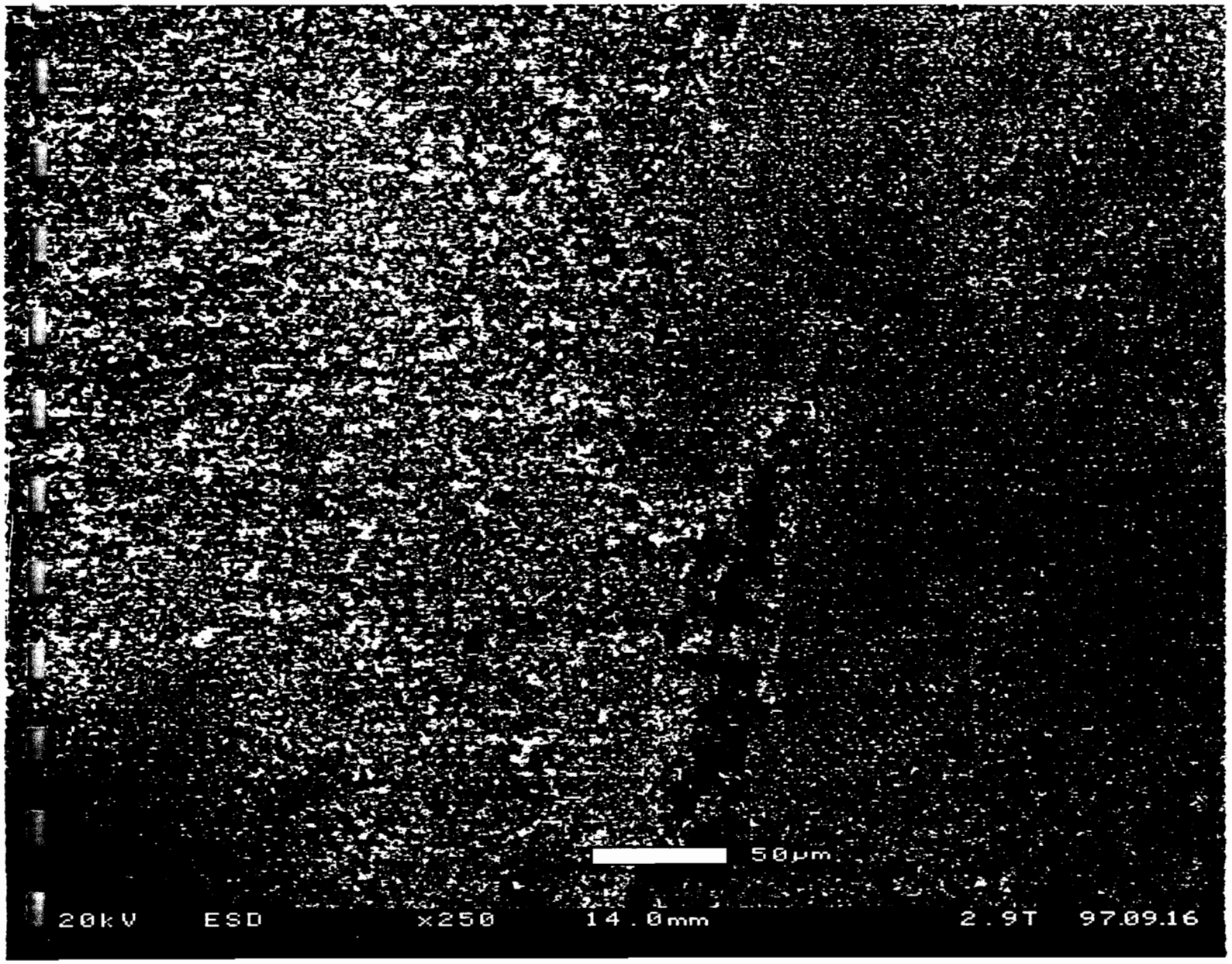
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-E1A**

Sample N°: **2-3-E**

Grain N°: **1AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-E**. Grain N°: **1AV**. Magnification 250.

SEMQuant results. Listed at 14:08:03 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-e2a

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
1 peak possibly omitted: 15.32 keV

Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.24	8.91
O K	0.11	3.00
Mg K	0.00*	0.00*
Si K	0.00*	0.04*
P K	0.00*	0.02*
S K	0.02*	0.23*
Cl K	0.00*	-0.03*
K K	0.00*	-0.03*
Ca K	0.01*	0.12*
Cr K	0.04	0.38
Mn K	0.02*	0.18*
Fe K	11.05	86.75
Ni K	0.04*	0.30*
Cu K	0.04*	0.27*
Zn K	0.01*	0.05*
Br L	0.00*	0.00*
Mo L	-0.04*	-0.18*
Cd L	0.00*	-0.01*
Total	11.54	100.00

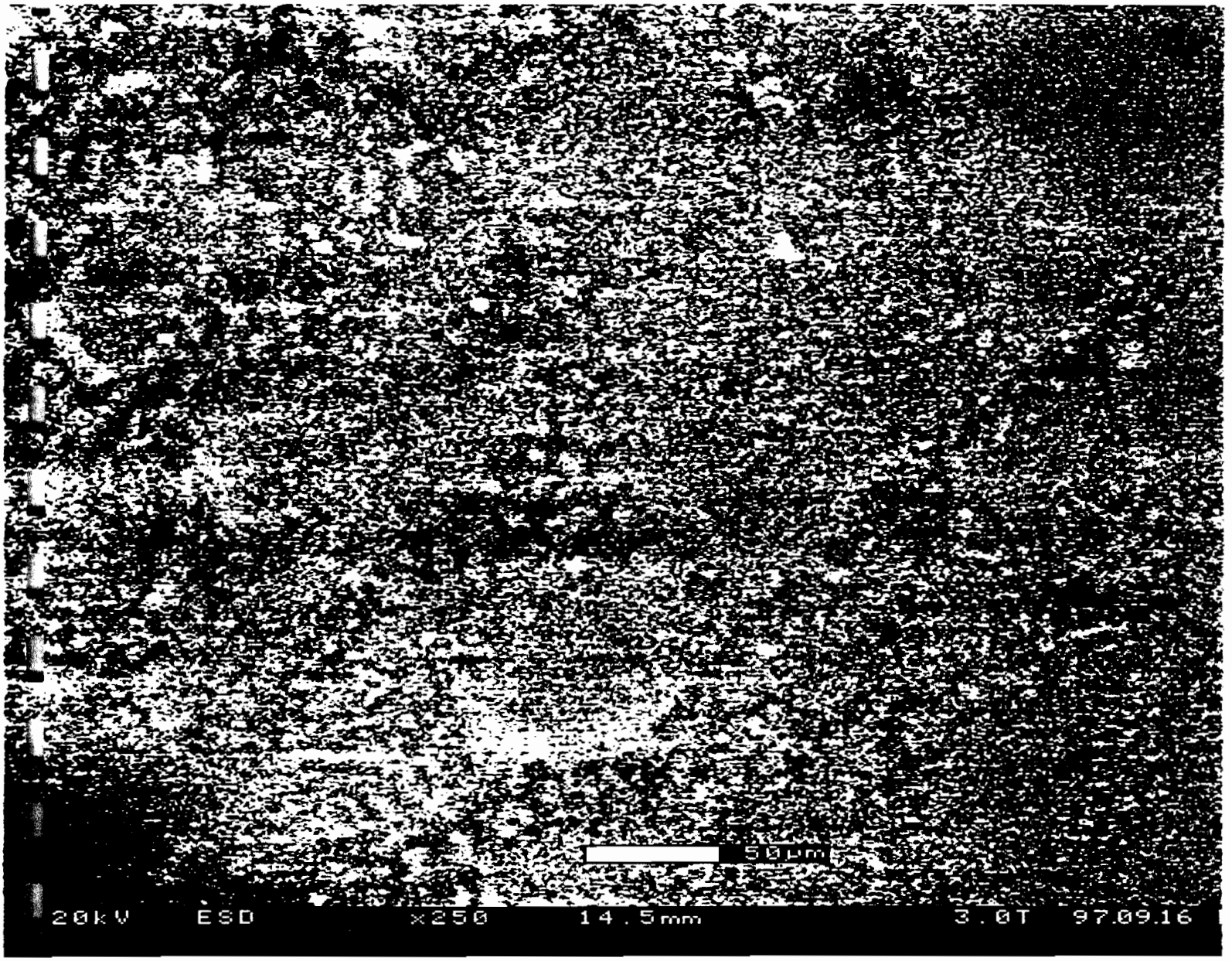
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-E2A**

Sample N°: **2-3-E**

Grain N°: **2AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-E**. Grain N°: **2AV**. Magnification 250.

SEMQuant results. Listed at 14:26:55 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3-g1a

System resolution = 95 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.24	20.42
O K	0.03	1.87
Mg K	0.00*	-0.05*
Si K	0.00*	0.08*
P K	0.00*	-0.11*
S K	0.00*	-0.13*
Cl K	0.00*	0.03*
K K	0.00*	0.08*
Ca K	0.01	0.22
Cr K	0.02	0.35
Mn K	0.01*	0.13*
Fe K	4.21	76.21
Ni K	0.03*	0.45*
Cu K	0.03*	0.50*
Zn K	-0.01*	-0.22*
Br L	0.00	0.04
Mo L	0.01*	0.15*
Cd L	0.00*	-0.02*
Total	4.57	100.00

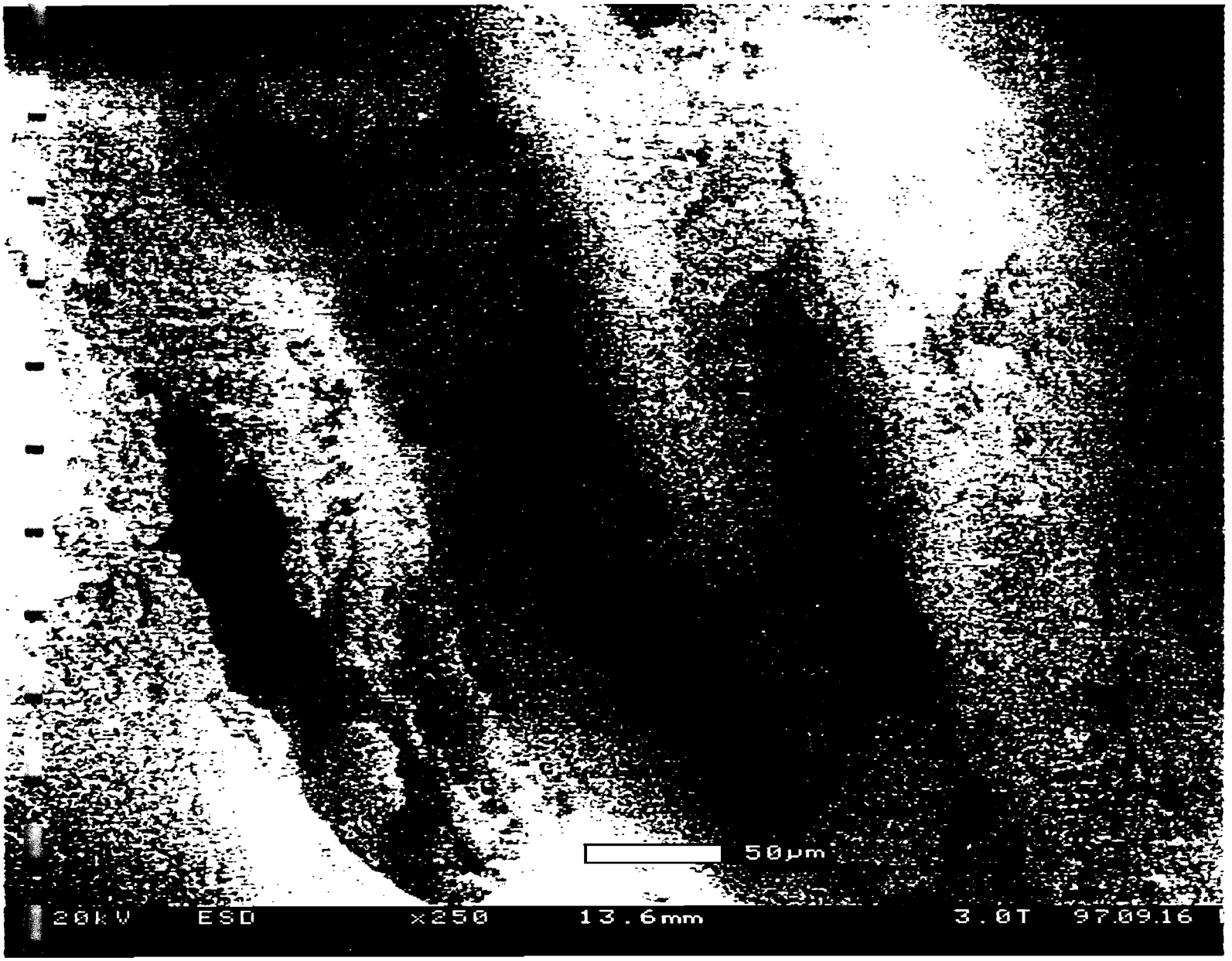
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-G1A**

Sample N°: **2-3-G**

Grain N°: **1AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-G**. Grain N°: **1AV**. Magnification 250.

SEMQuant results. Listed at 14:34:21 on 16/09/97
Operator: Marek Odziemkowski
Client: none
Job: core2eti
Spectrum label: 2-3g-2ga

System resolution = 97 eV

Quantitative method: ZAF (2 iterations).
Analysed all elements
Standards :

C	K	Calcium carbonate for C 02/04/93
O	K	Quartz - for Si 17/02/93
Mg	K	Magnesium oxide 14/02/93
Si	K	Quartz - for Si 14/02/93
P	K	Gallium phosphide - for Ga and P
S	K	Pyrite - for S 14/02/93
Cl	K	Potassium chloride - for Cl 16/0
K	K	Orthoclase - for K 16/02/93
Ca	K	Wollastonite - for Ca 14/02/93
Cr	K	Chromium metal 11/02/93
Mn	K	Manganese metal 11/02/93
Fe	K	Iron metal 11/02/93
Ni	K	Nickel metal 11/02/93
Cu	K	Copper metal 11/02/93
Zn	K	Zinc metal 11/02/93
Br	L	Potassium bromide - for Br 14/02
Mo	L	Molybdenum metal 11/02/93
Cd	L	Cadmium metal 11/02/93

Elmt	Element %	Atomic %
C K	0.24	7.82
O K	0.05	1.10
Mg K	0.00*	0.01*
Si K	0.00*	0.05*
P K	0.00*	-0.02*
S K	0.01*	0.14*
Cl K	0.00*	0.01*
K K	0.02	0.18
Ca K	0.01*	0.06*
Cr K	0.04	0.29
Mn K	0.08	0.55
Fe K	12.96	89.39
Ni K	0.04*	0.25*
Cu K	0.05*	0.31*
Zn K	0.00*	0.00*
Br L	0.00*	0.00*
Mo L	-0.02*	-0.08*
Cd L	-0.02*	-0.05*
Total	13.46	100.00

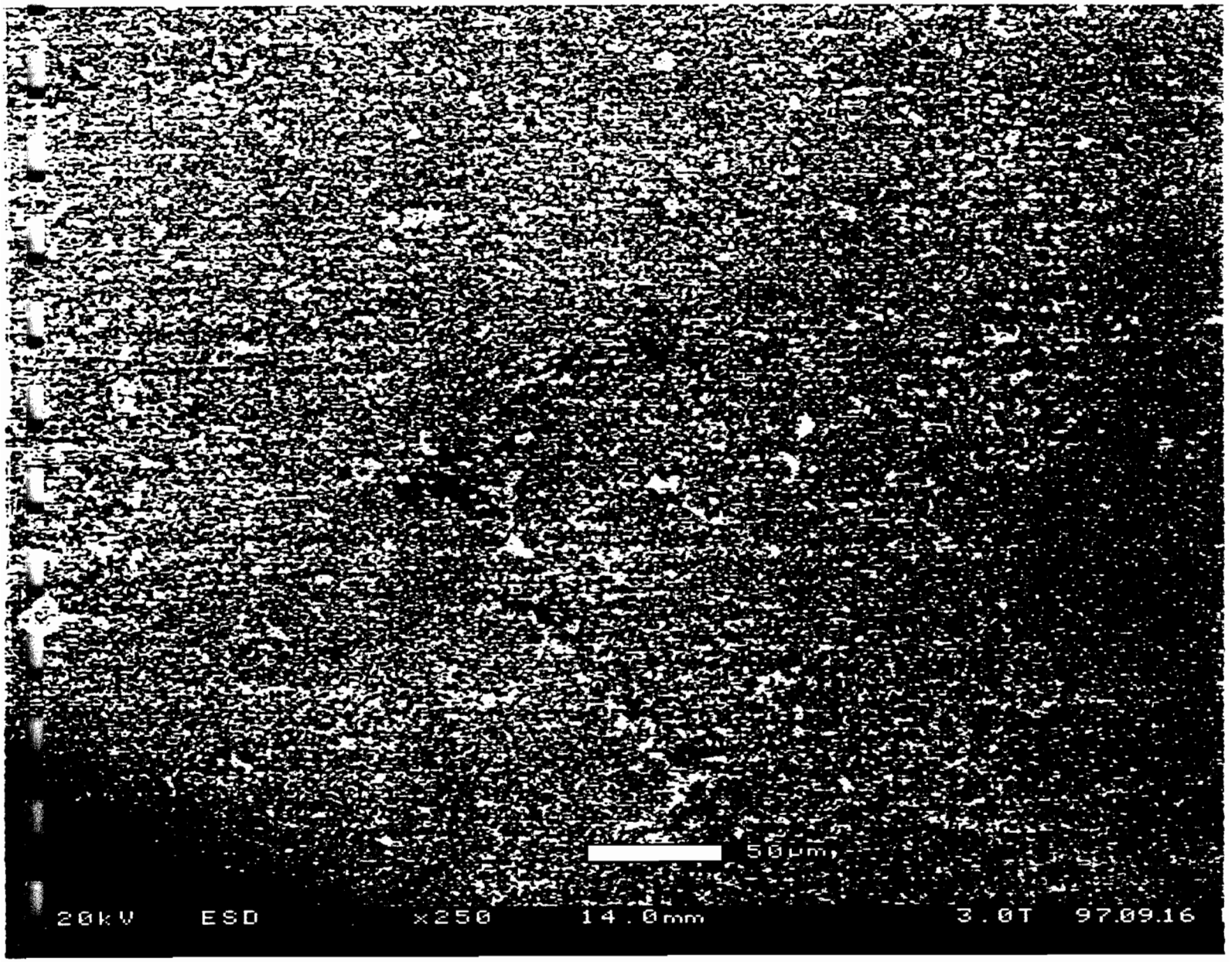
* = <2 Sigma

EDX analysis of core material.

EDX Spectrum N°: **2-3-G2A**

Sample N°: **2-3-B**

Grain N°: **2AV**



Copy of SEM micrograph of the analyzed area. Sample N°: **2-3-G**. Grain N°: **2AV**. Magnification 250.

APPENDIX B

Carbonate Analyses

TITRIMETRIC METHOD FOR DETERMINATION OF INORGANIC CARBON (CARBONATE) IN SOILS

Introduction

This simple procedure is used to determine quantitatively the total amount of carbonate carbon in a soil sample. Highly accurate and precise values can be obtained for very minute amounts of carbonate (< 0.3 mg/g) if extreme care is taken while preforming the analysis.

Basically soil samples are treated with strong acid to dissolve resident carbonate material and generate CO_2 gas. The CO_2 (g) evolved from the sample is subsequently collected in a solution containing strong a alkali (base) of known concentration. A back titration is then performed to determine the amount of CO_2 collected and thus estimate the amount of carbonate-carbon contained in the soil sample.

Reagents:

For the Preparation:

1. 2.0 mol/L HCl. Prepare by dissolving 167 mL concentrated (12 molar) HCl in 1 L of distilled H_20.
2. n-octyl-alchol (octanol), reagent grade, or some other surfactant. Optional; used to inhibit frothing in some samples high in organic matter.
3. 2.0 mol/L KOH. **Prepare fresh** just before using. Dissolve 56 g KOH in 500 mL distilled H_2O. Prepare only the minimum amount required for the number of samples to be run. This solution cannot be stored.

CAUTION: The dissolution of the KOH is slow and extremely exothermic. Cool the flask under cold running water. KOH is also very caustic. If any comes in contact with your skin wash it off immediately with plenty of water. The KOH solution will also rapidly adsorb/dissolve atmospheric CO_2, therefore it is important to minimize contact of the solution with the atmosphere at all times. Keep the flask capped!

For the Titration

1. 1.0 mol/L HCl. Prepare by dissolving 83 mL of concentrated (12 molar) HCl in 1 L distilled H_2O.
2. Standardized 0.100 mol/L HCl. Prepared by diluting 10.00 mL of 1.000 mol/L HCl (commercial) into 100.0 mL of distilled H2O.

3. **Phenolphthalein indicator.**
   Prepare by dissolving 0.05 g of commercial stock in 50 mL 95% ethanol and 50 mL distilled H_2O; pH range = 8.3-10.0; colorless/red.

4. Bromcresol Green indicator. Prepare by dissolving 0.1 g commercial stock in 250 mL 6 x 10-4 molar NaOH; pH range 3.6-5.2; yellow/blue.

Appratus:

- 250 mL widemouth flasks
- stopper assembly*
- 50 mL syringe with needle
- 10 mL syringe with needle
- 50 mL burette
- 10 mL burette
- burette stand and holder
- small magnetic mixer
- magnetic stir bar
- wash bottle
- 125 mL erlenmyer flask.

*STOPPER ASSEMBLY

Using a #4 cork borer tool, push a hole through the centre of a #8 rubber stopper. Using a #5 cork borer tool to assist you, insert a piece of glass tubing (about 170 mm long, 8 mm O.D., 6 mm I.D.) into the hole made in the stopper. The tube should be positioned so that it extends about 30 mm above the top of the rubber stopper but also remain about 10 mm above the bottom of the 250 mL widemouth flask when the stopper is tightly inserted. Try a flask for the fit before you go further. To the bottom (long) end of the tubing attach a 6 mL vial using two rubber bands positioned around the top and bottom of the vial holding it securely. The vial should be held upright with the bottom of the vial positioned about 10 mm from the bottom end of the glass tube. Fit the other (top) end of the glass tube with a small rubber septum (Authur H. Thomas Co., Philidalphia. PA 19105 USA, Cat. #1780-B10).

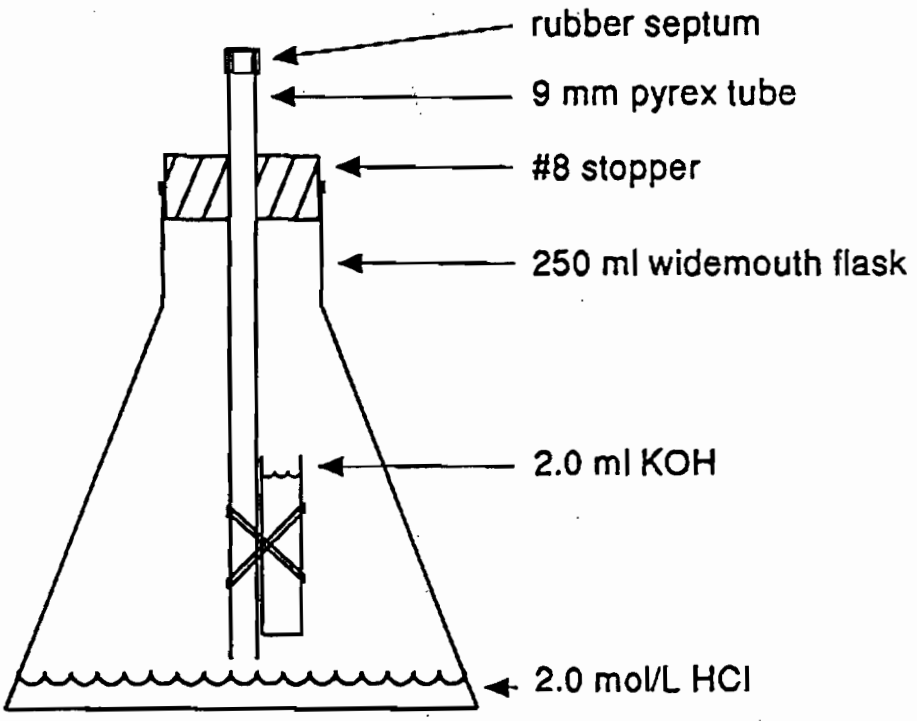


Figure 1: Sketch of the appratus

Procedure

Preparation

1. Weigh about 1.00 g** of ground soil (< 0.1 mesh) into a 250 mL widemouth flask making sure none of the sample clings to the inside walls of the flask.

** **Note:** If the sample contains a large amount of carbonate reduce the sample size to 0.50 g or less. If necessary as much as 8.00 g of soil can be used, provided it does not contain more than 30 mg inorganic carbon. All samples should be run in at least duplicate and blanks (no soil added to the flask) in triplicate. To test the accuracy of the method, analytical grade carbonate material can be substituted for samples instead of soil. Only quantities of pure carbonate less that 0.5 g should be used.

2. Record the exact weight of the sample.

3. Add 2 or 3 drops of surfactant (n-octanol) if required.

4. Pipette 5.0 mL of the freshly prepared 2.0 mol/L KOH into the small vial at the end of the stopper assembly (see above).

5. Carefully position the stopper assembly in the mouth of the sample flask making sure that no KOH spills from the vial and that the flask is tightly sealed.

6. Using a 50 mL syringe, withdraw about 150 mL (3 X 50 mL) of air from the tightly sealed flask through the rubber septum at the top of the stopper assembly.

7. Again using the 50 mL syringe inject 20 mL 2.0 mol/L HCl (30 mL for very alkaline samples) into the flask through the rubber septum.

8. Gently swirl the contents of the flask (being careful not to spill any KOH) so that all the soil in the flask comes in contact with the solution.

9. Let the flask stand for 16-24 hr at room temperature (25°C) to equilibrate. If a sample contains a large amount of carbonate, pressure from the CO_2 evolved may pop the stopper assembly out of the flask. If this occurs redo the above steps starting with less soil (about half the previous amount). Excess frothing will also disrupt the analysis. These also must be started again with the addition of a surfactant.

Titration

10. Fill the 50 mL burette with 1.0 mol/L HCl and the 10 mL burette with 0.100 mol/L HCl.

11. After reaction is complete (equilibrium obtained) carefully remove the stopper assembly (use a small syringe to relieve the vacuum if necessary) and quantitatively transfer the contents of the 6 mL vial into a clean 125 mL erlenmyer flask (marked in 50 mL increments).

12. Make the solution up to 50 mL with distilled H2O and add 6 to 8 drops of phenolphthalein indicator to the flask (pink color).

13. Insert a magnetic stir bar into the flask and titrate using 1.0 mol/L HCl until the pink color begins to fade. Blanks will require a total of about 10 mL of 1.0 mol/L HCl (9 mL can be delivered rapidly, the last mL dropwise). Samples will require less acid than the blank; usually 7 to 8 mL of acid depending on the amount of carbonate in the sample.

14. Using the 0.100 mol/L HCl continue to titrate until the clear end point is just reached. IT IS ABSOLUTELY CRITICAL THAT YOU DO NOT OVERSHOOT THIS END POINT!!!!

15. Record the reading on the 0.100 mol/L (10 mL) burette.

16. To the clear solution add 8 to 10 drops of bromcresol green indicator (blueish-green color).

17. Continue titrating with 0.100 mol/L HCl until the bright yellow end point is reached (blue to green to bright yellow transition).

18. Record the burette reading.

Calculations:

mg inorganic carbon = (S - B) X 1.20

mg carbonate CO_3^{-2} = (S - B) X 6.00

% CaCO3 equivalent = (S - B) / sample mass in grams.

Where:

S = mL of 0.100 mol/L HCl required to titrate the sample from the phenolphthalein end point to the bromcresol green end point.

B = mL of 0.100 mol/L HCl required to titrate the blank from the phenolphthalein end point to the bromcresol green end point.

Note: Low exposure of the KOH to the atmosphere can result in the blank reading (B) of less than 0.40 mL.

Theory:

The analytical procedure described above is based on the fundamental properties of the CO2-H2O (carbonate) system. By acidifying the soil sample any carbonate materials are rapidly dissolved and gaseous CO_2 is generated:

$$Ca(Mg)CO_{3\ (s)} + 2H^+ = CO_{2\ (g)} + H_2O + Ca^{+2} \qquad [1]$$

The CO_2 (g) evolved from the sample is dissolved in the KOH solution:

$$CO_{2\ (g)} + H_2O = H_2CO_{3\ (aq)} \qquad pKh = 1.5 \qquad [2]$$

In addition two other reactions occur in when the CO_2 gas dissolves:

H2CO3 (aq) = H+ + HCO3- pK1 = 6.3 [3]

HCO3- = H+ + CO3-2 pK2 = 10.3 [4]

The alkalinity of the solution facilitates the adsorption of the essentially all the CO_2 generated from the soil by reacting with the H+ generated through equations 3 and 4 and driving these reactions to the right. A reaction summarizing these reactions would be:

H2CO3 (aq) + 2KOH = 2H2O + K+ + CO3-2 [5]

During the titrations with HCl the above reactions are forced in the reverse directions. The first addition of HCl to the phenolphthalein end point (clear, about pH = 9) neutralizes excess KOH and converts the carbonate to the HCO3- (bicarbonate) form. The second titration to the bromcresol green end point (bright yellow, about pH = 4.5) converts the bicarbonate (HCO3-2) to H2CO3 (aq) on a one to one mole basis (i.e. the reverse of equation 3). Thus the total amount of carbonate adsorbed by the KOH solution is determined. Therefore if the KOH is kept free of CO_2 before being set in the flask with the soil sample, any carbonate detected in the KOH solution after acidification of the sample is attributable to the sample.

References:

1. Bundy, L.G. and J.M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc. 36:273-275.

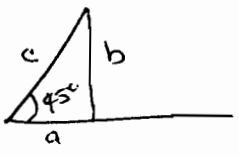
STEARNS and WHEELER CARBONATE ANALYSIS (core series #2)

Core length (Not flow Through).

Sample ID	Inorganic Carbon (mg)	Carbonate (mg. CO3-)	% CaCO3 equivalent
2-3-a 0-2" pea gravel.	3.36	16.8	5.16
2-3-a 2-4"	3.63	18.2	5.64
2-3-a	4.08	20.4	5.99
2-3-b 4-6"	1.20	6.0	2.51
2-3-b	1.26	6.3	2.08
2-3-c 6-8"	0.36	1.8	0.59
2-3-c	nd	nd	nd
2-3-d 8-10"	0.78	3.9	1.22
2-3-d	0.99	5.0	1.36
2-3-e	nd	nd	nd
2-3-e 10-12"	0.15	1.2	0.25
2-3-f	0.06	0.3	0.11
2-3-f 16-18"	0.24	1.2	0.34
2-3-g	0.06	0.3	0.08
2-3-g 20-24"	0.15	0.8	0.24
2-3-h	nd	nd	nd
2-3-h 28-32"	0.18	0.9	0.28
2-6-a 6" from front face	0.48	2.4	0.79
2-0 Virgin Material	0.18	0.9	0.26
2-0	0.06	0.3	0.09
2-3-c 6-8"	0.42	2.1	0.88
2-3-e 10-12"	1.02	5.1	1.42
2-3-h 28-32"	0.24	1.2	0.39
2-5-a 6" from	0.18	0.9	0.27
2-5-a front face	0.12	0.6	0.18
2-6-a 6" from front face	0.54	2.7	0.82
pea gravel	3.30	16.5	9.00
pea gravel	3.30	16.5	7.32

powder material only.

Core lengths must be adjusted. → flow



$a = b$

$a^2 + b^2 = c^2$

if $c = 2"$

$a = 1.4"$

most of ppt in first 3" of well

APPENDIX C

Results of Microbial Analyses

Microbial analysis, Stearns and Wheler, NY

September 3 1997

1. Sample handling:

Samples received were stored at 4°C under argon until analyzed. All subsampling was conducted in an anaerobic glovebox (N_2, 1% CO_2, 2.5% H_2 atmosphere).

2. Visual description of the samples:

The field-derived samples were moist, but not water-saturated. Samples 2-3-A and 2-3-B, and to a lesser extent 2-3-C were grey-black coloured solids, whereas the solids in other samples were black in colour.

3. Microbial enumeration:

In the anaerobic glovebox, five gram subsamples were removed from each sample bottle into 45 mL of Baars' diluent (see **section 4**). This suspension was shaken for 10 min on a rotary shaker operated at 400 rpm, then further serially diluted (5 mL into 45 mL) in Baars' diluent under anaerobic conditions. The Baars' diluent had been previously de-aerated and was under a N_2 atmosphere in bottles sealed with sterile Suba seals. Transfers from bottle to bottle were conducted by syringe. Triplicate one-mL aliquots from selected dilutions (10^{-1} to 10^{-3} inclusive) were transferred by syringe to deep tubes of molten anaerobic agar (see **section 4**), which were then mixed and allowed to solidify.

The sample dilutions were also used to spread plates of R2A agar (see **section 4**), to enumerate any culturable aerobic microorganisms present. This procedure was carried out under normal atmospheric conditions. Aliquots of 0.1 mL from selected dilution bottles (10^{-1} to 10^{-3} inclusive) were spread onto triplicate plates of R2A agar, using a flame-sterilized glass rod. After spreading, the plates were placed inside plastic bags to minimize drying of the agar.

The tubes and plates of medium were incubated at room temperature in the dark for up to 25 d. Colonies arising during the incubation period were counted, and appropriate dilution factors taken into account to determine the number of colony-forming units (CFUs) in the original sample.

3.1 Results:

The data for aerobic heterotrophs (i.e., able to grow aerobically on R2A medium) and fermentative heterotrophs (i.e., able to grow anaerobically on anaerobic agar medium) are reported in Table 1 as CFUs per gram (wet weight) of sample.

Table 1 Microbial enumerations - Stearns and Wheler site

Sample	Aerobic heterotrophs CFU/g wet wt mean (s.d.)	Fermentative heterotrophs CFU/g wet wt mean (s.d.)
2-3-A	3.3×10^4 (1.4×10^3)	2.0×10^3 est* (2.5×10^2)
2-3-B	9.6×10^3 (1.1×10^3)	1.1×10^3 (2.2×10^2)
2-3-C	5.5×10^3 (2.2×10^2)	3.4×10^2 (21)
2-3-D	2.0×10^3 est (1.6×10^2)	1.8×10^2 est (15)
2-3-E	1.1×10^3 est (4.2×10^2)	1.5×10^2 est (48)
2-3-F	5.0×10^2 est (82)	53 est (21)
2-3-G	2.7×10^2 est (1.7×10^2)	37 est (12)
2-3-H	7.5×10^3 (1.3×10^3)	2.2×10^3 (2.9×10^2)
2-5-A	5.1×10^4 (3.6×10^3)	1.3×10^3 (3.9×10^2)
2-6-A	8.7×10^2 est (1.9×10^2)	70 est (22)
2-0	33 est (47)	<3

*est: estimate - some/all plates (or tubes) with <30 colonies (supposed to be between 30 & 300 per plate for a "valid" count).
<33 on R2A: below detection (i.e., no colonies arose from least dilute sample)
<3 on anaerobic agar: below detection (i.e., no colonies arose from least dilute sample)

Most microbial species do not form highly distinctive colonies and therefore cannot be identified solely by colony type. However, there are some exceptions. *Bacillus mycoides* is one, a common soil bacterium that forms distinctive rhizoid colonies on the agar surface. This species was present in the samples from this site, growing on R2A media inoculated with 2-3-A, 2-3-B, 2-3-C, 2-3-D, 2-3-H, 2-5-A and 2-6-A materials. This does not necessarily indicate that the bacterium is active and growing in the treatment wall, however, as this species also forms endospores, dormant resistant bodies that allow survival of adverse environmental conditions. It is possible that only endospores are present in the treatment wall material samples, not vegetative cells. The endospores then germinate and grow when introduced into the growth medium in the laboratory.

Abundant gas was formed in tubes of anaerobic agar inoculated with 2-3-A, 2-3-B, 2-3-C, 2-3-D, 2-3-F, 2-3-H, and 2-5-A materials. Gases (e.g., CO_2, H_2) are products of fermentative metabolism.

4. Information on media and technique used for microbial enumeration

Baars' diluent contains 0.5 g K_2HPO_4, 1.0 g NH_4Cl, 1.0 g $CaSO_4 \cdot 2H_2O$, 2.0 g $MgSO_4 \cdot 7H_2O$ and 0.01% Na thioglycolate in 1 L, pH 7.4. It was prepared without the thioglycolate, dispensed into 120-mL dilution bottles (45 mL/bottle) and sterilized by autoclaving. The bottles were then sealed with sterile Suba seals (a type of red rubber seal), then evacuated and back-filled with sterile N_2 gas, using a vacuum pump and a gas manifold. The evacuation (2 min) and back-filling (2 min) procedure was repeated three times. About 30 min before use, Na thioglycolate was added to the individual dilution bottles from a 1% stock solution, which was filter-sterilized by passage through a sterile syringe filter (0.2 µm pore size). Thioglycolate is a chemical reducing agent and acts to both lower and poise the redox potential of the medium. With an E_0' of <-100 mV (Breznak and Costilow, 1994), it is probably insufficient to protect the most stringent anaerobes, i.e., methanogenic microorganisms. However, the intent of this analysis was to detect less stringent anaerobes, for example, fermentative bacteria such as *Clostridium* sp., and possibly sulfate-reducing bacteria, if able to grow on the anaerobic agar provided. (The recipe for Baars' diluent suggests that it is - or is derived from - a medium intended for the growth of sulfate-reducing bacteria. It is similar to Postgate's medium for sulfate reducers).

R2A agar is a low nutrient medium that was developed for enumerating bacteria in potable water samples (Reasoner and Geldreich, 1985). It contains 0.5 g yeast extract, 0.5 g proteose peptone #3, 0.5 g casamino acids, 0.5 g dextrose, 0.5 g soluble starch, 0.3 g Na pyruvate, 0.3 g K_2HPO_4, 0.05 g $MgSO_4$ and 15 g agar per L, pH 7.2, and is available commercially from Difco Laboratories (Detroit, MI). This is our "in-house" medium for enumerating culturable aerobic microorganisms from aquifer materials. It is a general purpose medium, intended to support the growth of a variety of heterotrophic microorganisms (i.e., those using organic C). However, neither this medium nor any other will allow "all" microorganisms to grow, divide and form visible colonies. There is no universal microbial growth medium. A "viable count" (i.e., the number of cells alive and capable of division) is always limited by the conditions (medium type, incubation temperature, pH, etc., etc.) provided for growth.

Anaerobic agar is a general purpose medium intended for cultivating microaerophilic and anaerobic bacteria, especially *Clostridium* sp. It would not support the growth of methanogens, but a variety of fermentative microorganisms should grow. Sulfate is not specifically supplied in the medium, but there may be enough available (e.g., from the diluent) for some sulfate reducers to grow. Anaerobic microbial communities typically contain fermentative members (see Table 2), so if there is a substantial anaerobic microbial community present on the Fe wall material, one would expect to isolate fermentative bacteria. The medium (obtained from Gibco Diagnostics, Madison, WI) contains 17.5 g peptone 140 (a pancreatic digest of casein), 2.5 g peptone 110 (a papaic digest of soy protein), 0.4 g L-cystine, 10.0 g dextrose, 2.5 g sodium chloride, 2.0 g sodium thioglycolate, 1.0 g sodium formaldehyde sulfoxylate, 0.002 g methylene blue and 15.0 g agar per 1 L, pH 7.2. The Anaerobic agar was sterilized by autoclaving, then aseptically dispensed into sterile 14 cm x 1.6 cm thick-walled test tubes (20 mL/tube) which were sealed with sterile Suba seals. The agar was maintained in a molten state in a waterbath set to 48°C. Before use, each tube was evacuated (~20 sec) and backfilled with N_2 gas (~20 sec) twice, using the gas manifold system. The methylene blue in the medium serves as a redox indicator (Eo' = 11 mV, Breznak and Costilow, 1994), and will turn the medium green if it becomes substantially oxidized. The presence of thioglycolate in the medium, filling of tube headspaces with N_2, and the use of deep, sealed tubes help achieve and maintain a low redox environment for microbial growth.

Table 2 is one example of relative numbers in an anaerobic microbial community. The community in question is an anaerobic enrichment culture able to dechlorinate PCE when fed methanol. I do not mean to imply that this is a "typical" population distribution - it probably is not, and it is also probable that no one knows what such a "typical" distribution might be, should one exist. Rather, the intent is to illustrate that such communities are complex, and that fermentative heterotrophs, i.e., those microorganisms expected to grow in the Anaerobic agar, are an integral part of such communities.

The theory of a **"viable count"** is that every microbial cell that is present and able to grow under the conditions provided will begin to grow, and divide into new, daughter cells. Bacteria typically divide by a process known as binary fission - one cell forms two daughter cells, then they each divide to give four cells, then eight, etc. If the original cell is embedded in, or affixed to, a solid medium, the initial cell (which might be 1 or 2 μm in size) will eventually give rise to a clump of biomass visible to the naked eye - a **colony** of its progeny. Therefore, every discrete colony that develops on the growth medium arises, in theory, from a single cell. In practice, we know that some types of microorganisms tend to grow in pairs, in short chains, in clumps, as well as those normally found as single cells. To waffle around this problem, viable counts are reported as **"colony-forming units" (CFUs)** rather than "cells" per mass or volume of sample.

Table 2 MPN determinations for various microbial populations in a methanol-PCE culture

Organism type	MPN /mL
H_2-CO_2-utilizing methanogens	2.3×10^4
methanol-utilizing methanogens	≤ 2.3
acetate-utilizing methanogens	≤ 2.3
H_2-CO_2-utilizing acetogens	$\leq 2.3 \times 10^4$
methanol-utilizing acetogens	9.3×10^6
H_2-utilizing thiosulfate reducers	9.3×10^5
fermentative heterotrophs	2.3×10^7
methanol-utilizing PCE dechlorinators	2.3×10^3
H_2-utilizing PCE dechlorinators	2.3×10^6

from Maymó-Gatell et al. (1995)

5. References:

Breznak, J.A. and Costilow, R.N. 1994. Physicochemical factors in growth. **In** Gerhardt, P., Murray, R.G.E., Wood, W.A. and Krieg, N.R. (eds), Methods for General and Molecular Bacteriology. American Society for Microbiology, Washington, D.C. pp. 137-154.

Maymó-Gatell, X., Tandoi, V., Gossett, J.M. and Zinder, S.H. 1995. Characterization of an H_2-utilizing enrichment culture that reductively dechlorinates tetrachloroethene to vinyl chloride and ethene in the absence of methanogenesis and acetogenesis. Appl. Environ. Microbiol. **61**:3928-3933.

Reasoner, D.J. and Geldreich, E.E. 1985. A new medium for the enumeration and subculture of bacteria from potable water. Appl. Environ. Microbiol. **49**:1-7.

Barbara J. Butler, PhD
Research Associate &
Adjunct Assistant Professor
Department of Biology
University of Waterloo
Waterloo, Ontario

Microbial Insights. Inc.

Project Name University of Waterloo
Date Received 8/25/97

Extraction Date	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97	7/15/97
Sample Number	1-0	2-0	2-3-A	2-3-B	2-3-C	2-3-E	2-3-6	1-2	1-4	Blank
Method:	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric	Colorimetric
Sample Weight (g)	25	25	25	25	25	25	25	25	25	25
MI Identifier	3loo1	3loo2	3loo3	3loo4	3loo5	3loo6	3loo7	3loo8	3loo9	3loo10
pmols Lipid Phosphate/sample	1,478	12,888	16,863	6,303	5,433	9,151	2,467	22,202	12,493	ND

Data Summary Sheet

Biomass:

Colorimetric method

Lipid Biomass/gram	59	516	675	252	217	366	99	888	500	NC
Conversion factor Lipid:PLF	0.166	0.166	0.166	0.166	0.166	0.166	0.166	0.166	0.166	0.166
Equivalent PLFA/gram	9.8	85.7	112.1	41.9	36.1	60.8	16.4	147.6	83.1	NC
Equivalent Cells/gram	1.97E+05	1.71E+06	2.24E+06	8.38E+05	7.23E+05	1.22E+06	3.28E+05	2.95E+06	1.66E+06	NC

Raw data

Adsorbance	0.12	0.7	0.901	0.367	0.323	0.511	0.173	1.171	0.68	0.042

APPENDIX D

General Electric CR&D Results

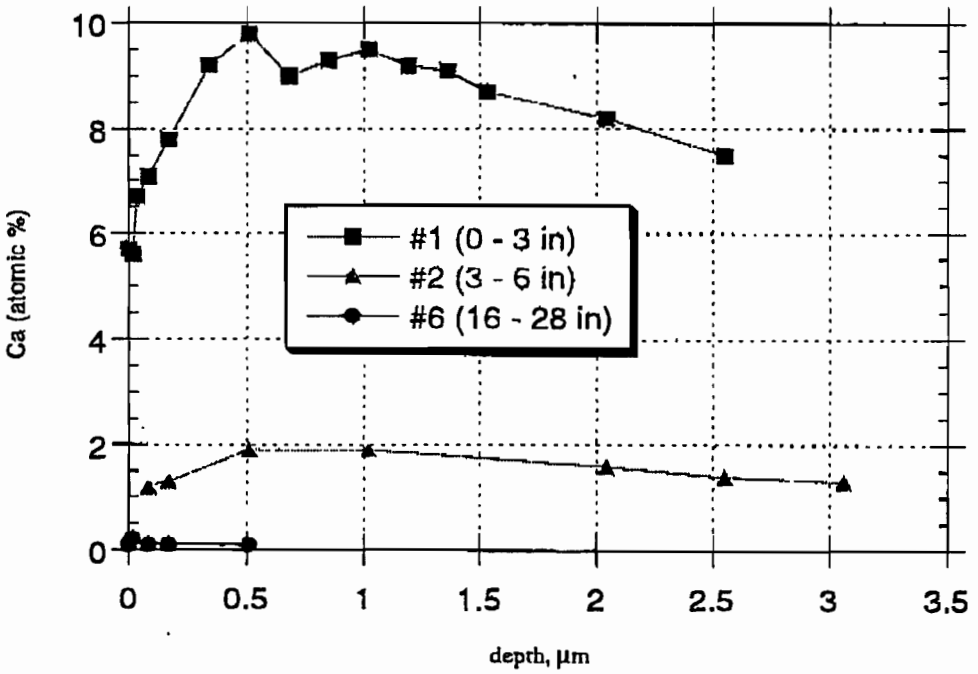
ANALYSIS OF GRANULAR IRON CORES FROM FIELD PILOT WALLS

Timothy M. Sivavec
General Electric Corporate Research and Development Center
Schenectady, NY 12301

Abstract: The use of iron walls to control groundwaters contaminated with chlorinated solvents and reducible metals is a very promising technology for many remediation sites, but there is still much uncertainty in predicting long-term performance. This is due mainly to uncertainty in predicting extent of mineral precipitation in field installations. In this work,corings taken from several field installations that have been in use over one year are analyzed by a variety of surface analytical techniques, including: scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and wavelength dispersive spectroscopy (WDS). These results are correlated to the aqueous inorganic profiles to determine the nature of the mineral precipitates that form under given field conditions. These results are compared with similar analyses performed on samples from laboratory and pilot columns. These studies have shown that in low hardness waters $FeCO_3$ is the main precipitate on the iron surfaces, while in high hardness waters $CaCO_3$ also forms. Laboratory and field data both show that the precipitation is greatest early in the treatment zone and that an equilibrium is reached further into the treatment zone, after which only minimal precipitation occurs.

Post-it® Fax Note 7671	Date 10/2/97	# of pages ▶
To John Vogan	From T. Sivavec	
Co./Dept. ETI	Co. GE CRD	
Phone #	Phone #	
Fax # (519) 763-2378	Fax #	

XPS Depth Profile of Granular Iron from a Sherburne, NY Coring



Tim Sivavec
97093 7/16/97

Iron Filings, Sherburne Core Samples
Surface Composition (atomic %)

Sherburne #1

	C	O	Fe	Si	Ca	Al	Mg	N	Fe/O
as rec'd	14.5	53.9	23.7	2.7	4.1	0.4	0.7	0.5	*0.44*
0.5 min. sputter (85Å)	3.6	51.2	34.5	2.3	5.7	1.3	1.4	X	*0.67*
1.0 min. sputter (170Å)	3.7	49.7	35.1	2.7	5.6	0.9	2.2	X	*0.71*
2.0 min. sputter (340Å)	2.6	48.6	36.1	3.0	6.7	1.4	0.6	X	*0.74*
5.0 min. sputter (850Å)	3.4	46.6	37.0	2.9	7.1	1.5	1.6	X	*0.79*
10 min. sputter (1700Å)	2.3	46.7	36.5	2.5	7.8	2.2	1.2	X	*0.78*
20 min. sputter (3400Å)	1.7	47.6	36.8	2.2	9.2	1.7	0.8	X	*0.77*
30 min. sputter (5100Å)	2.2	47.2	36.8	1.7	9.8	1.2	1.1	X	*0.78*
40 min. sputter (6800Å)	2.1	46.6	38.8	2.3	9.0	0.6	0.6	X	*0.83*
50 min. sputter (8500Å)	2.4	45.6	39.4	1.5	9.3	0.9	0.9	X	*0.86*
60 min. sputter (10200Å)	1.7	46.9	39.0	1.4	9.5	1.0	0.7	X	*0.83*
70 min. sputter (11900Å)	1.6	46.2	39.9	1.4	9.2	0.4	1.3	X	*0.86*
80 min. sputter (13600Å)	1.9	46.2	40.2	1.4	9.1	0.5	0.9	X	*0.87*
90 min. sputter (15300Å)	2.5	44.8	41.5	1.6	8.7	X	0.9	X	*0.93*
120 min. sputter (20400Å)	2.7	43.8	42.9	1.6	8.2	X	0.9	X	*0.98*
150 min. sputter (25500Å)	1.6	43.5	45.9	1.5	7.5	X	X	X	*1.06*

Tim Sivavec
97093 7/16/97

Iron Filings, Sherburne Core Samples
Surface Composition (atomic %)

Sherburne #2

	C	O	Fe	Ca	Si	Al	Mn	Mg	Fe/O
as rec'd	21.3	49.5	23.3	0.9	2.1	0.9	X	1.0	*0.47*
0.5 min. sputter (85Å)	5.5	45.8	41.6	1.2	2.4	2.4	X	1.1	*0.91*
1.0 min. sputter (170Å)	3.7	44.2	44.8	1.3	2.2	2.9	0.2	1.3	*1.01*
5.0 min. sputter (850Å)	1.2	43.2	47.1	1.5	2.1	4.7	0.1	< 1.0	*1.09*
10 min. sputter (1700Å)	1.1	43.4	47.5	1.8	2.2	2.7	0.4	< 1.0	*1.09*
30 min. sputter (5100Å)	0.8	43.4	49.5	1.9	1.7	2.5	0.3	< 1.0	*1.14*
60 min. sputter (10200Å)	0.8	42.0	51.4	1.9	1.3	2.3	0.1	<1.0	*1.22*
90 min. sputter (15300Å)	0.7	41.6	54.4	1.9	1.3	X	0.1	<1.0	*1.31*
120 min. sputter (20400Å)	0.7	39.9	55.7	1.6	0.8	0.9	0.4	<1.0	*1.40*
150 min. sputter (25500Å)	0.6	39.2	57.6	1.4	0.9	X	0.2	<1.0	*1.47*
180 mim. sputter (30600Å)	1.0	37.9	58.3	1.3	1.4	X	0.2	<1.0	*1.54*

trace levels (< 0.2) of potassium can be detected at the surface
magnesium is detected at about the 1%

Tim Sivavec
97093 7/16/97

Iron Filings, Sherburne Core Samples
Surface Composition (atomic %)

Sherburne #6

	C	O	Fe	Si	Ca	Al	Mn	N	Fe/O
as rec'd	36.1	38.3	19.3	4.4	0.3	1.2	X	0.3	*0.5*
0.5 min. sputter (85Å)	17.7	34.1	43.4	3.3	0.1	0.8	0.5	X	*1.28*
1.0 min. sputter (170Å)	15.8	32.0	48.4	2.0	0.2	1.0	0.7	X	*1.51*
5.0 min. sputter (850Å)	12.6	30.1	53.6	1.9	0.1	0.8	0.8	X	*1.78*
10 min. sputter (1700Å)	9.4	30.1	57.6	1.7	0.1	0.3	0.7	X	*1.91*
30 min. sputter (5100Å)	6.7	27.0	64.4	2.0	0.1	X	0.7	X	*2.39*
60 min. sputter (10200Å)	7.3	25.4	65.7	0.8	X	X	0.7	0.1	*2.59*
90 min. sputter (15300Å)	6.3	24.4	67.1	1.3	X	X	0.7	0.3	*2.7*