THE ASSOCIATION OF EXPLORATION GEOCHEMISTS

Exploration Geochemistry into the 21st Century
VANCOUVER
1999

GEOANALYSIS
With Emphasis on Selective Extractions

Presented by:

Joe Brenner	Varian and Ben Gurion University
Gwendy Hall	Geological Survey of Canada
Russell Birrell and Alan Mann	MMI Technology, Wamtech
Robert Clark and Eric Hoffman	Activation Laboratories
David Gray	CRC LEME, CSIRO
Brenda Caughlin	Chemex Laboratories
Dave Seneshen	WMC Exploration Inc
David Cohen	University of New South Wales
Stewart Hamilton	Ontario Geological Survey
Jan van Moort	University of Tasmania
David Garnett	Becquerel Laboratories

A Short Course presented during the 19th International Geochemical Exploration Symposium
April 10, 1999
Hotel Vancouver, Vancouver, British Columbia, Canada

Sponsored by the Association of Exploration Geochemists

Workshop Timetable

WELCOME 8.30 - 8.40

Joe Brenner 8.40 - 9.10
New instrumental developments for geoanalysis using ICP-AES

Gwendy Hall 9.10 - 9.55
Review of analytical considerations with respect to selective leaches

Russell Birrell and Alan Mann 9.55 - 10.40
Mobile Metal Ions in the A horizons of soils

TEA/COFFEE BREAK 10.40 - 11.00

Robert Clark and Eric Hoffman 11.00 - 11.45
Concepts and models for interpretation of enzyme leach data for mineral and petroleum exploration

David J. Gray, J.E. Wildman and G.D. Longman 11.45 - 12.30
Selective and partial extraction analyses of transported overburden for exploration

Brenda Caughlin 12.30 - 13.00
Selective leaches – laboratory analysis

LUNCH 13.00 - 14.00

Dave Seneshen 14.00 - 14.30
Sources of variability associated with the use of partial extractions

David R. Cohen, N.F. Rutherford, X.C. Shen and A.C. Dunlop 14.30 - 15.00
Some comments on the use of selective extractions in geochemical exploration in arid terrains

Stew Hamilton 15.00 - 15.30
Transport mechanisms responsible for selective leach anomalies

TEA/COFFEE BREAK 15.30 - 16.00

Jan van Moort 16.00 - 16.30
Quartz and the acid insoluble residue of rocks and regolith as a sample medium in mineral exploration

David Garnett 16.30 - 16.50
Who needs total analyses?

DISCUSSION 16.50 - 17.30

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Joe Brenner

New instrumental developments for geoanalysis using ICP-AES

CURRENT STATUS OF PLASMA-BASED SPECTROMETRY USING ICP-AES AND MS

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ADVANTAGES OF THE ICP-AES

- *HIGH TEMPERATURE OF THE INERT Ar DISCHARGE*
- *EFFICIENT ATOMIZATION OF SAMPLE AEROSOLS*
- *EXTENDED LINEARITY OF SIGNAL-CONCENTRATION FUNCTIONS*
- *MINIMUM MATRIX EFFECT*

ICP as an Ion Source for ICP-MS

- *Source and sample introduction at atmospheric pressure*
- *Most elements 90 % ionized at 6000-8000 °C except As 52 %, Se 33 %, S 14 %, F $9x10^{-4}$ %*
- *Singly charged M^+ predominate (> 90 %)*
- *Small M^{++} populations - worst case Ba^{++} 1 - 2 % of Ba^+*
- *Bulk plasma is 99.9 % Ar^+*
- *Ion energies 2 - 10 eV - optimum QMS*

ADVANCES IN SAMPLE PREPARATION

PARTIAL DECOMPOSITION FOR GEO-ENVIRONMENTAL STUDIES

- *Church procedure (Church et al., J. Geochem. Explor. 29, 207, 1987.*
- *Oxalic acid > secondary minerals*
- *Aqua regia > primary sulfides*
- *"Speciation" of elements in the solid phase*
- *Labile (mobile) elements in geochemical exploration*
- *Rapid, automated, inexpensive*
- *Low dissolved salt content*
- *Problem of PURE reagent blanks*

SEQUENTIAL EXTRACTION

- *Exchangeable - 1M $MgCl_2$, pH 7, 1 h 25°C, continuous agitation*
- *Carbonate - 1 M Na Acetate, pH 5, 5 h, 25 °C, continuous agitation*
- *Fe-Mn oxides - 0.04 M $NH_2OH.HCl$ in 25 % v/v acetic acid, 6 h, 96°C, occasional agitation*
- *Organic fraction - 0 .02 M HNO_3 and 30 % H_2O_2, pH 2, 2 h, 85°C. 3.2 M NH_4 acetate in 20 % (v/v) HNO_3 diluted 20 ml*
- *Residual and total metals - $HF-HClO_4$*
- *A. Tessier, P.G.C. Cambell, and M. Bisson, Anal Chem., 51, 844, 1979*

ADVANCES IN SAMPLE INTRODUCTION

Sample intro - challenges in ICP-MS

- ○ ***Analysis of high salt solutions***
- ○ ***Analysis of small volumes - FIA, MCN, ETV***
- ○ ***Analysis of volatile organics -membranes, DIN***
- ○ ***Enhanced aerosol generation - USN***
- ○ ***Preconcentration and matrix elimination***
- ○ ***On-line sample decomposition and handling***
- ○ ***Automation***
- ○ ***Speciation - HPLC, GC, CE***
- ○ ***Direct solids analysis - slurries and slurry ETV and laser ablation***
- ○ ***Desolvation - minimum plasma loading***
  - ***USN, ETV, Laser, low consumption nebulizers***

ADVANCES IN SAMPLE INTRODUCTION

- ○ ***LOW CONSUMPTION NEBULIZERS FOR HIGH EFFICIENCY TRANSPORT AND REDUCED LOADING IN PLASMA***
- ○ ***DESOLVATION OF AEROSOLS FOR REDUCED WATER LOADING AND POLYATOMIC INTERFERENCES***
- ○ ***MEMBRANES FOR REMOVAL OF VOLATILE ORGANIC SOLVENTS***
- ○ ***DIRECT SAMPLE INSERTION FOR REDUCED MEMORY EFFECTS***
- ○ ***ELECTROTHERMAL VAPORIZATION FOR SMALL VOLUME SAMPLES AND PARTICLE ANALYSIS***

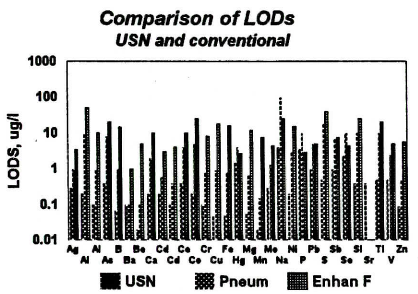
ADVANCED SAMPLE INTRODUCTION

ULTRASONIC NEBULIZATION

- ☺***High frequency crystal transducer - fine aerosol formed by ultrasonic waves.***
- ☺***Solution is fed to the surface of piezoelectric transducer. Aerosol formed by the geyser effect.***
- ☺***Desolvation reduces liquid load***
- ☺***Increased efficiency to about 20 %***
- ☺***Enhances LOD by approximately 5-20***

USN - ANALYTICAL CONSIDERATIONS

- ☺ ***Due to high sensitivity, less sensitive spectral lines and M/z can be employed***
- ☹ ***LOD degradation in the presence of high salt (> 0.5 %)***
- ☹ ***Volatile species (B, As, Ge, Os) are lost in the desolvation process***
- ☹ ***Interferences in transport system and in plasma (enhancement and depression - spectral lines behave differently according to EP and IP***
- ☹ ***Problems of calibration - matrix match***
- ☹ ***High price***



ADVANCES IN PLASMA

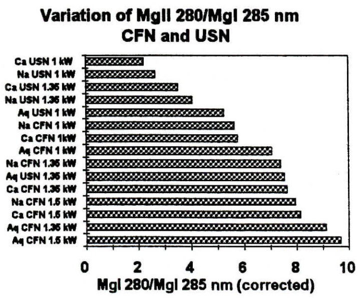
- ❍ *Better RF generators - efficent transfer of energy from coil to plasma column - robust ICPs*
- ❍ *Use of Mg II/MgI ratios and M^{++}/M^{+}*
- ❍ *Axial viewing of robust ICPs*

ASPECTS OF EXCITATION

- ❍ *Robust plasma Mg II 280/ Mg I 285 > 8. Lower values indicate matrix interferences*
- ❍ *Wide central injector - avoiding clogging, enhancing residence time (Mermet).*
- ❍ *Mixed gases*
- ❍ *Oxygen - pyrolysis of organic matrices*
- ❍ *Hydrogen and nitrogen - higher plasma temperature and thermal conductivity*

Mg II 280.270/MgI 285.213 nm

- ❍ *Convenient criterion for excitation, atomization, ionization, solute interferences, transport*
- ❍ *Ratio is related to:*
  - ❍ *Excitation temperature via Saha equation*
  - ❍ *Residence time*
  - ❍ *Energy transfer*



PLASMA CONFIGURATION

ICP-AES

Enhancing limits of detection

LODs of ICP-AES insufficent for analysis of environmental materials

- ○ ***Increasing efficiency of aerosol generation USN and desolvation, thermospray***
- ○ ***Preconcentration - Chelating resins, solvent extraction***
- ○ ***Reduce noise level in generator, detector - signal filtering, reduce background***
- ○ ***Mixed gas ICPs - hydrogen, nitrogen***
- ○ ***Plasma configuration - axial viewing, pinch plasma***

ICP-AES - AXIAL VIEWING

- ○ ***Horizontal - conventional***
- ○ ***Axial - up to 10-fold increase in LODs - CLOSING THE GAP WITH ICP-MS***
- ○ ***Axial - presence of EIE effects***
- ○ ***Shear gas - removal of the cold fringe***
- ○ ***Reduced dynamic range***
- ○ ***The detection gap between ICP-AES and MS decreases for some elements***

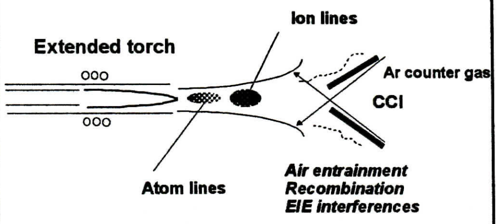
Axial viewing systems

- ○ ***ARL - Maxima - not commercially available***
- ○ ***JY-ISA - Panorama, Ultima***
- ○ ***Leeman - PS 1000 AT***
- ○ ***PE - Optima 3000 XL, DV, SC***
- ○ ***Spectro - EOP (low UV < 150 nm)***
- ○ ***TJA - 61E, Trace scan, Atomscan 25, Iris***
- ○ ***Varian - Series II, Vista CCD***

Current status of axial plasmas

- ○ ***5-20 improvement in LODs***
- ○ ***Reduced dynamic range***
- ○ ***Increased EIE interferences***
- ○ ***Two approaches to minimize interferences:***
- ○ ***Shear gas (air, nitrogen) directed at 90 degrees to the plasma axis to remove perturbed plasma tail***
- ○ ***End-on argon gas to symmetrically peel away cool plasma fringe***

Schematic structure of plasma for axial viewing

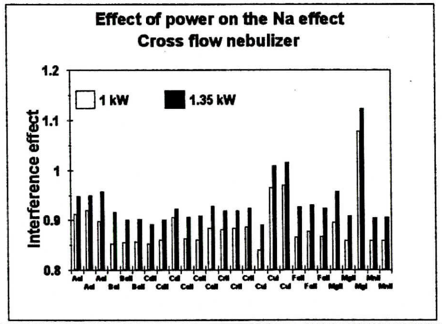


Limits of detection, ng/ml. Axial plasma and comparisons

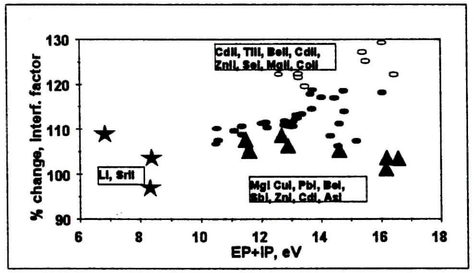
Element	Wave, nm	RP	RP+USN	AP	AP+USN
Al	I 396.152	5	0.5	1	0.15
As	I 193.759	10	10	4	1
Be	II 234.861	0.15	0.01	0.05	0.005
Cd	II 226.502	2	0.3	0.3	0.05
Co	II 238.892	4	0.2	0.15	0.05
Cr	II 267.716	4	0.2	0.2	0.03
Mo	II 202.030	4	0.2	0.6	0.04
Ni	II 231.604	5	0.5	0.75	0.06
Pb	II220.353	12	1.5	1.5	0.2
Se	II 196.090	30	4	3	0.8
V	II 292.402	2	0.3	0.8	0.05

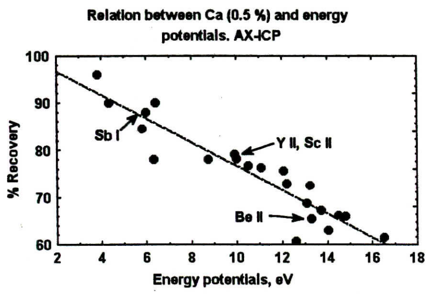
Matrix effects in axial ICPs

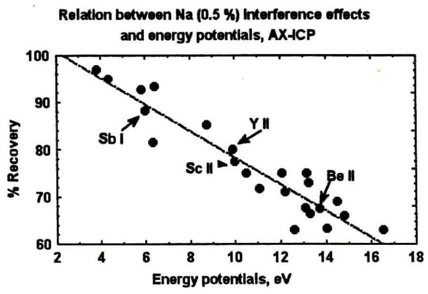
- ○ *Depends on generator robustness*
- ○ *Concentrations of EIEs, Ca and acids*
- ○ *Mode of cold plasma fringe removal*
- ○ *Evidently the "depth" of focus*
- ○ *Energy potentials of spectral lines - the higher the energy the higher intensity depression*
- ○ *Plasma loading amount of aerosol*

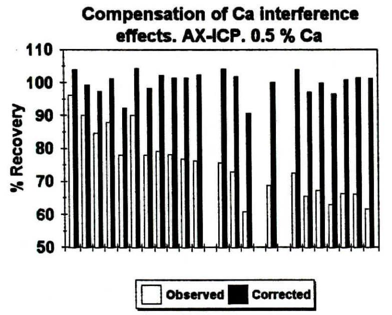

Effect of power on the Na effect
Cross flow nebulizer

Effect of the change of RF power, Axial ICP, Optima 3000 XL




Relation between Ca (0.5 %) and energy potentials. AX-ICP


Relation between Na (0.5 %) interference effects and energy potentials, AX-ICP


Compensation of Ca interference effects. AX-ICP. 0.5 % Ca

ICP-AES INSTRUMENTATION

THE IDEAL AES SPECTROMETER

- ○ *Spectral range from 150-800 nm and even less*
- ○ *Purge for low UV range*
- ○ *High sensitivity across the spectral range*
- ○ *High precision for major elements - enhanced detection for trace elements*
- ○ *High resolution 160-450 nm range (< 8 pm)*
- ○ *Simultaneous real time background correction*
- ○ *Transient signal acquisition for DC arc, ETV, FIA and laser analysis*

CONVENTIONAL AES SPECTROMETERS DISADVANTAGES

- ○ *SEQUENTIAL*
  - *Low sample throughput*
  - *High solution consumption*
- ○ *POLYCHROMATORS*
  - *Inflexible spectral selection*
  - *High cost*
- ○ *POLYSCANS and SIM-SEQ*
  - *High price for flexibility*

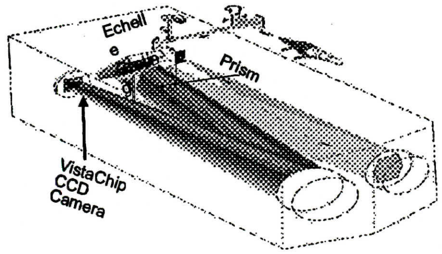
ICP-AES SPECTROMETERS NEW GENERATION ECHELLE BASED CTDS

- ○ *CTDs - ability to monitor a vast amount of spectral information*
- ○ *Echelles - high dispersion in a compact configuration*

Vista CCD Simultaneous ICP Spectrometer

- ○ *Echelle 0.4 m spectrometer, thermostatted to 35°C*
- ○ *94.74 lines/mm grating used in 19 to 88 orders*
- ○ *7-9 pm resolution in UV*
- ○ *CaF_2 prism cross-disperser for order sorting*
- ○ *Ar or N_2 purge allows low UV detection (167 nm)*
- ○ *Axial viewing with end-on gas*

Vista CCD Simultaneous ICP Schematic



Vista CCD
Axially viewed ICP

- ❍ *40 MHz free running air-cooled generator*
- ❍ *DISC - Direct Serial Coupling System*
  - ❍ *> 75% coupling efficiency*
- ❍ *Power output stability - better than +/- 0.1 %*
- ❍ *Produces robust ICP (MgII / MgI = 12)*
- ❍ *Capable of atomizing high salt loads, 5 % NaCl*

DETECTOR and SIGNAL PROCESSING

- ❍ *I-MAP technology*
- ❍ *Anti-blooming on each pixel*
- ❍ *70,000 uninterrupted pixels that match the echelle image*
- ❍ *Full range from 176-785 nm*
- ❍ *High speed signal processing due to dual read out circuitry - 2 elements/s - NO SEQUENTIAL PROCESSING*
- ❍ *AIT (Adaptive Integration Technology) simultaneous processing of very high and low signals based on optimum SBRs*

Background and spectral corrections

- ❍ *Background Correction*
  - ❍ *1 or 2 points - free selection*
  - ❍ *Automatic Fitted Gaussian*
- ❍ *FACT (Fast Automated Curve-fitting Technique) Spectral line interference corrections using on-line deconvolution for resolution of complex spectra - up to 3 models can be constructed*

Comparison of VISTA AX LODs with Radial plasma and EPA USN data,

3 σ, µg/L

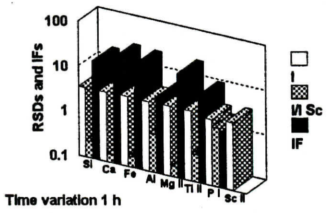
200.15	Rad Liberty	Ax	Ax Vista	EPA USN
Ag 328.068	2	0.7	0.5	0.3
As 188.980	12	5	3	
B 249.773	1	0.4	0.07	2
Ba 455.403	0.06	0.01	0.04	0.2
Be 234.861	0.15	0.05	0.05	0.05
Bi 223.061	9	0.8	3	
Cd 228.802	1.2	0.3	0.3	0.2
Co 238.892	4	0.25	0.5	0.4
Cr 267.716	3	0.2	0.5	0.9
Cu 324.754	2	0.6	0.3	0.3
Fe 259.940	1	0.2	0.4	0.3

Comparison of VISTA AX LODs with Radial plasma and EPA USN data,

3 σ, µg/L

215	Rad Liberty	Ax	Ax Vista	EPA USN
Mn 257.610	0.2	0.06	0.05	0.2
Mo 202.032	4	0.6	0.8	1
Ni 231.604	5	0.6	1.3	0.8
Pb 220.353	10	1.5	2	2
Sb 217.582	14	2.5	2	1
Se 196.026	30	3	5	8
Sr 407.771	0.03	0.01	0.01	0.1
Tl 190.790	12	3	5	5
V 292.401	2	0.8	0.4	0.6
Zn 213.857	1	0.4	0.3	0.4

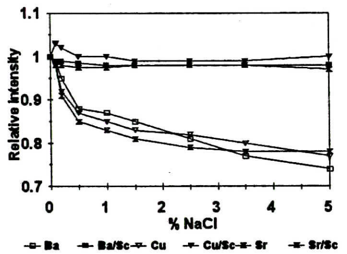
Role of Sc II internal standard in precision. IF : Improvement factor



Time variation 1 h

Myers, S.A., and Tracy, D.H., Spectrochim. Acta, 38B, 1227, 1983
Schmidt, G.J., and Slavin, W. Anal. Chem., 54, 2493, 1982
Brenner, I.B., Watson, A.E., Russell, G.M., and Goncalves, M., Chem. Geol., 28, 321, 1980

Role of Sc II as internal standard



○ICP-MS

CURRENT STATUS OF ICP-MS

- ○*Trace element determinations*
- ○*Environmental and geoanalysis*
- ○*Clinical analysis*
- ○*Semiconductors*
- ○*Nuclear*

ICP-QMS Instrumentation

- ○ *Chicane lens for low background < 1 cps*
- ○ *Single lens on the fly*
- ○ *S option enhanced sensitivity*
- ○ *Collision cells*
- ○ *Simultaneous dual detector*
- ○ *Plasma screen and shield*

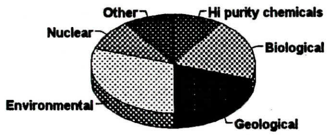
Historical Perspectives

- ○ *1975: Atmospheric plasma sampled into MS with capillary DC arc [Gray at ARL]*
- ○ *1978: ICP as ion source with QMS [Houk at Ames, Iowa]*
- ○ *1981: Practical plasma/MS interface [Douglas -SCIEX and French - Univ. of Toronto]. Date and Gray at VG and BGS in UK*
- ○ *1982: Introduction of ELAN 250 and VG Plasmaquad*
- ○ *1985: ICP-MS established for routine analysis*
- ○ *1990: VGE HiRes and multiple collector*
- ○ *1990: TOF ICP-MS (Hieftje, Bloomington)*
- ○ *1995: Double quad (Houk at Ames Iowa)*
- ○ *1996: Enhanced interface, VG*
- ○ *1996: Ion trap - Kopenaal at PNL and Finnigan*
- ○ *1997: Collision chamber, HEXAPOLE - Micromass, PE-Sciex, VGE*
- ○ *1998 - Time of flight - Leco and GBC*

ADVANTAGES OF ICP-MS

- ○ ***Multielement capability with LODs in the ppt range. Environmentally important elements can be determined with out preconcentration***
- ○ ***Determination of the REEs, HFSE, PGMs - important geological indicators***
- ○ ***Analysis of saline solutions (20 % salt) by dilution - fusion solutions, biological fluids, industrial wastes***
- ○ ***Wide dynamic range - 8 orders with dual detector***
- ○ ***Rapid isotope ratio determinations 0.1-0.5 %***
- ○ ***Isotope dilution - accurate determinations***
- ○ ***Advanced techniques of sample introduction***

Distibution of ICP-MS instruments as a function of applications



DISADVANTAGES OF ICP-MS

○ *Maximum salt content - 0.1-0.2 % using conventional nebulization. Higher with flow injection*
○ *Mass overlap with polyatomic ions in LR quads*
○ *Matrix induced signal depression*
○ *Ionization interferences*
○ *Degraded RSDs relative to TIMS*
○ *Space charge effects and mass discrimination*

1998 ICP-MS highlights

○ *VGE*	*Axiom MC*
○ *GBC*	*Optimass TOF*
○ *Leco*	*Renaissance TOF*
○ *Micromass*	*Platform ICP, hexapole*
○ *TJA electronics*	*Poems 3, impoved PQ3 quad with TJA*
○ *PE*	*Collision cell*
○ *PE*	*Ultrawave OLP*
○ *Cetac*	*LSX 200 and 300*
○ *Merchantek*	*UV laser*
○ *HP*	*4500 plus - improved support*

Liquid handling techniques in ICP-MS

● *Micro injection and low flow nebulizers*
● *FIA for high salt nebulization*
● *On-line dilution*
● *On-line addition of reagents and ISs*
● *Hydride generation and cold-vapor*
● *Matrix separation and preconcentration*
● *On-line digestion*
● *In-line reactions*

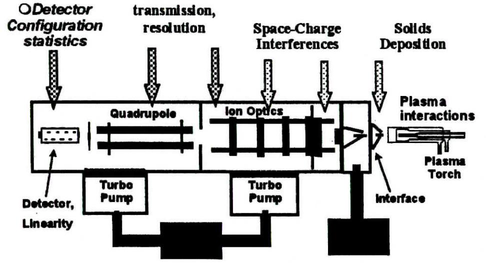
SAMPLE INTRODUCTION CHALLENGES IN ICP-MS

○ *Analysis of high salt solutions*
○ *Analysis of small volumes - FIA, MCN, ETV*
○ *Analysis of volatile organics -membranes, DIN*
○ *Enhanced aerosol generation - USN*
○ *Low consumption nebulizers*
○ *Preconcentration and matrix elimination*
○ *On-line sample decomposition and handling*
○ *Automation*
○ *Speciation - HPLC*
○ *Solids analysis - slurries*
○ *Laser ablation*

LIQUID HANDLING TECHNIQUES IN ICP-MS

● *Micro injection and low flow nebulizers*
● *On-line dilution*
● *On-line addition of reagents*
● *Hydride generation and cold-vapor*
● *Matrix separation and analyte preconcentration*
● *Speciation*
● *On-line digestion*
● *In-line reactions*

ICP-QMS Sources of interference and error



Inteferences in ICP-MS

- ○ *Spectral*
  - ○ *Isobaric - overlap*
  - ○ *polyatomic - reagents, plasma and entrained gases*
- ○ *Nonspectroscopic*
  - ○ *Ionization, EIEs - shift in plasma equilibrium - signal supression and enhancements (low m/z)*
  - ○ *Plasma conditions*
  - ○ *Space charge effects*
  - ○ *Deposition on interface - condensation on cold surface, restriction, resampling, memory*
- ○ *Mass discrimination*
- ○ *Sample transport*
  - ○ *Change of sample viscosity*
  - ○ *Memory effects*

MATRIX, SOLVENT AND PLASMA GAS INDUCED IONS

- ○ ***Ions derived from plasma gases and their interaction with sample sample preparation elements***
- ○ ***Molecular ions due to ion-molecule reactions, recombination-clustering***

ICP-MS SPECTRAL INTERFERENCES

POLYATOMIC IONS

^{51}V - ^{35}Cl^{16}O
^{52}Cr- ^{52}ArC
^{53}Cr-^{37}ClO
^{63}Cu-^{47}TiO
^{71}Ge- ^{40}Ar^{31}P
^{75}As-^{40}Ar^{35}Cl
^{80}Se -^{40}Ar$_2$
^{152}Gd- ^{136}Ba^{16}O
^{158}Gd -^{146}Ce^{16}O
^{107}Ag, ^{113}Cd -ZrO

ISOBARIC

^{40}Ar - ^{40}K
^{114}Cd -^{114}Sn

DOUBLY CHARGED IONS

^{38}Ba^{++} - ^{69}Ga^{+}

Oxide and doubly charged Ions

- ○ ***Effected by ICP operating conditions and sample introduction***
- ○ ***Minimized by desolvation and dry plasmas. Expressed as %CeO+/Ce+***
- ○ ***Oxide ions appear at M + 16 amu. 40Ar16O (56Fe), 137BaO+ (153Eu+)***
- ○ ***Doubly charged ions appear at M+/2 e.g., 138Ba+ at 69 amu (69Ga)***

PROCEDURES FOR SOLVING INTERFERENCE EFFECTS IN ICP-MS

- ○ ***<u>O, H and Cl species</u>***
- ○ ***Nitrogen in plasma or aerosol carrier gas***
- ○ ***Avoid the use of HCl and HClO$_4$***
- ○ ***Cold plasma - Plasma screen, shielded torch***
- ○ ***Cooled spray chamber***
- ○ ***Cryogenic and membrane desolvation***
- ○ ***High resolution mass spectrometer***

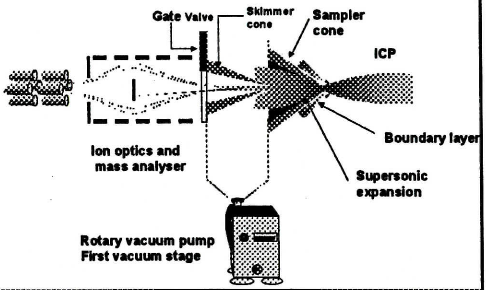
Recent instrumental developments

- ○ *S option - enhanced sensitivity*
- ○ *Collision cells- reduced polyatomic*
- ○ *Simultaneous dual detector - extended linearity*
- ○ *Advanced sample introduction devices FIA, on-line processing, membrane desolvation*
- ○ *ETV*
- ○ *UV - Laser ablation*
- ○ *Multiple collectors*

Collision Cells, multipole ion guides

- ○ *1989 Houk - buffer gas*
- ○ *1994 Kopenaal, Ion Traps, H2*
- ○ *1997 Micromass hexapole, off set collision cell, He,H2*
- ○ *1998 PE-Sciex DRC reaction cell*
- ○ *1999 VGE - PQXCELL*

ICP-MS Interface



MULTICOLLECTOR ICP-MS - history

- ○ *Problem with TIMS, thermodynamic and kinetic fractionation*
- ○ *Mass bias*
- ○ *Low sample throughput*

Reduction of ArO+ polyatomic interferences and Ar+

- ○ *Enable Ca to be determined at m/z 40*
- ○ *Supress 40Ar+ by 9 orders of magnitude (eg. 40Ca+, 80Se+)*
- ○ *Reduce ArO+ to determine Fe using 56Fe+*
- ○ *Reduce REE-O+*
- ○ *<u>Aerosol desolvation</u>*
- ○ *<u>High resolution MS</u>*
- ○ *<u>Collision Cells</u>*

Gases used -

- ○ *NH3 - charge and proton tranfer reactions*
  ArO+ +NH3 -> O + Ar + NH3+
  ArH+ + NH3 -> NH4+ +Ar
- ○ *H2 -chemical reaction*
- ○ *He thermalize to increase collisions*

High Resolution ICP-MS

- ○ *Finnigan Element 2*
- ○ *VGE Axiom*
- ○ *Sensitivity 107-109 - reduced at high resolution*
- ○ *Background 0.1 cps*
- ○ *Linear dynamic range 109 with pulse and analog counting*
- ○ *Matrix effects - similar to quads*
- ○ *Precision for ratio determination 0.04-0.1 %*

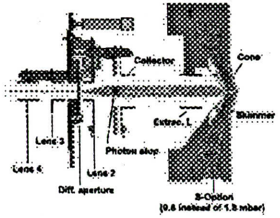
OVERCOMING EFFECTS OF SOLVENT LOAD

- ○ *Ultrasonic nebulization - not universally applicable to all solvents*
- ○ *Low flow - low consumption*
- ○ *Cooled spray chamber*
- ○ *Cryogenic desolvation*
- ○ *Solvent decomposition - tedious*
- ○ *Oxygen bleeding*

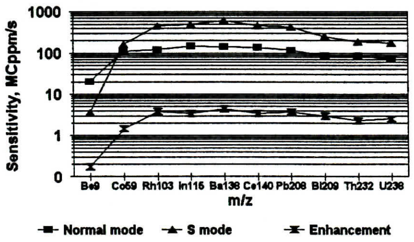
Enhancing LODs in ICP-MS

- ○ ***Matrix rejection- analyte preconcentration***
- ○ ***USN-Desolvation***
- ○ ***High ion transmission interface***

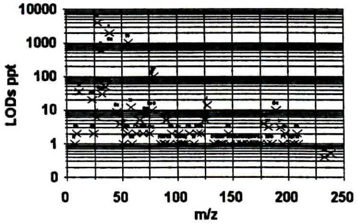
The enhanced ion transmission interface (S option) in the VGE PlasmaQuad 3

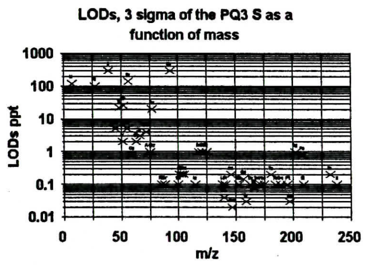


Sensitivity comparisons, VGE PQ3 Normal and S modes



LODs, 3 sigma of the PQ3 as a function of mass



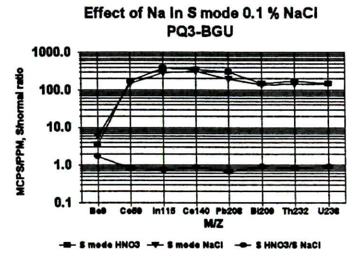

LODs, 3 sigma of the PQ3 S as a function of mass

Current applications of S mode

- ○ *Microanalysis of minerals and inclusions using UV Laser ablation*
- ○ *Determination of actinides in very low salt solutions*
- ○ *Has not been characterized for Geo and Environmental Analysis*

Multicollector ICP-MS

- ○ *Accurate and precise isotope ratio determinations 0.001 %*
- ○ *86Sr/87Sr*
- ○ *204Pb/208/206Pb*
- ○ *11B/10B*
- ○ *Lu/Hf*
- ○ *Nd/Sm*
- ○ *Th/U*


Effect of Na in S mode 0.1 % NaCl
PQ3-BGU

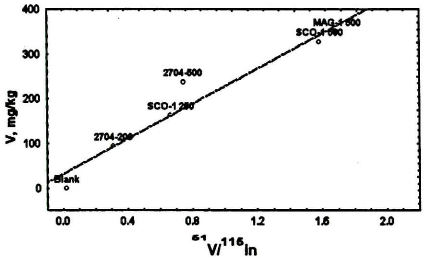
REEs in NRCC SLRS-2. Data in ppt
Values compared with Hall et al, (1997)

New applications of the S mode in Geoanalysis

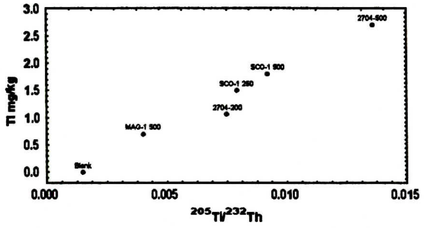
- ○ *Determination of the rare elements in geological samples*
- ○ *Determination of ultratrace elements in surface and subsurface waters at the ppt level*
- ○ *Analysis of sample extracts for low abundance elements and speciation - enzyme leach etc..*

Slurry nebulization

Determination of V by slurry nebulization ICP-MS
0.05 % solid in slurry



Determination of Tl by slurry nebulization
ICP-MS, 0.05 % solid in slurry
Correlation: r = .98763



Calibration statistics for common elements in sediments by SN-ICP-MS. N SRMs = 5-7. R ser - R values ($p < 0.05$) for 5 serial dilutions of Red Mountain illite slurry (0.002-0.05 % suspension)

Element	Mass	R	t	p	*R ser**	Range
Li	7	0.9905	12.45	0.0011	*0.9990*	0-200
B	11	0.9999	66.39	0.0096	*0.9993*	0-350
Ti	49	0.9703	5.67	0.03	*0.9992*	0-2 % TiO_2
V	51	0.9711	7.05	0.0059	*0.9989*	0-350
Cr	52	0.996	15.77	0.004	*0.9875*	0-350
Mn	55	0.9096	3.79	0.032	*0.9981*	0-0.25
Co	59	0.9961	15.87	0.004	*0.9080*	0-50
Ni	60	0.9969	21.83	0.00021	*0.9085*	0-150
Cu	63	0.9772	7.97	0.0041	*0.9746*	0-250
Zn	64	0.9704	6.957	0.0061	*0.9358*	0-1100
Rb	85	0.9887	11.4	0.0015	*0.9990*	0-400
Ba	137	0.9695	6.85	0.0064	*0.9998*	0-1500

Laser Ablation

TYPES OF LASERS

- ○ *IR Nd-YAG 1064 nm*
- ○ *VIS Nd-YAG 532 nm*
- ○ *UV Nd-YAG 266 nm*
- ○ *EXCIMER XeCl 308 nm*
- ○ *EXCIMER KrF 248 nm*

COMPARISON OF UV and IR LASERS

- *Small vs large craters*
- *Enhanced sample-laser interaction with UV lasers - the "transparent minerals"*
- *Minimum fractionation vs thermal differentiation*
- *Similar response for element groups vs large differences in response*
- *Problems with calibration in both cases*

Modes of Ablation and Applications

- *Single pulse - analysis of a small area - single mineral grains*
- *Spatial profiling - variation of elemental composition by continous laser ablation of the sample area without stage movement*
- *Examples fluid inclusions, weathering crusts.*
- *Zoned minerals and grain boundaries analysed by moving sample stage whilst firing the laser repetively*
- *Bulk analysis of powders and Li borate glasses*

REQUIREMENTS OF A LASER ABLATION SYSTEM FOR ICP-MS

- *Good shot-to-shot stability*
- *< 10 microns for inclusion analysis*
- *Minimum fractionation effects*
- *Good image quality*
- *Petrographic-metallurgical microscope*
- *Variable image magnification for feature definition, identification and location*

REQUIREMENTS OF ICP-MS FOR LASER ABLATION

- *Transient analysis*
- *Simultaneous dual range detector - measurement of pulse and analog signals in one mass scan*
- *Large dynamic range*
- *Rapid work cycle of quadrupole, capability of scanning the mass range in 100 msec*
- *High sensitivity for small feature analysis*
- *3-D software for elemental zoning studies*

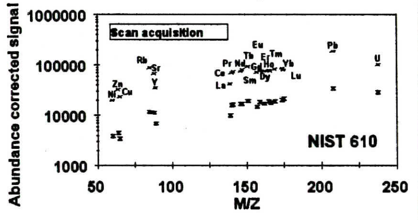
LASER SAMPLING ICP-MS BENEFITS

- *Minimum sample preparation and contamination*
- *High sample throughput - 1-2 min/sample*
- *Very wide elemental coverage*
- *Applicable to all types of geological and related materials*
- *Bulk and small feature analysis, zonation*
- *Minimizes sample waste disposal for RADWASTE analysis*
- *Reduced polyatomic interferences - oxides [illegible] plasma*

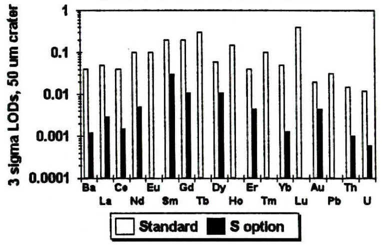
FACTORS EFFECTING LA-ICP-MS PERFORMANCE

- *Laser - sample interaction - fractionation*
- *Laser operation conditions - power, frequency, energy, active focusing, shot duration*
- *Particle- plasma interaction*
- *Spectrometer sensitivity, S option*
- *Mode of signal detection, dual, transient*

COMPARISON OF MASS RESPONSE CURVES NORMAL AND S OPTION, LASER ABLATION



LOD comparison for laser ablation glass. PQ3 standard and S option



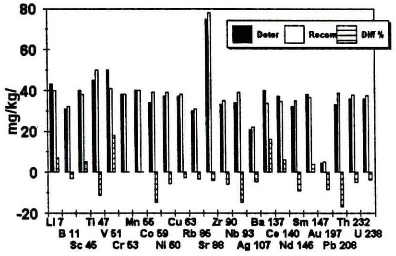
CALIBRATION STRATEGIES IN LA-ICP

- ○ *Conversion to glasses*
- ○ *Pressed powders - matrix match*
- ○ *Capillaries for liquid inclusions*
- ○ *Dry aerosols*
  - ○ *desolvated aqueous aerosols*
  - ○ *ETV*
  - ○ *Desolvated microslurries*

Calibration strategies

- ○ *Matrix match using SRMs - NIST 610-616, BCR-1, BCR-2G, AGV-1, BHVO-1, SL13 zircon*
- ○ *Pressed pellets*
- ○ *Vitrified SRMs*
- ○ *Solutions- dual sample introduction, liquid ablation*
- ○ *Desolvated slurries*

Analysis of NIST 612 glass by LA-ICP-MS. Calibration with NIST 610



Analysis of USGS BHVO-1 using AGV-1 as a calibration standard

Element	[redacted]	*Rec*	Element	[redacted]	Rec
Li	[redacted]		La	[redacted]	*15.8*
Be	[redacted]	*1.1*	Ce	[redacted]	*39*
Sc	[redacted]	*31.8*	Pr	[redacted]	*5.7*
V	[redacted]	*317*	Nd	[redacted]	*19*
Cr	[redacted]	*289*	Sm	[redacted]	*6.2*
Co	[redacted]	*45*	Eu	[redacted]	*2.06*
Cu	[redacted]	*136*	Gd	[redacted]	*6.4*
Zn	[redacted]	*105*	Tb	[redacted]	*0.96*
Sr	[redacted]	*403*	Dy	[redacted]	*5.2*
Y	[redacted]	*27.6*	Ho	[redacted]	*0.99*
Zr	[redacted]	*179*	Er	[redacted]	*2.4*
Nb	[redacted]	*19*	Th	[redacted]	*1.08*
Pb	[redacted]		U	[redacted]	*0.42*

Isotope ratios of Sr and Pb using S mode.
% HNO3, N=10. No IS

^{87}Sr	181296	0.79
^{88}Sr	2.125×10^{6}	0.71
$^{87}Sr/^{88}Sr$	0.0853	0.17
$^{86}Sr/^{88}Sr$	0.1183	0.12
^{207}Pb	223565	0.78
^{208}Pb	548569	0.63
$^{207}Pb/^{208}Pb$	0.4075	0.21

MULTIPLE COLLECTOR MASS SPECTROMETERS

- *Double focusing sector mass spectrometer - 7 Faraday collectors*
- *Isotope ratios: $^{147}Sm/^{144}Nd$,*
- *% RSDs $^{87}Sr/^{88}Sr$ - 0.008*
  $^{143}Nd/^{144}Nd$ - 0.0038
- *Comparable to TIMS*
- *Correction of mass bias - SRMs, internal standards, isotope dilution, isobaric corrections*

Pb ISOTOPE RATIOS WITH DOUBLE FOCUSING MULTIPLE COLLECTOR LA-ICP-MS

	208/204	SD	207/204	SD
Mean	36.948	0.038	15.509	0.018
TIMS	36.989	0.024	15.506	0.01

Double focusing sector mass spectrometer - 7 Faraday collectors

Comparable to TIMS.Correction of mass bias - SRMs, internal standards, isotope dilution, isobaric corrections

Walder, A.J., Platzner, I., Freedman, P.H., and Abell., I.D., JAAS, 1993, 8, 19 and Spectrochim. Acta 48B, 397, 1993

UV laser abaltion ICP-MS
Advantages of the S mode and active focussing

- *ICP-Mass spectrometers with enhanced ion transmission interface (VGE S mode) provides enhanced sensitivity and LODs for trace element geoanalysis - about 5-10 times enhancement*
- *ppb LODs can be attained with LA*
- *Active focusing reduces in-crater and peripheral thermal effects*
- *Discriminant analysis shows that Si can be used to compensate for signal variations*
- *Time studies indicate that stability is attained after a brief 10 s pre-ablation followed by a stable meaurement time of 20-30 s*
- *SRMs calibration can be used to provide accurate data*

Gwendy Hall

Review of analytical considerations with respect to selective leaches

Gwendy E.M. Hall, Geological Survey of Canada

This talk is taken from one of the"distinguished lecture" series and presents essentially a review of analytical considerations with respect to selective leaches. Rather than copy the slides for this notebook, I have selected some of my recent papers on this subject which go into much more detail; others can be obtained by request (hall@gsc.nrcan.gc.ca). Many of us are attempting to understand the various mechanisms of element transport from depth; this is an extremely challenging area of research. We must start by ensuring that the results of selective or partial/unselective extractions are optimised in terms of their precision and accuracy, that we are analysing exactly what we are aiming for (i.e. the methods are robust). From that point, we can go on to discern whether anomalies reflect mineralisation below or whether they reflect changes in surficial and bedrock geology, fault systems, landscape, soil type, topography, drainage, aerial deposition and so on. Here are some pertinent considerations to the application of partial extractions:

- What sample medium (e.g. organic-rich humified horizon, peat, well developed B-horizon..) is most prevalent and consistent throughout the survey area and therefore what "phase" is most appropriate to analyse?
- Is there adequate scavenging phase present throughout the samples so that all available/labile element is fixed? If not, is normalisation to the major element of that phase really appropriate?
- How should the sample be prepared to minimise any change in element distribution (air-dried, kept wet)?
- What size fraction should be selected? Do results reflect grain size distribution?
- What is the precision of sampling and analysis (the latter is usually much better than the former, as it ought to be)?
- Is the analysis accurate with respect to dissolving only that "phase" or "form" of element targeted, i.e. is the leach selective (if desired) or are other minerals also being dissolved to a significant extent? Is *all* the phase being dissolved by one application and if not, does it matter?
- Is the analysis accurate, are all interferences corrected for?
- Is the element stable in solution *during* the leach (i.e. no readsorption/precipitation) and *after* the leach prior to analysis?
- Is the leach pH-controlled or do results depend upon the sample pH?

Five papers are included here.

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Analytical perspective on trace element species of interest in exploration

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Accepted 21 October 1997

Abstract

Analysis of soil and sediment samples, using selective extraction methods to distinguish different phases, is of particular interest in exploration geochemistry to locate deeply buried mineral deposits. There are various mechanisms of binding labile elements in the secondary environment, including physical and chemical sorption, precipitation, chelation and complexation. Phases present in soils and sediments which are likely to scavenge 'free' elements include amorphous Mn and Fe oxides, the humic and fulvic components of humus, and clays. This paper reviews these forms of trace elements and the methods in current use to quantify them. Examples of precision data, both for control and survey samples, are given with respect to trace elements dissolved from the 'soluble organic' component of humus, Mn oxides and amorphous Fe oxides. The high sensitivity of inductively coupled plasma mass spectrometry (ICP–MS) is required to measure accurately and precisely a large suite of trace elements, especially where only small fractions of elements are dissolved by such leaches as the commercially available Enzyme and MMI (Mobile Metal Ion) extractions. The relative standard deviations (RSD) obtained for 33 elements (e.g. Ag, Cd, In, I) in the standard reference sample (SRM), TILL-2, are in the range 0.5–8% for the hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) leach designed to extract hydrous Fe and Mn oxides. The corresponding RSDs for elements in the reactive Mn oxide phase extracted by the Enzyme leach are in the range 3–19% except for some trace elements at levels close to detection limit (e.g. Cd, Bi). The RSDs obtained for field duplicates are inferior to those for analytical replicates (i.e. sample splits), probably a reflection of different concentrations of the host phase. In one soil survey, the Fe extracted by a 0.25 M $NH_2OH \cdot HCl$ leach ranged conservatively from 0.2 to 1.7% whereas the Mn extracted by the Enzyme leach varied extensively, from 0.3 to > 999 ppm. In contrast, precision, at 1–7% RSD, for field duplicates was found to be comparable with that for both analytical duplicates and the SRM, LKSD-4, for elements associated with the humic and fulvic component of humus samples sieved to < 177 μm. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: selective leach; analysis; precision; soil; sediment; element speciation

1. Introduction

Interest in the use of selective leaches in geochemical exploration was rekindled by the reported successes of the Russians in using this methodology to locate deeply buried mineralisation in glaciated and non-glaciated terrains (Ryss et al., 1990; Antropova et al., 1992; Goldberg, 1998). Although this approach has found application outside Russia since the 1970s (Bradshaw et al., 1974; Chao, 1984; Hall, 1996), until recently relatively few surveys employed selective leaching, probably because of

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PII S0375-6742(97)00046-0

inadequate detection limits and relatively high analytical costs. Electroanalytical (e.g. polarography) and solid sample emission spectroscopic techniques were designed in Russia to play key roles in measuring elements bound to fulvic and humic material (designated 'MPF') and to amorphous Fe oxyhydroxides ('TMGM'). Transfer of the analytical technique ICP–MS, generally more sensitive than ICP–ES by several orders of magnitude, from research-oriented laboratories to commercial labs in the 1990s has opened the door to high-production, affordable selective analysis. Two popular commercially available leaches are known as: the Enzyme leach (Activation Laboratories, Ancaster, ON; Clark, 1993), designed to dissolve the amorphous or 'more reactive' Mn oxide phase; and the MMI (Mobile Metal Ion) leach, designed to dissolve loosely held metals (Mann et al., 1998). The strengths and weaknesses of different leaches used at the Geological Survey of Canada (GSC) and at other commercial labs have been described previously (Hall et al., 1996a,b). This paper focusses on these various extractions and the reproducibility of results obtained by their implementation. Interpretation of results is addressed in other papers of this special issue.

The objective of selective leaching in the exploration context is to map specifically that fraction of an element which was previously in a labile (free) form and has been 'trapped' or immobilised in the surficial environment. Controversy abounds as to the dominant mechanisms of transport of the element from oxidising mineralisation at depth, whether it be by diffusion or 'fast-ion migration' (Goldberg, 1998), through faulting, water-borne or gaseous. However, there is agreement that the principal resident sites in the secondary environment for these migrating elements comprise hydrous Fe and Mn oxides, humic and fulvic components of humus material, and clay minerals. Thus, leaches have been developed to extract these 'phases' (used in a broad sense) in their entirety or to dissolve elements loosely adsorbed to them. These phases are generally not discrete, but rather exist linked together as colloids. Furthermore, binding mechanisms are not simple, comprising physical and chemical adsorption at surfaces, occlusion within structures, chelation, complexation and coprecipitation. These factors confound the design of a *selective* extraction which is often based on changing the pH and/or Eh environment of the sample to promote specific dissolution. Thus, true specificity is almost impossible to achieve and the term 'operationally defined' is used to describe more loosely the phase or form measured.

Sometimes it is necessary to carry out a 'pre-extraction' in order to improve the accuracy of the extraction of interest. For example, the various leaches employed to dissolve amorphous Mn and/or Fe oxides will also bring into solution elements physically and chemically sorbed at surfaces or elements precipitated as carbonates; an initial 'wash' in an appropriate solution would remove such forms. This approach then, in essence, forms a segment of a *sequential* extraction scheme. Such schemes are used in the sister disciplines of exploration and environmental geochemistry and have been compared recently by Hall and Pelchat (1997b). It is interesting that the tendency exists in environmental studies to attribute an *anthropogenic* source, particularly airborne, to labile elements leached out early in these schemes, whereas the philosophy underpinning these selective extractions in exploration assumes a *geogenic* source from buried mineralisation.

In a soil survey, the question of which selective leach to use cannot be answered without first examining the soil profile and thereby identifying the horizon most likely to have trapped the elements migrating from depth. The characteristics of the soil profile depend not only on the parent rock (or transported till) material but also on climate, topography and biological activity. Fig. 1 and Table 1 describe, in a generalised sense, characteristics of some idealised soil profiles. Soils in humid regions tend to be thoroughly leached and possess well defined Fe-rich B-horizons whereas much less extensive downward leaching occurs in semiarid warm climates, often producing calcareous soils with the formation of a caliche layer ($CaCO_3$ precipitation) which may be the target phase in exploration. In regions of significant rainfall with good drainage, leaching is usually extensive, and therefore A- and B-horizons are strongly differentiated. However, where drainage is poor and hence leaching minimal, reducing conditions prevail and a thick organic-rich surface layer may form over a mottled subsoil. Young soils often lack a B-horizon. Of particular interest in well developed Podzols are the organic-rich humus layer (A_1),

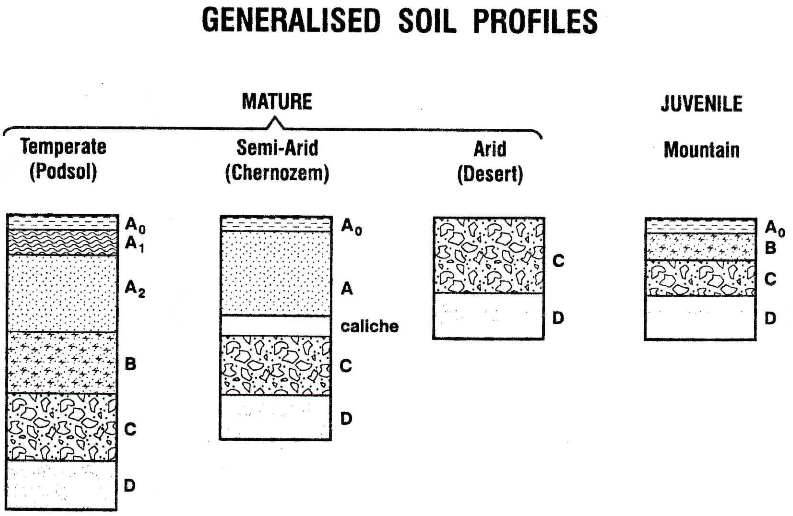

Fig. 1. Generalised soil profiles for four different climatic environments (taken from Levinson, 1974).

and the reddish-brown B-horizon, rich in hydrous Fe, Mn and Al oxides and clay minerals. Clearly, the light-coloured A_2-horizon (Fig. 1), zone of maximum leaching ('eluvation') and minimum cation exchange capacity, is not a good sampling medium.

Fig. 2 is a generalised representation of the distribution of Cu in four different soil types, taken from Levinson (1974). Copper accumulates in the upper humic layer and in the illuvial B-horizon of the Podzol and forest soils. Trace metals tend to be enriched in the organic-rich layers of soils in less humid regions where leaching is low. In Chernozems (e.g. in fertile grasslands), Cu collects in the organic-rich upper layer, and in Chestnut (brunisol) soils under conditions of less precipitation, Cu is directly related to the amount of organic matter. In laterite profiles, the trace elements tend to be concentrated in the upper ferruginous B-horizon, but rela-

Table 1
Simplified description of soil profiles

Horizon	Description
A_0	Partly decomposed organic debris. Should reflect chemistry of vegetation.
A_1	Dark-coloured organic-rich material mixed with mineral matter. Good sample for elements bound to humates and fulvates.
A_2	Light-coloured zone of maximum eluviation (leaching) of soluble bases, clays, colloidal oxides and organic matter by percolating rainwater. Well developed in Podzols, faint in Chernozems and may be absent in arid regions or young soils. Very low in trace elements.
B	Brownish colour due to illuviation (accumulation) of Fe/Mn oxides, organic matter and clays. Blocky or prismatic structure. High capacity for trace elements. Zone of illuviation in semiarid regions, forming caliche (coarse $CaCO_3$ precipitate) which would be near surface under very dry conditions.
C	Zone of weathering bedrock or till, loose and partly decayed. Parent material for overlying A- and B-horizons. Minimal organic material and illuviation. Relic rock structures. Sometimes intensely gleyed layers or layers of $CaCO_3$ in some soils. Sampled when A and B are missing or in some laterites.
D	Bedrock.

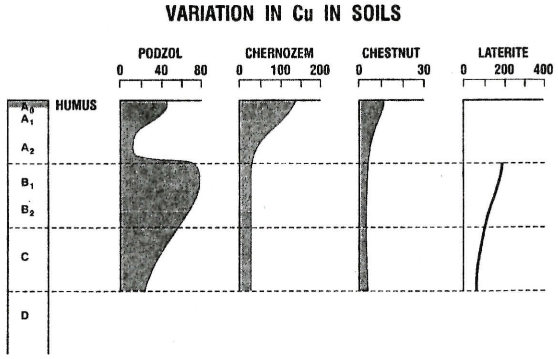

Fig. 2. Generalised representation of Cu in four soil types (taken from Levinson, 1974).

tively mobile elements such as Zn can accumulate at an intermediate montmorillonite-rich C-horizon (Zeissink, 1971). A thorough appreciation of the secondary environment and considerations relevant to geochemical exploration can be gleaned from numerous sources. Readers are referred to the classic books of Levinson (1974) and Rose et al. (1979), and more specifically, related to climatic zones, to those by Kauranne et al. (1992) for Arctic and temperate terrains, and Butt and Zeegers (1992) for tropical and subtropical terrains.

Undoubtedly the success or failure of a selective leach approach rests, initially, on the sampling strategy. If substantial amounts of another horizon are included with the target (e.g. A_2 mixed in with B or with A_1; Fig. 1), then results will be affected by the mixing ratio of two matrices. Thus, recognition of the selected horizon is critical and instructions should not be given to field personnel based solely on *depth* of sampling unless the survey area has an unusually consistent soil profile. On a global scale, Levinson (1974) makes the generalisation that: the A-horizon can range from ca. 30 cm to > 1 m in thickness; the B-horizon from ca. 5 cm to 2 m; and the C-horizon is usually thicker than A or B, exceeding 100 m in some tropical soils.

Since the scavenging phases of hydrous Fe, Mn and Al oxides occur in the fine clay and silt fraction, it is advantageous to sieve the soil to at least < 63 μm. This size fraction also serves to separate out the 'soluble organic' scavenging phase in humus material. Coatings of hydrous Fe oxide on the coarse particles of stream sediments may dictate the use of this fraction in quantifying hydromorphically dispersed elements held in this phase (see Hale and Plant, 1994, for design concepts in drainage geochemistry). Numerous case histories comparing the geochemical response of different size fractions using 'conventional' total or near-total sample decomposition (e.g. $HF–HClO_4–HNO_3$ or aqua regia) have been documented in the aforementioned texts, but more study of sample preparation is needed in the application of selective leaches. Furthermore, the question of drying the sample is particularly critical when extracting a certain species of element. Redistribution of element species on drying (air-, oven-, freeze-) well aerated samples is of less concern than for anoxic samples, but nevertheless, storage of samples between collection and analysis remains an area for further investigation (Kersten and Forstner, 1989). The preference at the GSC, when collecting wet samples such as peat, is to keep them wet and cool in 'zip-lock' bags until analysis. Results are calculated on a dry-weight basis, the moisture being determined on a separate aliquot. If samples are to be dried before analysis, then air-drying is preferable to maintain the integrity of element distribution.

2. Trace element forms of interest in exploration

2.1. Adsorbed and exchangeable forms

Adsorption of metals and metalloids by soil constituents may be described as *specific* or *non-specific*. A soil's Cation Exchange Capacity (CEC) is a measure of its ability to provide sites for *non-specific* adsorption. The forces involved in the adsorption of ionic species at charged surfaces are electrostatic, governed by Coulomb's Law of Attraction and Repulsion. The CEC of most soils ranges from a few to several hundred meq/100 g and far exceeds anion exchange capacity as negative rather than positive charges dominate on colloidal surfaces. These negative charges can be classified as: (1) independent of pH, where permanent charge is due to isomorphous substitution of major element ions within 2 : 1 clay minerals and edge effects on clay minerals; and (2) pH-dependent charges on humus polymers and hydrous oxides (Alloway, 1990). Although the important role played by clay minerals in the sorption of trace elements from soil solutions is widely recognised, the exact mechanisms of adsorption remain to be thoroughly clarified. Generally, a soil solid phase with a large surface area has a high CEC, as is shown in the descending CEC sequence for the clay mineral groups: montmorillonite, vermiculite (700–800 m^2/g surface area and a CEC of 70–150 meq/100 g) > illite, chlorite > kaolinite > halloysite (30 m^2/g, CEC of 3–50 meq/100 g). Amorphous aluminosilicates (allophane, imogolite) are probably significant adsorbers of trace elements in warm, humid climates. Clays rarely exist in soils in pure form; rather, they are bound together with humic colloids and hydrous oxide precipitates.

The negative charges on humus polymers are due to the removal of protons from carboxyl and phenolic hydroxyl groups, whereas those on the surface of hydrous oxides are created by proton dissociation from O and OH groups. Below a pH of 8, newly formed hydrous oxides of Fe and Al contribute little to the CEC of soils as the hydrogen ion concentration inhibits proton dissociation, and they have essentially no charge. In contrast, carboxyl groups in humic polymers have dissociation constants (pK) of 3–5 and phenolic groups have pK values of greater than 7. Thus, the high adsorptive capacity of humic substances at pHs above 5 contributes significantly to the overall CEC of a soil.

Specific adsorption implies the exchange of metallic cations and anions with surface ligands to form partly covalent bonds with lattice ions (i.e. not simple electrostatic attraction). Thus the degree to which metal ions are held may be much greater than that suggested by the CEC of the soil. Metals most able to form hydroxy complexes, as shown below, are specifically adsorbed to the greatest extent:

$$M^{2+} + H_2O \rightleftarrows MOH^{+} + H^{+}$$

Hence, Pb with a pK of 7.7 is more strongly adsorbed than Cd with a pK of 10.1. Hydrous oxides of Fe, Mn and Al are the major soil constituents responsible for specific adsorption, though surface chelation of metals with various functional groups (e.g. $-COOH$, $-NH_2$, $-C_6H_5OH$) on organic substances does occur.

Although the Langmuir and Freundlich adsorption isotherms are used to quantify this overall process, neither provides information as to the mechanisms involved and both are simplistic in that they assume a uniform distribution of adsorption sites and an absence of any reaction between adsorbed ions. The distribution of an element between soil solution and solid phases at equilibrium is governed by: (1) the density of surface binding sites for each component (e.g. clay mineral, hydrous Fe oxide); (2) the binding intensity of the metal ion to each component; (3) the abundance of each component; (4) the chemical characteristics (e.g. pH, ligands and their concentration) of the solution phase; and (5) the concentration of other ions, major or trace, competing for binding sites. In order to dissolve adsorbed elements selectively without dissolving the substrate itself (i.e. clays, hydrous oxides, humics), the adsorption equilibrium must be shifted to the free-ion side. Neutral salts such as $MgCl_2$, $CaCl_2$ and $NaNO_3$ are used to perform this function by displacing adsorbed metal ions. As the affinity of Group I and II cations for these sites is usually much lower than that of metal ions, a high concentration (e.g. 1 *M*) is often employed. In numerous studies, the cation displacement efficiency for oxic soils and sediments has been demonstrated to decrease in the order Cd > Zn > Cu ≈ Pb (Kersten and Forstner, 1989), which is consistent with the decreasing pH values of their adsorption edges. The solid-to-solution ratio (or 'dilution factor') is an important influence on desorption efficiency: the higher the dilution factor, the greater the amount of metal extracted.

In his review of speciation in soils and sediments, Pickering (1986) reported that $MgCl_2$ leachates typically extract very low amounts of Al, Si, Fe and organic matter, showing that attack on the substrates (clay minerals, organic matter, oxides and sulphides) is minimal. However, other reagents used for the same purpose, such as NH_4Cl and NH_4OAc, have been shown to dissolve considerable amounts of carbonates and sulphates (of Ca and Mg), an undesirable feature in this application (Robbins et al., 1984). The various affinities of neutral salts for surface binding sites generally appear to be in the order $H^{+} >> Ca > Mg > Na = NH_4^{+}$. Thus, 1 *M* H^{+} would desorb more metal ions than would 1 *M* Mg^{2+}. It should also be noted that the anion can play a role in complexation (especially for Cd); chloro-complexes of transition elements are slightly less stable than those formed with acetate. Pickering (1986) found that 0.05 M $CaCl_2$ displaced 10–20% more metal ions than did 1 M $MgCl_2$ or 0.5 M NaCl, indicating that differences in the affinity for the sorption site ($Ca > Mg > Na$) was more important than chloro-complex formation. The use of $CaCl_2$ as an extractant seems to be limited, despite its desirable features. Kersten and Forstner (1989) have selected, admittedly arbitrarily, 1 M NH_4OAc (at a solid/solution ratio > 1 : 10) for 2 h to dissolve adsorbed elements. In the well-known sequential extraction scheme designed by Tessier et al. (1979), 1 M $MgCl_2$ at pH 7 for 1 h was chosen over: (1) 1 M NH_4OAc at pH 7, because of the latter's reputed attack on carbonates (and organics); and (2) 1 M NaOAc at pH 8.2, because complexation of Ca^{2+} (from $CaCO_3$) as $CaOAc^+$ was again evident.

The Mobile ('unbound') Metal Ion (MMI) leach approach, described by Mann et al. (1998), is designed to release loosely held adsorbed elements, without attacking the substrate. Unlike the use of electrolytes to displace weakly bound elements, the two MMI leaches contain ligands which, through complexation, specifically bring the analytes into solution (e.g. acetate, EDTA, CN). A mildly acidic leach (proprietary to Mann's company, Wamtech), containing both organic and inorganic reagents, is employed for the metals Cu, Pb, Zn and Cd whereas a mildly basic solution, also comprising organic and inorganic ligands, is used for Au, Ag, Ni, Co and Pd. The leaches are carried out at room temperature for 24 h, apparently on large sample sizes (e.g. 100 g) sieved to remove coarse fragments (1–4 mm).

2.2. Bound to carbonates

Depending upon climate and local conditions, carbonates may be the dominant sink for some trace elements. The major control on trace element uptake by carbonates, often in metastable and polymorphic forms, is pH. Trace elements may be coprecipitated as their carbonates or, like Cd, may actually replace Ca^{2+} in the lattice. The preferred method of selective dissolution of the carbonate phase is an acidified acetate-buffered extraction, namely 1 M NaOAc/HOAc at pH 5 (Chao, 1984; Kersten and Forstner, 1989; Hall et al., 1996a). Robbins et al. (1984) have shown that this buffering capacity is sufficient to dissolve all the calcite in a carbonate-rich (68% $CaCO_3$) sediment, resulting in a final pH of 5.5 with a solid/solution ratio of 1 : 40. The method used at the GSC involves 6 h of constant agitation, at a ratio of 1 : 20, to ensure complete dissolution of the carbonate phase.

In soils, the greatest affinity for reaction with carbonates has been observed for Co, Cd, Cu, Fe, Mn, Ni, Pb, Sr, U and Zn; up to 1000 ppm of Sr and Co may occur in secondary calcite minerals (Kabata-Pendias and Pendias, 1984). In determining the carbonate-bound trace elements in marine sediments, Span and Gaillard (1986) found that only Cd and Mn correlated well with Ca. The other elements, Fe, Mn, Pb and Zn, were inferred to be only weakly associated, probably simply adsorbed and therefore would have been removed by prior application of a $MgCl_2$ or NH_4OAc leach.

2.3. Bound to 'soluble' organic matter (humic and fulvic component)

The bulk of organic matter in most soils consists of humic substances: amorphous, brown or black, hydrophyllic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tens of thousands. They are usually classified into three groups: humic acids, soluble in dilute alkaline solution; fulvic acids, soluble in acid and alkali; and humin, insoluble in dilute acid or base. These groups are structurally similar, but differ in molecular weight and functional group content, with the fulvic fraction having a lower molecular weight but higher content of oxygen-containing functional groups per unit weight than the others. Important characteristics of these compounds include their ability to form water-soluble and insoluble salts, and complexes with metal ions and hydrous oxides, and to interact with clay minerals (for thorough review, see Schnitzer and Khan, 1972).

The term 'organically bound' metal covers a broad spectrum of binding mechanisms, including adsorption, complexation and chelation. The high scavenging capacity of these organic substances is usually attributed to their carboxylic acid (COOH) functional groups, with contributions from other groups such as $-NH_2$ (amino) and –SH (thiol). The maximum amount, based on equivalents, of any given metal

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bound is approximately equal to the number of carboxyl groups. The total binding capacity of marine humic acid for metal ions was determined to be 200–600 μmol/g (Kersten and Forstner, 1989). Metals adsorbed on the surfaces of humic substances are removed by extraction with $MgCl_2$ or NH_4OAc (see Section 2.1); a stronger attack is required to bring complexed or chelated metals into solution for analysis. Two approaches are employed: destruction of the organic matter by oxidation with reagents such as H_2O_2 or NaOCl; or the use of an alkaline complexing agent such as $Na_4P_2O_7$, sodium pyrophosphate. The former approach has drawbacks in that other phases such as sulphides, Mn oxides and silicates can be partially dissolved and precipitation (e.g. as oxalates, hydroxides) may occur. The action of a neutral salt such as $Na_4P_2O_7$ in the extraction of humic substances depends upon: (1) the ability of the anion to interact with Ca, Fe and Al and other polyvalent cations combined with the humic material, to form either insoluble precipitates (e.g. $Ca_2P_2O_7$) or soluble complexes with the metals; and (2) the formation of soluble salts of the humic material by reaction with the cation. This is represented as, where X = Fe or Al and R is the organic molecule:

$$R(\mathrm{COO})_4\mathrm{Ca}_2 + \mathrm{Na}_4\mathrm{P}_2\mathrm{O}_7 \rightarrow R(\mathrm{COONa})_4 + \mathrm{Ca}_2\mathrm{P}_2\mathrm{O}_7\downarrow$$

$$2[R\mathrm{COO}X(\mathrm{OH})_2](\mathrm{COO})_2\mathrm{Ca} + \mathrm{Na}_4\mathrm{P}_2\mathrm{O}_7 \rightarrow 2[R\mathrm{COO}X(\mathrm{OH})_2](\mathrm{COONa})_2 + \mathrm{Ca}_2\mathrm{P}_2\mathrm{O}_7\downarrow$$

At a relatively high pH of 10, 0.1 *M* $Na_4P_2O_7$ does not dissolve amorphous Fe oxides (Bascomb and Thanigasalam, 1978). Results for Fe, however, may be erroneously high for some samples due to peptisation and dispersion of finely divided ferruginous particles present in the soil (Jeanroy and Guillet, 1981). Ultracentrifugation or ultrafiltration would negate this error, but the extra effort compared to simple centrifugation prior to analysis seems impractical for exploration purposes as Fe is not a critical analyte. Previous work has shown that the 16 h extraction often employed by soil scientists (McKeague et al., 1971) could be reduced to 1 h without significant decrease in the amount of Co, Cu, Fe, Ni, Pb or Zn extracted (Hall et al., 1996b). Thus, a 1 h 0.1 *M* $Na_4P_2O_7$ leach at room temperature and a sample-to-solution ratio of 1:100 (g:ml) is recommended for extraction of the labile organic component of humus, soil or sediment samples.

The earliest reagent applied to extract humic substances is NaOH and remains that suggested by the International Humic Substances Society, despite its drawbacks. These disadvantages include: unacceptable dissolution of clay minerals; and the metals' tendency to hydrolyse and readsorb onto reactive surface sites following removal of their organic coatings (Kersten and Forstner, 1989). In a comparison study of the 0.1 *M* $Na_4P_2O_7$ leach at pH 10 and 0.5 *M* NaOH at pH 12, Hall and Pelchat (1997a) demonstrated that there was minimal change in the amount of organic C, Hg or Zn leached from reference lake sediment, LKSD-4, when parameters of sample weight-to-reagent volume (w/V) and contact time are altered. In contrast, the 0.5 *M* NaOH leach showed an exponential increase in Hg and Zn extracted with decrease in w/V which did not correspond to the behaviour of organic C. Clearly the two reagents are extracting different groups of organic substances and results for both cannot be equated to the same nominal phase. A sequential extraction procedure developed by Schnitzer and Schuppli (1989), to define various organic fractions in soil, placed 0.1 *M* $Na_4P_2O_7$ before 0.5 *M* NaOH to dissolve organic matter complexed specifically to metals and clays as opposed to 'free' organic matter including less decomposed material which would finally be leached with the latter reagent.

2.4. Bound to Mn oxides

Although most soils contain much greater amounts of Fe oxides than Mn oxides, the latter possess greater sorption capability for trace elements. Such reactivity is due to characteristics of Mn such as: (1) it exists in several oxidation states (II, III, IV); (2) it forms non-stoichiometric oxides with different valencies; (3) its higher valence oxides exist in several crystalline (e.g. birnessite, lithiophorite, pyrolusite) or pseudocrystalline (manganite) forms; and (4) it forms coprecipitates and solid solutions with Fe oxides, owing to their similar chemical properties (Chao and Theobald, 1976). Although crystalline forms of

Mn oxide do occur in soils, the predominant species are amorphous (Kabata-Pendias and Pendias, 1984). Manganese oxides can have surface areas of several hundred m^2/g and larger CECs than some clay minerals (e.g. in the order of 150 meq/100 g). The internal structure of poorly crystallised Mn oxides can have an effect on the uptake of trace elements. For example, Anderson et al. (1973) found that the uptake of Ag by such Mn oxides depended upon the amount of internal Na and K, indicating exchange of these elements by Ag. In a study by Loganathan and Burau (1973) of the adsorption by synthetic hydrous Mn oxide of Co, Zn, Ca and Na, Mn was released to solution during the adsorption of the first two elements but not the latter. It was deduced that Co interchanged with surface-bound H and structural Mn^{2+} and Mn^{3+}, Zn with H and Mn^{2+}, and Ca only with H.

The relative importance of Mn and Fe oxides as scavengers will depend upon: (1) pH–Eh conditions; (2) degree of crystallinity of the oxides and hence their reactivity; (3) their relative abundances; (4) the presence of organic matter as a competing adsorbing and chelating fixing agent. Thus, elements will show a preference for uptake by either Mn or Fe oxide depending upon local conditions, as demonstrated in a study of uptake of Cu in a suite of soils (McLaren and Crawford, 1973). Removal of Cu from solution followed the order Mn oxides > organic matter > Fe oxides > clay minerals.

Selective extraction of Mn oxides and Fe oxides is usually based upon progressively increasing the reducing strength of the reagent, hydroxylamine hydrochloride being the popular choice. Two pH levels, 2 and 4.5, in a matrix of 0.1 M $NH_2OH \cdot HCl$ have been widely employed according to the literature (Chao, 1984). Manganese oxides are efficiently dissolved by agitation of the sample with 0.1 M $NH_2OH \cdot HCl$ in 0.01 M HNO_3 at a solid/solution ratio of ≥ 50 for 30–60 min at room temperature (Chao, 1972). Freshly precipitated hydrous Fe oxide may dissolve to a few percent, whereas dissolution of crystalline Fe oxides is negligible. Some authors replaced the unbuffered 0.01 M HNO_3 (pH 2) medium with 1 M NH_4OAc buffered at pH 4.5 (Gatehouse et al., 1977; Sondag, 1981). The extraction designed by Chao (1972) is rapid, simple to carry out, inexpensive and easy to automate.

The 'Enzyme Leach', marketed by Activation Laboratories (Ancaster, ON, Canada), is designed to solubilise selectively the most reactive forms, amorphous and pseudocrystalline, of Mn oxides present in soils and sediments. The key feature is that hydrogen peroxide is produced in relatively small concentrations (< 0.01 M) in which state it acts as a weak reducing (rather than oxidising) agent. The leach solution comprises essentially glucose (or dextrose) and glucose oxidase (Clark, 1993; US Patent 5491078). The enzyme catalyses the reaction of the sugar with oxygen (air) and water, to form gluconic acid and hydrogen peroxide:

$$\text{glucose} + O_2 + H_2O \underset{\text{(glucose oxidase)}}{\rightarrow} \text{gluconic acid} + H_2O_2$$

Hydrogen peroxide then reacts with the most reductive forms of Mn oxide and H^+ (from gluconic acid) to produce soluble manganous ions:

$$MnO_2(s) + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + O_2(aq) + 2H_2O$$

Gluconic acid has the advantage that it can stabilise some metals by complexation. Typically, 15 ml of leach solution containing 1% glucose and 0.03% glucose oxidase are added to 1 g of sample, the mixture periodically agitated during the 1 h extraction and finally centrifuged. The solution is made 1% in HNO_3 to inhibit precipitation of trace elements prior to analysis by ICP–MS. Acidification, however, causes rapid volatilisation of halides as halogen gases and thus is avoided if these elements (Cl, Br, I) are to be determined. A modification of the Enzyme leach involves the addition of ascorbic acid to the extractant (to a concentration of 0.1%) in order to lower the oxidation potential of the mixture (by destroying excess H_2O_2). (The enzyme, catalase, performs the same function but does not lower the oxidation potential as much.) The modified leach then dissolves more Mn oxide and amorphous Fe oxide, though the degree to which this occurs is unclear. In general terms, the leach modified with ascorbic acid appears to dissolve about an order of magnitude more Mn (US Patent 5491078). A weak feature of the Enzyme leach is that it is unbuffered; hence a significant change in pH amongst the soil samples analysed will cause a change in the amount of element extracted.

Table 2

Summary of forms of elements and common approaches to their dissolution

Form of element	Binding	Dissolution
Adsorbed/exchangeable	*Non-specific* (quantified by CEC), through electrostatic attraction: (1) pH-independent (e.g. on clays); and (2) pH-dependent (negative charges on humus polymers and, to a lesser extent, on hydrous oxides).	By displacement rather than dissolution of phase itself. Reagents such as 1 M $MgCl_2$, 0.1 M $CaCl_2$, 1 M NH_4OAc (pH 7) and 1 M NaOAc (pH 8.2).
	Specific: partial covalent bonding, especially with hydrous oxides of Fe, Mn and Al.	Affinity for displacement in the order of $H^+ \gg Ca^{2+} > Mg^{2+} > Na^+ = NH_4$. Also MMI-A and MMI-B proprietary reagents.
Organically bound	Besides being *adsorbed* to humates and fulvates, elements form 1 : 1 or 1 : 2 complexes through –COOH (mainly), NH_2 and SH functional groups.	Two approaches: via *dissolution* of organics using 0.1 M $Na_4P_2O_7$ at pH 10 at room temperature (preferable to NaOH which also dissolves clays);
		or via *destruction* of organics using NaOCl or H_2O_2 (these are less specific, attacking sulphides, etc.).
With Mn oxides	Variety of mechanisms including: adsorbed onto, coprecipitated with, occluded in, isomorphous substitution for Mn, to give a wide range of bond strengths. Mn often occurs as a mixed oxide with Fe.	By reducing agents: hydroxylamine hydrochloride, 0.1 M $NH_2OH \cdot HCl$ in 0.01 M HNO_3 at room temperature; or by the commercialised Enzyme leach where H_2O_2 is the reducing agent.
With hydrous Fe oxides	Variety of binding mechanisms as with Mn oxide above. Hydrous Fe oxide also adsorbs anions (e.g. molybdates, selenites).	By reducing agents: hydroxylamine hydrochloride, 0.25 M $NH_2OH \cdot HCl$ in 0.1 M HCl at 60°C; or Tamm's reagent, ammonium oxalate in the dark.

Whether it is preferable to dissolve only the more 'reactive' forms of Mn oxide to highlight previously mobile elements is a moot point since the scavenging capacities of all forms of Mn oxide are considerable. Both the hydroxylamine hydrochloride and the Enzyme leaches can also be considered to dissolve loosely adsorbed elements.

2.5. Bound to amorphous Fe oxides

The degree of fixation of trace elements by Fe oxides ranges from adsorption at the surface, through coprecipitation, to relatively strong binding within the oxide structure. As with Mn, the geochemistry of Fe in the terrestrial environment is complex, its behaviour being closely linked with the cycling of O, C and S (Taylor, 1990). Amorphous Fe oxide ($Fe(OH)_3 \cdot nH_2O$) is chemically more reactive than its pseudocrystalline and crystalline forms, which provides the basis for its chemical separation. For example, moderate reducing conditions are required for dissolution of amorphous Fe oxides compared to those for poorly crystallised goethite (α-FeOOH) or lepidocrocite (γ-FeOOH), whereas highly crystallised magnetite (Fe_3O_4) and hematite (Fe_2O_3) require a strong reductant or aggressive attack.

Chao and Zhou (1983) compared the specificity of reagents in the extraction of amorphous Fe oxyhydroxides from soils and sediments and concluded that hydroxylamine hydrochloride was optimal. Design of the GSC protocol for this phase was based largely on their findings, supported by later work. Their results confirmed that Tamm's reagent (0.175 *M* ammonium oxalate in oxalic acid at a pH of 3.2) in the dark was selective for amorphous Fe oxide only in the absence of magnetite and organic complexes. Magnetite is known to contain a host of trace metals and hence its dissolution is undesirable (Overstreet et al., 1978). Dissolution of magnetite by Tamm's reagent was also demonstrated by Borggaard (1982) who recommended the selective extraction of amorphous Fe oxides to be carried out using 0.02–0.1 *M* EDTA at pH 8–10 over a time period of > 30 days, hardly practical. Although extraction of amorphous Fe oxides in 1 *M* HCl for 30 min at room temperature appears to be specific for amorphous Fe oxide with respect to crystalline Fe oxides (dissolves < 1% of the hematite, goethite and magnetite minerals tested), this attack may well bring into solution metals from clays, amorphous allophanic materials and some sulphides (Chao and Zhou, 1983). They demonstrated that, after about 30–60 min in 0.25 *M* $NH_2OH \cdot HCl/0.25$ *M* HCl at 70°C, further dissolution of the two amorphous Fe oxides examined (synthetic and natural) was minimal while < 1% of the crystalline Fe oxides was dissolved except for one magnetite (ca. 2%). They concluded that this was the optimum, most selective extraction but reduced the temperature to 50°C to minimise the degree of dissolution of the crystalline Fe oxides below 1% total Fe.

Extensive application of the 0.25 *M* $NH_2OH \cdot HCl$ leach (at 60°C) at the GSC showed that the selectivity of the procedure should be improved (Hall et al., 1996a). Firstly, the acidity of the HCl medium should be reduced from 0.25 to 0.05 *M* in the presence of sulphides such as galena and sphalerite, to minimise their dissolution to < 1%. This less acidic pH is still low enough to prevent reprecipitation of Fe but should probably be monitored when the leach is applied to highly alkaline samples. Secondly, significant dissolution of the labile organic component occurs, as shown by the C concentration in solution for the reference sample LKSD-4, at 63% of that extracted by 0.1 *M* sodium pyrophosphate solution. Clearly, where the organic component of a sample is comparable in concentration to the amorphous Fe oxide phase, the pyrophosphate leach should precede the hydroxylamine hydrochloride extraction if specificity is desired. The GSC protocol involves leaching of a 1 g sample in 20 ml of 0.25 *M* $NH_2OH \cdot HCl$ in 0.1 *M* HCl at 60°C for 2 h, followed by centrifuging of the mixture at ≥ 2000 rpm for 10 min. This leach also dissolves the Mn oxide phase.

Table 2 summarises the forms of elements discussed above, and common approaches to their dissolution.

3. Analytical figures of merit

As previously stated, the accuracy obtained in selective leaching is difficult to assess. Even the use of separate minerals to test the degree of concurrent dissolution is subject to criticism as it does not take

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into account the confounding, interactive effects of other phases present in soils and sediments. Precision is much easier to measure and, from experience at the GSC is, perhaps surprisingly, comparable to that obtained for total element content. The reproducibility of sampling, preparation and methodology impact on the final precision. Variability at the analysis step is usually the minimum component, unless the element concentration is near the instrumental detection limit. These limits are mostly in the ppt (ng l^{-1}) and ppb ($\mu g\ l^{-1}$) range in analysis by ICP–MS, several decades below those of ICP–ES. Previous applications (Hall et al., 1996a,b) have shown that ICP–ES has been adequate for elements such as Zn and Cu bound to organic material in humus or to amorphous Fe oxide but the less abundant elements (e.g. Cd, Pb, Ag) require ICP–MS, especially in the application of the Enzyme and MMI leaches.

3.1. Precision associated with the $Na_4P_2O_7$ leach for organically bound elements

The previous report (Hall et al., 1996b) for two in-house humus control samples and the international standard reference lake sediment, LKSD-4, demonstrated long-term relative standard deviations in the range 2–7% when element concentrations were a decade above instrumental detection limits. Similar precision was shown by replicate samples of 37 humus samples sieved to < 80 mesh (177 μm). However, data obtained by AAS and ICP–ES for some trace elements such as Co, Cu and Ni showed poor precision, in the order of 20–50% RSD at several ppm of the organically bound element. This was due to the relative insensitivity of the analytical technique employed, rather than to inherent variability in the method itself. Later work, using direct ICP–MS to determine most elements in the LKSD-4 control sample, demonstrated that precision (as measured over several months) could be improved to be better than 10% RSD for these elements. The data in Table 3 show that RSDs for most elements are in the range 1–7%, the exceptions being for Sb, Tl and As which, however, remain acceptable at 12–19%. Note the excellent reproducibility for Hg, determined by cold vapour ICP–MS, of ±7% at the 14 ppb level in LKSD-4. In order to minimise instrumental drift, the ICP–MS method is based on a 50-fold dilution of the leached solution, thereby producing an overall dilution factor of 5000. This limits the capability to measure some elements at their true 'background' levels in this leach. For example, method detection limits of As and Sb — at 500 and 50 ppb (ng g^{-1}), respectively, by direct ICP–MS — should be improved by several orders of magnitude by employing hydride generation ICP–MS (Hall et al., 1997a).

The reproducibility of results obtained for 'real' humus samples, sieved to < 177 μm, is expected to

Table 3
Mean and standard deviation (SD) for elements bound to soluble organic phase in LKSD-4 ($n = 4$) (0.1 *M* $Na_4P_2O_7$ leach) (units as shown by detection limit, DL)

Element (DL)	Mean ± SD (%RSD)	Element	Mean ± SD (%RSD)
Ti (1 ppm)	65.0 ±1.8 (3)	Ba (1 ppm)	13.5 ± 0.57 (4)
V (0.5 ppm)	10.7 ±0.3 (3)	Ce (0.05 ppm)	24.6 ±0.8 (3)
Cr (0.5 ppm)	2.9 ±0.2 (7)	Tl (25 ppb)	189 ±35 (19)
Co (0.1 ppm)	1.71 ± 0.13 (8)	Pb (0.5 ppm)	55.2 ±0.8 (1)
Cu (0.5 ppm)	7.6 ±0.3 (4)	Th (25 ppb)	1148 ±15 (1)
Zn (2 ppm)	63.5 ±1.3 (2)	U (0.02 ppm)	23.2 ±0.6 (2)
Rb (0.2 ppm)	0.62 ± 0.01 (2)	As (0.5 ppm)	3.6 ±0.4 (12)
Sr (2 ppm)	24.0 ±0.8 (3)	Mn (2 ppm)	202 ±4 (2)
Y (0.05 ppm)	11.4 ±0.46 (4)	Fe (15 ppm)	3195 ±50 (1)
Mo (250 ppb)	770 ±48 (6)	Al (15 ppm)	2664 ±47 (2)
Cd (250 ppb)	654 ±41 (6)	Hg (6 ppb)	14.2 ±0.9 (7)
Sb (50 ppb)	218 ±26 (12)	C_{org} (0.1%)	2.32 ± 0.03 (2)

Most elements determined by direct ICP–MS, the exceptions being: Mn, Fe and Al by ICP–ES; Hg by cold vapour ICP–MS; and C_{org} by IR spectrometry.

Table 4
Results for field and analytical duplicates for 0.1 *M* $Na_4P_2O_7$ leach of humus samples from the Restigouche deposit, New Brunswick

Dup.	Cu, ppm	Zn, ppm	Cd, ppb	Ba, ppm	Ce, ppb	Pb, ppm	U, ppb	As, ppm	Hg, ppb	C_{org}, %
Field duplicates										
11	2.8/1.6	69/80	472/507	64/67	767/701	52/46	62/51	< 0.5/< 0.5	30/24	2.82/2.44
14	2.0/1.9	50/48	370/371	51/44	669/680	42/58	51/52	< 0.5/0.9	21/35	2.42/2.88
28	1.6/2.3	70/91	627/622	55/71	909/882	69/59	67/94	2.8/1.9	20/28	2.24/2.59
38	1.9/1.8	48/44	848/689	127/154	1160/1358	35/42	65/40	0.8/0.8	53/44	3.20/3.00
Analytical duplicates										
04	2.6/2.8	23/22	279/< 250	20/22	836/972	19/22	101/109	1.3/1.0	38/37	3.52/3.52
18	2.7/3.1	81/86	832/790	88/91	818/824	51/54	109/76	2.0/1.9	34/33	3.12/3.04
26	2.9/2.4	164/153	846/899	74/73	1124/1118	117/117	74/83	14.6/14.8	38/40	3.56/3.54
43	1.1/0.9	33/31	261/275	64/62	596/606	34/32	55/79	0.6/1.3	58/55	3.42/3.32

be inferior to that shown by an SRM (e.g. as in Table 3). Examples of both field and analytical duplicate data obtained in a humus survey over the Restigouche volcanogenic massive sulphide deposit (Zn–Pb–Ag–Cu) are given in Table 4. Two humus samples taken within several metres of each other constitute *field* duplicates, whereas an *analytical* duplicate is taken as a separate 1 g sample after sieving. The data in Table 4 indicate that analytical precision for these humus samples is comparable to that shown by the control, LKSD-4, and, perhaps more importantly, is only slightly superior to that of field sampling and analytical precision combined. Instrumental variability, as measured by replicate analysis of the same leach solutions, is typically only 1–3%.

3.2. Precision associated with the $NH_2OH \cdot HCl$ leach for oxide-bound elements

As happened during the development of the pyrophosphate leach, the initial values obtained for the precision typical of the 0.25 *M* $NH_2OH \cdot HCl$ leach (for amorphous Fe and Mn oxides) suffered from the use of ICP–ES rather than ICP–MS. At concentrations at least a decade above detection limits, long-term (over 18 months) RSDs for 14 elements in two till SRMs were in the range 6–18% (Hall et al., 1996a). Typical precision values shown by 75 soil and till analytical duplicates were: 10% (i.e. ±5% RSD) for Al and Y; 15% for Ca, Cr, Fe and Sr; 20% for Ba, Cu, La, V and Zn; 25% for Mg, Mn and Ni; and 30% for Co and Pb, which are present at levels below about 10 ppm in this phase. Precision is greatly improved when ICP–MS is employed, particularly as the overall dilution factor required is only 500 (cf. 5000 for the $Na_4P_2O_7$ leach) and consequently detection limits are excellent. Table 5 shows more data from the survey at Restigouche, indicating that RSDs for the SRM TILL-2 (over a 2-month period) were in the range 0.5–8% for 33 elements. Only Te suffered from an inadequate detection limit of 0.2 ppb, creating significant analytical variability at the 0.5 ppb level (Table 5). The SRMs, TILL-2 and TILL-3, were interspersed in a batch of samples submitted for Enzyme leach/ICP–MS analysis at Activation Laboratories; their data are presented in Table 6. Here most RSDs are in the range 3–19%, the noticeable exceptions being for Cd (25%) and Bi (80–100%) present at concentrations close to detection limits. A major contributor to the inferior precision by this leach compared to the 0.25 *M* $NH_2OH \cdot HCl$ leach for amorphous Fe oxide is the analytical variability at the much lower levels of elements present. Note the much lower amount of Mn extracted from TILL-2 (6 vs. 326 ppm).

The survey of B-horizon soils over the Restigouche deposit provides more examples of field and analytical duplicate data for the 0.25 *M* $NH_2OH \cdot HCl/0.1$ *M* HCl leach of the amorphous Fe oxide phase (Tables 7 and 8). This suite of samples was analysed for the Mn oxide phase using the Enzyme leach at Activation Laboratories; these data are also shown in Tables 7 and 8. In this instance, the precision associated with analytical duplicates is comparable to the good precision shown in the previlew Brunswick

b	C_{org}, %
	2.82/2.44
	2.42/2.88
	2.24/2.59
	3.20/3.00
	3.52/3.52
	3.12/3.04
	56/3.54
	42/3.32

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Table 5
Mean and standard deviation (SD) for elements bound to amorphous Fe (and Mn) oxide phase in TILL-2 ($n = 5$) (0.25 M $NH_2OH \cdot HCl$/0.1 M HCl leach) (units as shown by detection limit, DL)

Element (DL)	Mean ± SD (%RSD)	Element	Mean ± SD (%RSD)
Li (2 ppb)	1712 ±72 (4)	Ba (0.08 ppm)	61 ±0.3 (0.5)
Be (2 ppb)	542 ±28 (5)	La (4 ppb)	5748 ±44 (0.7)
Ti (0.2 ppm)	18.3 ±0.4 (2)	Ce (0.004 ppm)	15.2 ±0.07 (0.5)
Cr (0.04 ppm)	3.75 ± 0.15 (4)	Hf (4 ppb)	75.2 ±2.1 (3)
Co (0.02 ppm)	4.09 ± 0.04 (1)	Tl (2 ppb)	65.8 ±2.5 (4)
Ni (0.08 ppm)	2.81 ± 0.10 (3)	Pb (0.1 ppm)	12.9 ±0.2 (2)
Cu (0.04 ppm)	35.7 ±0.7 (2)	Th (20 ppb)	856 ±64 (8)
Zn (0.2 ppm)	14.6 ±0.6 (4)	U (2 ppb)	658 ±37 (6)
Rb (0.02 ppm)	5.01 ± 0.10 (2)	I (50 ppb)	1062 ±66 (6)
Sr (0.2 ppm)	7.22 ± 0.12 (2)	Bi (1 ppb)	1912 ±35 (2)
Y (4 ppb)	4695 ±146 (3)	Sb (1 ppb)	17.0 ±1.1 (7)
Zr (0.02 ppm)	1.71 ± 0.02 (1)	Te (0.2 ppb)	0.50 ± 0.10 (23)
Nb (4 ppb)	133 ±6 (5)	As (10 ppb)	1599 ±126 (8)
Ag (20 ppb)	226 ±5 (2)	Hg (0.2 ppb)	6.3 ±0.8 (12)
Cd (20 ppb)	180 ±11 (6)	Mn (0.1 ppm)	326 ±5 (2)
In (4 ppb)	25.3 ±1.9 (8)	Fe (6 ppm)	5944 ±247 (4)
Cs (4 ppb)	582 ±16 (3)	Al (30 ppm)	7255 ±180 (2)

Elements not determined by direct ICP–MS comprise: Bi, Sb, Te and Hg by hydride (or Hg°) generation ICP–MS; As by hydride generation QTAAS; Mn, Fe and Al by direct ICP–ES.

ous table for TILL-2, but is noticeably better than that shown by field duplicates. It is interesting that the behaviour is element-specific and is certainly independent of concentration level. For example, field duplicate data for Cr, Ti, Zn, Y and Fe are relatively 'noisy' whereas those for Pb, Th, U, Sb and Hg are excellent in the same samples (sample 38 appears to be the worst case overall). Note that the amount of amorphous Fe extracted in the field duplicates varies more than any other element but is

Table 6
Mean and standard deviation (SD) for SRMs TILL-2 ($n = 4$) and TILL-3 ($n = 3$) by Enzyme leach and ICP–MS (all data in ppb except for Cl and Mn in ppm)

Element (DL)	Mean ± SD (%RSD) for TILL-2	Mean ± SD (%RSD) for TILL-3
Cl (3 ppm)	22.94 ± 1.95 (9)	21.74 ± 2.06 (9)
Mn	6.21 ± 1.21 (19)	4.75 ± 0.40 (8)
Co	51 ±5 (10)	83 ±10 (12)
Ni	32 ±6 (19)	94 ±7 (7)
Zn	183 ±18 (10)	168 ±20 (12)
As (5 ppb)	21 ±1 (5)	887 ±81 (9)
Br (30 ppb)	1033 ±52 (5)	301 ±16 (5)
Cd (0.2 ppb)	4.8 ±1.2 (25)	0.8 ±0.2 (25)
I (10 ppb)	155 ±4 (3)	126 ±5 (4)
Ba	1733 ±161 (9)	508 ±67 (13)
La (1 ppb)	60 ±5 (8)	30 ±1 (3)
Pb (1 ppb)	29 ±2 (7)	45 ±5 (11)
Bi (1 ppb)	5 ±4 (80)	3 ±3 (100)
Th (1 ppb)	11 ±1 (9)	7 ±2 (28)
U (1 ppb)	10 ±1 (10)	5 ±1 (20)

All subsamples submitted in the same batch (i.e. short-term precision).

Table 7
Results for field and analytical duplicates for 0.25 *M* $NH_2OH \cdot HCl/0.1$ *M* HCl leach of B-horizon soils

Dup.	Li	Be	Ti	Cr	Co	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ag	Cd	In	Cs
Field duplicates																	
11A	361	291	4.11	5.68	227	959	856	8.7	1.88	1058	531	2.25	27	528	102	24	46
11B	328	341	2.83	4.68	327	1146	815	12.2	2.09	1018	708	1.99	211	474	107	18	36
11A					*23*	*80*	*18*	*0.509*	*0.179*	*188*	*6*	*0.011*			*6.4*		
11B					*24*	*68*	*16*	*0.472*	*0.211*	*170*	*8*	*0.008*			*4.7*		
14A	341	144	6.46	6.90	285	793	1063	11.5	1.12	480	337	1.71	50	258	93	32	25
14B	302	222	5.21	6.09	368	786	1095	14.9	1.64	440	420	2.039	37	267	110	27	49
14A					*29*	*70*	*28*	*0.990*	*0.134*	*54*	*5*	*0.015*			*5.5*		
14B					*19*	*44*	*24*	*0.746*	*0.086*	*39*	*3*	*0.011*			*3.4*		
38A	323	196	2.43	4.33	985	828	516	9.6	1.50	564	520	1.11	20	143	154	21	53
38B	178	245	2.49	3.38	878	1060	560	16.0	1.90	351	811	1.13	11	152	152	9	47
38A					*28*	*55*	*< 5*	*0.476*	*0.087*	*151*	*6*	*0.011*			*12.1*		
38B					*20*	*52*	*< 5*	*0.402*	*0.096*	*114*	*6*	*0.002*			*13.2*		
Analytical duplicates																	
8A	62	664	4.09	3.12	4656	1754	395	8.3	1.25	1661	927	1.02	23	95	326	11	33
8B	76	678	4.30	3.07	4827	1767	412	8.3	1.24	1648	946	0.99	23	97	342	10	36
68A	363	163	1.99	6.22	1172	820	1627	10.2	2.65	209	1016	1.83	12	78	157	29	68
68B	353	149	1.94	5.82	1099	756	1615	9.6	2.58	201	988	1.75	11	74	158	27	63
93A	373	240	2.37	10.2	2320	1825	809	13.8	1.43	433	580	0.70	6	137	115	10	37
93B	369	255	2.45	9.89	2312	1700	905	13.8	1.37	436	592	0.67	5	131	125	11	34
100A	340	344	5.25	6.02	2312	1800	1651	31.7	2.68	468	625	1.71	20	507	324	27	57
100B	340	339	5.48	6.18	2443	1830	1547	31.7	2.58	493	636	1.71	20	495	323	26	55

Data shown in italics are by the Enzyme leach; all data, by ICP–MS, are in ppb except for Ti, Cr, Zn, Rb and Zr in ppm.

consistent in the analytical duplicates. The much greater amount of Fe extracted in sample 38A (0.54 vs. 0.19% in 38B) is not reflected in a greater amount of trace elements released, suggesting perhaps that the scavenging capability of this phase is far from saturated at these levels. A consistent and relatively elevated concentration of Al is evident in all duplicate results.

As expected, the concentrations of elements released from the Mn oxide phase dissolved by the Enzyme leach are 1–3 orders of magnitude lower than those released from the combined Fe and Mn oxide phase (Tables 7 and 8). Thus, the Enzyme leach demands higher analytical performance than does the acidic $NH_2OH \cdot HCl$ leach. The greatest differential in trace element concentration between the two phases exists for Pb, Th, Y, Zr and the REEs, and the least for elements such as I, Sb and As. In scanning the complete data set for the 102 B-horizon soil samples at Restigouche, one observes that the Fe released from the combined amorphous Fe and Mn oxide phase ranges from 0.18 to 1.7%, whereas the corresponding Mn dissolved by the Enzyme leach from the 'host' oxide phase ranges from 0.3 ppm to > 999 ppm. The scavenging capacity attributable to a Mn content of less than a ppm is negligible and, hence, the interpretation of these data is in doubt. For example, a sample containing 0.3 ppm Mn also reports 0.5 ppm Zn, 4.6 ppm Cl, 0.9 ppm Ba and 1.1 ppm Pb by the Enzyme leach; clearly the results reflect dissolution of other phases.

A study of geochemical signatures in soils in Nevada (Hall et al., 1997b) provides more quality-control data, specifically to compare the precision of analytical duplicate results obtained by application of the two $NH_2OH \cdot HCl$ leaches designed to dissolve (1) the Mn oxide phase and (2) the combined amorphous Fe and Mn oxide phase. Thompson and Howarth (1978) log–log plots have been used to estimate precision for some selected elements in 24 analytical duplicate soil samples (Fig. 3). The control line has been drawn at the 95th percentile for the precision (twice the RSD) indicated. For the most part, RSDs are similar between the two leaches and

Table 8
Results for field and analytical duplicates for 0.25 *M* $NH_2OH \cdot HCl$/0.1 *M* HCl leach of B-horizon soils

Dup.	Ba	La	Ce	Hf	Tl	Pb	Th	U	I	Bi	Sb	Te	As	Hg	Mn	Fe	Al
Field duplicates																	
11A	11.3	921	1625	103	21	65	1045	123	1204	5	6	< 0.2	6	4.1	6.0	0.547	1.84
11B	13.0	1411	2323	93	19	57	965	102	1349	3	6	< 0.2	23	3.8	5.6	0.344	1.81
11A	*0.36*	*7*	*16*			*0.133*	*5*	*2*	*90*		*< 1*		*9*		*0.64*		
11B	*0.42*	*12*	*20*			*0.092*	*4*	*2*	*66*		*< 1*		*5*		*0.49*		
14A	16.1	804	1364	79	18	17	864	106	1579	6	7	< 0.2	27	5.0	40	0.910	1.47
14B	13.8	873	1528	94	20	13	915	104	1614	4	8	< 0.2	18	4.8	41	0.546	1.69
14A	*0.43*	*7*	*16*			*0.029*	*5*	*2*	*73*		*< 1*		*11*		*2.11*		
14B	*0.39*	*7*	*12*			*0.029*	*5*	*2*	*74*		*< 1*		*12*		*1.33*		
38A	19.7	689	1159	50	26	5.9	459	122	1547	9	39	< 0.2	219	4.2	163	0.539	1.38
38B	21.4	801	1399	53	30	5.5	435	124	1558	6	42	< 0.2	277	3.5	124	0.191	1.36
38A	*0.96*	*6*	*10*			*0.008*	*4*	*2*	*130*		*4*		*6*		*7.09*		
38B	*1.30*	*5*	*10*			*0.006*	*3*	*2*	*143*		*4*		*< 5*		*6.59*		
Analytical duplicates																	
8A	35.1	1215	1793	45	28	4.6	232	33	2536	< 1	11	0.3	22	3.6	513	0.514	1.90
8B	34.3	1214	1815	45	27	5.0	251	37	2465	1	11	0.3	16	3.5	510	0.501	1.87
68A	14.2	927	1656	87	23	8.4	1281	170	1218	6	19	< 0.2	52	5.1	93	0.336	1.49
68B	13.7	894	1588	85	21	8.4	1226	174	1068	7	19	< 0.2	74	4.9	97	0.334	1.54
93A	21.0	651	1076	32	13	10.8	251	71	861	2	15	0.3	103	4.5	72	0.278	1.56
93B	21.5	649	1090	31	12	10.9	292	75	1054	3	15	0.2	103	4.5	71	0.247	1.53
100A	17.3	847	1837	86	34	49.7	759	122	1190	6	14	< 0.2	121	7.5	86	0.353	1.44
100B	17.6	837	1840	87	33	51.5	889	123	1393	6	14	< 0.2	126	7.7	89	0.347	1.47

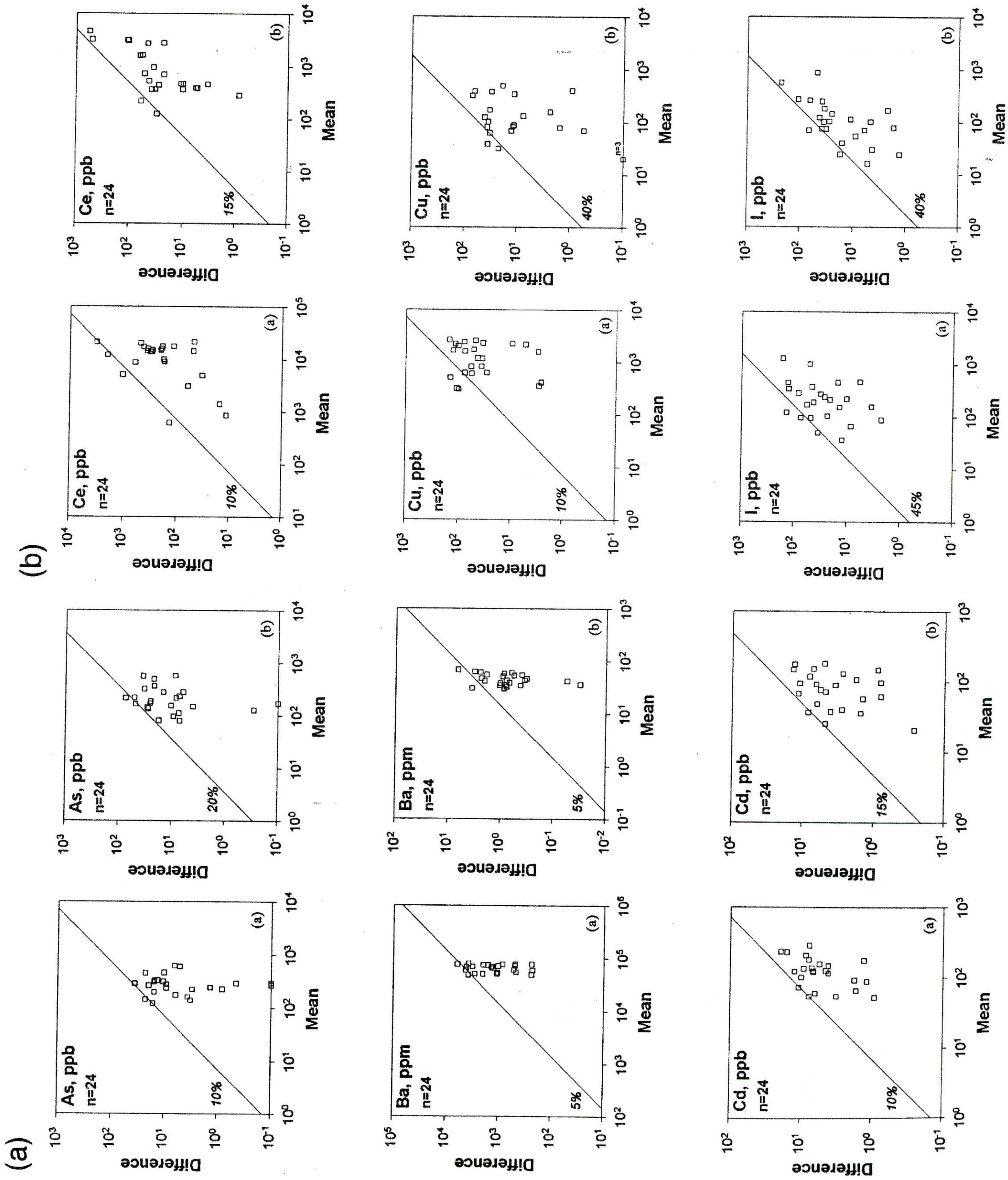
Data shown in italics are by the Enzyme leach; all data are in ppb except for Ba, Pb, Mn in ppm and Fe and Al in %.

in the range 5–10% except for: I (at ±20%) which tends to suffer from memory effects during analysis; and elements present at levels close to detection limits, such as Cu in the Mn oxide phase. In these soils, elements predominantly associated with the Mn oxide phase include Mo, Cd, Th, U, As, I, Sr and Ba whereas those at much higher concentrations when the amorphous Fe oxide phase is analysed include Be, Cu, Pb, Al, Y and the REEs. Typically in this survey, both 'host' Mn and Fe are present consistently at several hundred ppm in the 0.1 *M* $NH_2OH \cdot HCl$/0.1 *M* HNO_3 and 0.25 *M* $NH_2OH \cdot HCl$/0.1 *M* HCl leaches, respectively. Little Fe is dissolved in the 0.1 *M* $NH_2OH \cdot HCl$/0.01 *M* HNO_3 leach and usually is present at 1–2 orders of magnitude below Mn.

4. Readsorption

The accuracy of a selective leach is affected not only by the degree to which unwanted phases are concurrently dissolved with the phase of interest, but also by the extent to which the analyte is redistributed between solution and solid during the leach. Analyte loss during extraction could be the result of adsorption, (co)precipitation and complexation, but is often simply referred to as 'readsorption'. Too few publications exist on this topic and those that do are controversial, probably due to the widely differing experimental conditions used (Rendell et al., 1980; Belzile et al., 1989). Recent work by Qiang et al. (1994), in an effort to negate criticism of the use of artificial phases, employed model soils to study the readsorption of Cu and Pb during extraction by 1 *M* NaOAc/HOAc of the 'adsorbed/exchangeable/carbonate' phase. Pyrolusite and humic acid, constituents of the model soils, showed much stronger affinities for Cu and Pb redistribution than hematite, illite and montmorillonite. The relative importance of the constituent phases depended upon both the binding ability and the abundance of components. The leach itself may well create fresh binding sites on a soil or sediment sample as a particular phase is dissolved.

Tests for readsorption of analytes by the various selective leaches used at the GSC have identified Au


(a)
(b)
As, ppb
n=24
10%
20%
Ba, ppm
n=24
5%
Cd, ppb
n=24
10%
15%
Ce, ppb
n=24
10%
15%
Cu, ppb
n=24
10%
40%
n=3
I, ppb
n=24
45%
40%
(a)
(b)
Difference
Mean

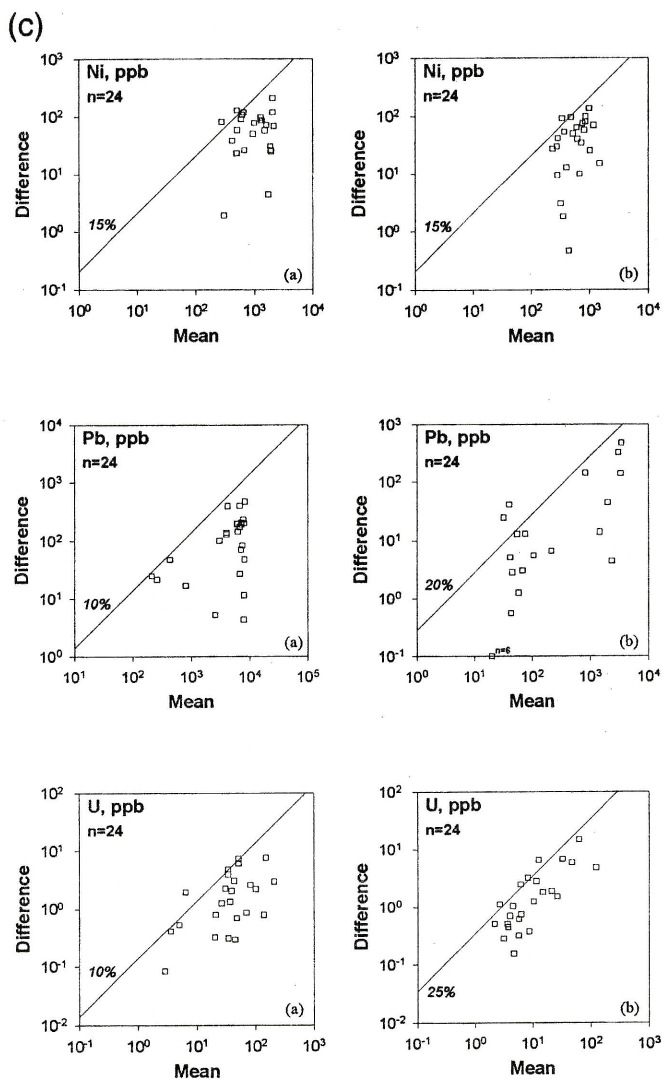


Fig. 3. (a) Thompson and Howarth (1978) plots for As, Ba and Cd in analytical duplicate soil samples collected in Nevada, by $NH_2OH \cdot HCl$ leaches for (a) amorphous Fe oxide phase and (b) Mn oxide phase. (data from Hall et al., 1997b). (b) Thompson and Howarth (1978) plots for Ce, Cu and I in analytical duplicate soil samples collected in Nevada, by $NH_2OH \cdot HCl$ leaches for (a) amorphous Fe oxide phase and (b) Mn oxide phase (data from Hall et al., 1997b). (c) Thompson and Howarth (1978) plots for Ni, Pb and U in analytical duplicate soil samples collected in Nevada, by $NH_2OH \cdot HCl$ leaches for (a) amorphous Fe oxide phase and (b) Mn oxide phase (data from Hall et al., 1997b).

as being the element of concern (Hall et al., 1995). Studies of soils and sediments indicated that significant readsorption was occurring in both $NH_2OH \cdot HCl$ and $Na_4P_2O_7$ leaches. Recovery of organically bound Au, by application of the latter leach to an organic-rich lake sediment, was found to be dependent on sample weight/leach volume ratio, ranging from 59 (3 g sample) to 128 ppb Au (0.5 g sample). Recoveries of 30% or less were obtained for Au spikes added to soil and sediment samples undergoing both leaches. Analysis of the residues confirmed that the ‘lost’ Au was indeed on the sample; that is, ‘lost’ Au was not in a colloidal form in solution which required digestion prior to analysis. The MO-

MEO procedure used in China to quantify various labile forms of elements involves a second treatment for Au specifically, to release Au from a colloidal form present in the leach solution after extraction (see Wang, 1998). This is *not* the problem of readsorption discussed by Hall et al. (1995).

The degree of readsorption of Au taking place in an iodide extraction of various soil matrices has been studied by Gray et al. (1998). A sachet of activated carbon served to preferentially sorb the Au released from these soils and was therefore subsequently analysed. However, the dependency of results on leaching time seriously limits the practicality of this partial extraction. Other work has suggested that readsorption may be occurring in slightly acidic leaches for elements such as Sb and Mo which form oxyanions and are more stable under alkaline conditions (Hall et al., 1997b). The degree of readsorption occurring depends upon the element itself, the chemical characteristics of the extractant, the sample constituents and the conditions of extraction. More research is needed in this area to elucidate the mechanisms of redistribution and to ascertain its effect on geochemical patterns obtained in selective leach surveys.

5. Concluding remarks

The application and development of selective leaches in exploration geochemistry is in a growth period. The degree of accuracy achieved in their application affects the interpretation of survey data and elucidation of mechanisms of element migration. More studies are needed to assess this accuracy, especially for the Enzyme and MMI leaches where publications are few. Evaluation of precision should be more extensive, particularly to gain insight into the relative contributions of field sampling reproducibility and analytical method variation. Research at the GSC has shown that analytical precision is excellent for the hydroxylamine hydrochloride and pyrophosphate leaches, with RSDs generally below 10%. Some low-abundance elements such as Sb, Bi, Se and Te require additional sensitivity of measurement by introducing them as their gaseous hydrides rather than direct ICP–MS analysis. The optimum method of sample preservation for the various modes of occurrence also needs to be better defined. With these basic requirements recognised, the question *which phase (or binding mechanism) should be analysed, in which sample type, at what size fraction, and under what field conditions* will be easier to answer.

References

Alloway, B.J., 1990. Heavy Metals in Soils. Blackie, Glasgow, 339 pp.

Anderson, B.J., Jenne, E.A., Chao, T.T., 1973. The sorption of silver by poorly crystallised manganese oxides. Geochim. Cosmochim. Acta 37, 611–622.

Antropova, L.V., Goldberg, I.S., Voroshilov, N.A., Ryss, Ju.S., 1992. New methods of regional exploration for blind mineralization: application in the USSR. J. Geochem. Explor. 43, 157–166.

Bascomb, C.L., Thanigasalam, K., 1978. Comparison of aqueous acetylacetone and potassium pyrophosphate solution for selective extraction of organic-bound Fe from soils. J. Soil Sci. 29, 382–387.

Belzile, N., Lecomte, P., Tessier, A., 1989. Testing readsorption of trace elements during partial chemical extractions of bottom sediments. Environ. Sci. Technol. 23, 1015–1020.

Borggaard, O.K., 1982. Selective extraction of amorphous iron oxides by EDTA from selected silicates and mixtures of amorphous and crystalline iron oxides. Clay Miner. 17, 365–368.

Bradshaw, P.M.D., Thomson, I., Smee, B.W., Larsson, J.O., 1974. The application of different analytical extractions and soil profile sampling in exploration geochemistry. J. Geochem. Explor. 3, 209–225.

Butt, C.R.M., Zeegers, H., 1992. Regolith Exploration Geochemistry in Tropical Terrains and Subtropical Terrains. Elsevier, Amsterdam, 607 pp.

Chao, T.T., 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. Soil Sci. Soc. Am., Proc. 36, 764–768.

Chao, T.T., 1984. Use of partial dissolution techniques in geochemical exploration. J. Geochem. Explor. 20, 101–135.

Chao, T.T., Theobald, P.K., 1976. The significance of iron and manganese oxides in geochemical exploration. Econ. Geol. 71, 1560–1569.

Chao, T.T., Zhou, L., 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. Soil Sci. Soc. Am., Proc. 47, 225–232.

Clark, J.R., 1993. Enzyme-induced leaching of B-horizon soils for mineral exploration in areas of glacial overburden. Trans. Inst. Min. Metall. 102, B19–B29.

Gatehouse, S., Russell, D.W., Van Moort, J.C., 1977. Sequential soil analysis in exploration geochemistry. J. Geochem. Explor. 8, 483–494.

Goldberg, I.S., 1998. Vertical migration of elements from mineral deposits. J. Geochem. Explor. 61, 191–202, (this volume).

r defined. With
.l. the question
should be anal-
size fraction,
ll be easier to

Blackie, Glasgow,

The sorption of
oxides. Geochim.

N.A., Ryss, Ju.S.,
for blind mineral-
chem. Explor. 43,

parison of aqueous
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ls. J. Soil Sci. 29,

sting readsorption
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f amorphous iron
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Miner. 17, 365-

., Larsson, J.O.,
l extractions and
stry. J. Geochem.

ration Geochem-
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nese oxides from
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chniques in geo-
0), 101–135.

ance of iron and
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ues for selective
soils and sedi-
2.

-horizon soils for
den. Trans. Inst.

1977. Sequential
eochem. Explor.

nts from mineral
his volume).

Gray, D.J., Lintern, M.J., Longman, G.D., 1998. Readsorption of gold during selective extraction — observations and potential solutions. J. Geochem. Explor. 61, 21–37, (this volume).

Hale, M., Plant, J.A., 1994. Drainage Geochemistry in Mineral Exploration. Elsevier, Amsterdam, 766 pp.

Hall, G.E.M., 1996. Twenty-five years in geoanalysis, 1970–1995. J. Geochem. Explor. 57, 1–8.

Hall, G.E.M., Pelchat, P., 1997a. Comparison of two reagents, sodium pyrophosphate and sodium hydroxide, in the extraction of labile metal organic complexes. Water Air Soil Pollut., in press.

Hall, G.E.M., Pelchat, P., 1997b. Comparability of results obtained by the use of different selective extraction schemes. Water Air Soil Pollut., in press.

Hall, G.E.M., MacLaurin, A.I., Vaive, J.E., 1995. Readsorption of gold during the selective extraction of the 'soluble organic' phase of humus, soil and sediment samples. J. Geochem. Explor. 54, 27–38.

Hall, G.E.M., Vaive, J.E., Beer, R., Hoashi, M., 1996a. Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction. J. Geochem. Explor. 56, 59–78.

Hall, G.E.M., Vaive, J.E., MacLaurin, A.I., 1996b. Analytical aspects of the application of sodium pyrophosphate reagent in the specific extraction of the labile organic component of humus and soils. J. Geochem. Explor. 56, 23–36.

Hall, G.E.M., MacLaurin, A.I., Pelchat, J.C., Gauthier, G., 1997a. Comparison of the techniques of atomic absorption spectrometry and inductively coupled plasma mass spectrometry in the determination of Bi, Se and Te by hydride generation. Chem. Geol. 137, 79–89.

Hall, G.E.M., Vaive, J.E., Button, P., 1997b. Detection of past underground nuclear events by geochemical signatures in soils. J. Geochem. Explor. 59, 145–162.

Jeanroy, E., Guillet, B., 1981. The occurrence of suspended ferruginous particles in pyrophosphate extracts of some soil horizons. Geoderma 26, 95–105.

Kabata-Pendias, A., Pendias, H., 1984. Trace Elements in Soils and Plants. CRC Press, Boca Raton, FL, 315 pp.

Kauranne, L.K., Salminen, R., Eriksson, K., 1992. Regolith Exploration Geochemistry in Arctic and Temperate Terrains. Elsevier, Amsterdam, 443 pp.

Kersten, M., Forstner, U., 1989. Speciation of trace elements in sediments. In: Batley, G. (Ed.), Trace Element Speciation: Analytical Methods and Problems. CRC Press, Boca Raton, FL, pp. 245–317.

Levinson, A.A., 1974. Introduction to Exploration Geochemistry. Applied Publishing, Calgary, 612 pp.

Loganathan, P., Burau, R.G., 1973. Sorption of metal ions by a hydrous manganese oxide. Geochim. Cosmochim. Acta 37, 1277–1293.

Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B., Perdrix, J.L., 1998. Application of the mobile metal ion technique to routine geochemical exploration. J. Geochem. Explor. 61, 87–102, (this volume).

McKeague, J.A., Brydon, J.E., Miles, N.M., 1971. Differentiation of forms of extractable iron and aluminium in soils. Soil Sci. Soc. Am., Proc. 35, 33–38.

McLaren, R.G., Crawford, D.V., 1973. Studies on soil copper II. The specific adsorption of copper by soils. J. Soil Sci. 24, 172–181.

Overstreet, W.C., Lowering, T.G., Rosenblum, K., Hubert, A.E., Crenshaw, G.L., 1978. Minor elements in magnetic concentrates from Alaska. U.S. Geol. Surv. Rep. USGS-GD-78-004, 596 pp.

Pickering, W.F., 1986. Metal ion speciation — soils and sediments (a review). Ore Geol. Rev. 1, 83–146.

Qiang, T., Xiao-Quan, S., Jin, Q., Zhe-Ming, N., 1994. Trace element redistribution during extraction of model soils by acetic acid/sodium acetate. Anal. Chem. 66, 3562–3568.

Rendell, P.S., Batley, G.E., Cameron, A.J., 1980. Adsorption as a control of metal concentrations in sediment extracts. Environ. Sci. Technol. 14, 314–318.

Robbins, J.M., Lyle, M., Heath, G.R., 1984. A sequential extraction procedure for partitioning elements among coexisting phases in marine sediments. College of Oceanography, Rep. 84-3, Oregon State Univ., Corvallis.

Rose, A.W., Hawkes, H.E., Webb, J.S., 1979. Geochemistry in Mineral Exploration. Academic Press, New York, 655 pp.

Ryss, J.S., Cherfas, M.A., Goldberg, I.C., Voroshilov, N.A., Siegel, H.O., Kinrade, J., Chance, P., 1990. Final report on the 1990 geochemical test program conducted by NPO Rudgeofizika and Scintrex Limited. Unpublished, 41 pp.

Schnitzer, M., Khan, S.U., 1972. Humic Substances in the Environment. Marcel Dekker, New York, 327 pp.

Schnitzer, M., Schuppli, P., 1989. Method for the sequential extraction of organic matter from soils and soil fractions. Soil Sci. Soc. Am. J. 53, 1418–1424.

Sondag, F., 1981. Selective extraction procedures applied to geochemical prospecting in an area of old mine workings. J. Geochem. Explor. 15, 645–652.

Span, D., Gaillard, J.F., 1986. An investigation of a procedure for determining carbonate-bound trace metals. Chem. Geol. 56, 135–141.

Taylor, R.M., 1990. Some observations on the formation and transformation of iron oxides. In: De Boodt, M.F. (Ed.), Soil Colloids and Their Associations in Aggregates. Plenum Press, New York, pp. 85–103.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51, 844–850.

Thompson, M., Howarth, R.J., 1978. A new approach to the estimation of analytical precision. J. Geochem. Explor. 9, 23–30.

Wang, X., 1998. Leaching of mobile forms of metals in overburden: development and application. J. Geochem. Explor. 61, 39–55, (this volume).

Zeissink, H.E., 1971. Trace element behaviour in two nickeliferous laterite profile. Chem. Geol. 7, 25–36.

Pergamon

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Pb isotopic ratios and elemental abundances for selective leachates from near-surface till: implications for mineral exploration

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Abstract—Pb isotope ratios obtained from fine-grained fractions (<63 and <2 μm) from near-surface (<1 m depth) till surrounding ore deposits show isotopic overprinting from the underlying sulfide mineralization, and provide a new approach to mineral exploration for massive sulfide deposits (VMS) in glaciated terrains.

In this study, Pb isotopic measurements, and selective leaching of 6 near-surface till samples down-ice from the Chisel Lake (Manitoba) and Manitouwadge (Ontario) VMS deposits were carried out in order to determine the location and nature of the Pb within till. Elemental abundances from selective leachates for all 6 samples display similar patterns and show that chalcophile elements (Cu, Ni, Pb and Zn), derived predominantly from the underlying VMS deposits, occur as (i) adsorbed/exchangeable metals; (ii) associated with oxyhydrous Fe and Mn; (iii) crystalline Fe oxides, and/or (iv) silicate. Despite the relative proximity of some of the till samples to the VMS deposits, only a very small component of the chalcophile elements is present as sulfide. This result is consistent with those from studies of weathered (oxidized) tills, which show that labile minerals such as sulfides have been completely destroyed and their chemical constituents reprecipitated or scavenged locally by clay-sized phyllosilicates and secondary oxides/hydroxides.

Pb isotopic ratios for selective leachates from till samples with VMS-like (anomalous) signatures are similar to those from ore (galena) within the proximal VMS deposits. This indicates that the Pb is of a secondary nature and was probably scavenged and deposited after destruction of original sulfide minerals during till formation. The lack of a predominant sulfide-held Pb component within the selective leachates supports this interpretation. In contrast, Pb isotopic ratios for the same selective leachates from "background" samples are significantly higher and show that the Pb is not derived from proximal VMS deposits but from a more radiogenic source.

Till samples were also leached using 2.5 M HCl ("conventional" leaching). The Pb isotope ratios from the conventional leachates are similar to those obtained from the selective leachates, and show a large difference in Pb isotopic ratios between anomalous and background samples. We propose, therefore, that the conventional leaching rather than selective leaching or complete dissolution of a particular grain-size fraction be adopted for mineral exploration purposes using glacial sediments.

The results from this study support the effective use of Pb isotope ratios from near-surface till as an exploration tool despite the weathered nature of the latter. We feel that this represents a more cost-effective technique over traditional geochemical prospecting methods, if used in conjunction with Pb abundance data. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Mineral exploration for ore deposits in glaciated terrains is complicated by glacial dispersal of mineralized bedrock and burial of ore beneath glacigenic sediment. Pb isotopic analysis of overburden, such as gossans, soils, stream sediments, and weathered bedrock, however, has been used as an effective exploration tool for concealed mineralization (e.g. Gulson, 1986 and references within; Gulson *et al.*, 1992). The application of Pb isotopes in mineral exploration for base and precious metal deposits using surficial sediments has been successful because: 1) Pb isotope ratios are not altered in the transition from the ore body to the secondary weathering environment (Gulson, 1986); 2) the isotope signature of some VMS deposits can be quite different to those of the country rock; and 3) Pb isotopic ratios are quantitatively and objectively measured.

Recently, Pb isotope ratios from glacigenic sediments overlying several known volcanogenic massive sulfide deposits (VMS) in Canada, such as Chisel Lake

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(Manitoba: Bell and Franklin, 1993), Buchans (Newfoundland: Bell and Murton, 1995), and Manitouwadge (Ontario: Bell and Card, in prep.) clearly indicate an overprint from the adjacent ore deposits and may provide a new method for detecting buried ore bodies. Pb isotopic ratios from the <63 and <2 μm fractions of till from Buchans (Bell and Murton, 1995), and Chisel Lake (Bell and Franklin, 1993) show a large variation; in general, till samples with overprinted Pb isotopic ratios usually contain higher abundances of Pb, and are close to the ore deposit (< 1 km). On the basis of their Pb abundances, Pb isotopic ratios, and down-ice location with respect to ore deposits (Figs 1 and 2), 6 till samples (< 63 μm fraction), 4 from Chisel Lake (Manitoba) and 2 from Manitouwadge (Ontario), have been selected for this study. The samples from both deposits include those with lower, "ore-like" Pb isotopic ratios ($^{206}Pb/^{204}Pb$ < 18.00), here referred to as "anomalous" samples, whereas those with higher, more radiogenic (crust-like) isotopic ratios are referred to as "background" samples. Although studies have shown the important use of Pb isotopes in glacial geology (Bell and Murton, 1995) and mineral exploration (Bell and Franklin, 1993), the exact location and nature of the Pb being held within glacigenic sediments is still unknown. Identification of the main binding sites for trace metals is important, providing both insight concerning the geochemical processes during and after till formation, and discrimination between trace-metal sources.

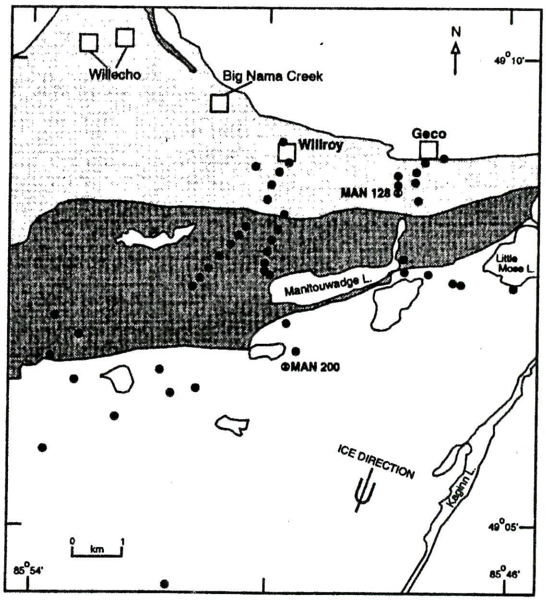

Fig. 2. Simplified geological map of the Manitouwadge area showing till sample locations (solid dots, Bell and Card, in prep.). Samples used in this study are indicated as labelled circles. Lighter shading ("Grey Gneiss Group")—is composed of both metasedimentary and minor felsic volcanic rocks; Darker shading ("Hornblende Schist Group") consists of highly deformed mafic, pillowed metavolcanic rocks (Williams *et al.*, 1990); Squares—massive sulfide deposits.

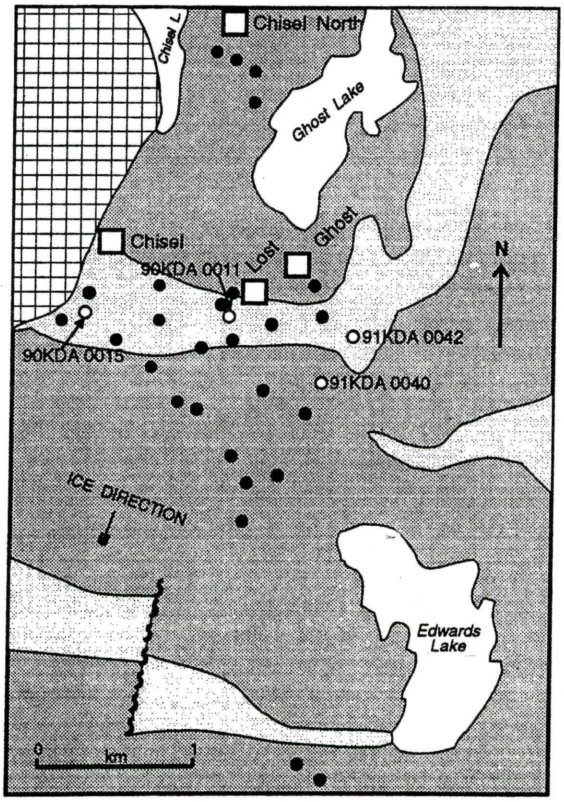

Fig. 1. Simplified geological map of the Chisel Lake area showing location of till samples (solid dots). Samples used in this study are indicated by labelled circles. Grid pattern—Chisel Lake gabbro; light shading—felsic flows, wackes, and breccias; dark shading—mafic flows, wackes, and breccias; Squares—massive sulfide deposits (modified after Bell and Franklin, 1993).

Ore and pathfinder elements are transported by various mechanisms from the source to the surficial environment, where they are held in relatively labile forms associated with different reaction sites (Hall *et al.*, 1993, in press). Organic matter and hydrous coatings of Fe and Mn are the most important surface-active phases ("scavengers"), which are widely distributed in subaerial and subaqueous environments, and have long provided an exploration tool (e.g. Hawkes and Webb, 1962; Levinson, 1980). Formation of Fe and Mn oxides and their metal capture is dependent on the Eh and pH of aqueous solutions, and the activities of many heavy metals are at a minimum in equilibrium with their hydroxides (Jenne, 1962). Selective extraction methods, therefore, have been used in exploration geochemistry to examine only those metals adsorbed on, or included in, specific mineral phases. A summary of the theory, analytical procedures and applications of selective leaches can be found in Chao (1984). Recently, a sequential leaching technique has been developed by the Analytical Method Development section of the Geological Survey of Canada (Hall *et al.*, 1993, in press). The technique was designed to mimic the action of 2 Soviet selective leaching methods — "MPF" and "TMGM" (e.g. Antropova *et al.*, 1992). The "MPF" method is based on the extraction of metal-organic complexes, whereas the "TMGM" technique is intended to extract elements adsorbed by amorphous forms of Fe and Mn oxyhydroxides (Hall *et al.*, 1993, in press).

Selective leaching was conducted on the <63 μm size fraction from 6 till samples because this grain size fraction is widely used in mineral exploration, and it is much cheaper to extract than other finer-grained size fractions (e.g. <2 μm). The aims of this study are to determine the concentration of Pb and other trace metals in selective leachates and measure the Pb isotopic ratio of each Pb-bearing leachate in an attempt to assess its source — i.e. crustal or VMS-derived. The applied objective is to identify the leaching method (selective vs conventional) which best serves for VMS exploration in glaciated terrains, using Pb isotopes.

GEOLOGY

Two locations were chosen for this study, one in Manitoba and the other in Ontario. Both are associated with Precambrian VMS deposits associated with greenstone belts. Sampling of both areas was carried out during an evaluation programme of the use of Pb isotopes for mineral exploration in glacial sediments.

Chisel Lake

Sampling of the Quaternary cover that overlies the Zn–Cu sulfide deposits at Chisel Lake, near Snow Lake, northern Manitoba (Fig. 1) was completed in 1991 by the Geological Survey of Canada, and material was supplied for Pb isotope analyses. Four sulfide deposits, the Chisel Lake, Chisel Lake North, Lost and Ghost deposits, are present in the bimodal volcanic suite of the early Proterozoic-age Amisk Group (Fig. 1 of Bailes and Galley, 1989; Galley *et al.*, 1990). The deposits and country rocks have been dated at 1889 Ma (U/Pb data; Bailes, 1992). The ore bodies are composed of at least 7.4 million tonnes (t) with an average grade of 10.9% Zn, 1.4% Pb and 0.5% Cu. They contain pyrite, sphalerite, chalcopyrite and galena, as well as trace amounts of arsenopyrite, tetrahedrite and native gold. The deposits are immediately above and adjacent to rhyolite domes and below dacitic ash and breccia. Extensive metamorphosed alteration pipes consisting of muscovite, staurolite, chlorite, gedrite, garnet and pyrite underlie the deposits. Lateral to and slightly below the deposits are zones of garnet–chlorite–muscovite–staurolite and for several hundred meters below the ore horizon the rocks are silicified and albitized. Lower in the succession thick mafic flows are intercalated with felsic ash and flow sequences. The country rocks are part of the juvenile core of the Trans-Hudson orogen, an arc-related sequence that formed between 1950 and 1835 Ma ago and which was tectonized during the Hudsonian collisional event. All of the rocks are metamorphosed to middle amphibolite grade. Till samples were collected (Fig. 1) from sites <4 km down-ice of the deposits. On the basis of pebble content (C. Kaszycki, 1993, personal commun.), the till (<3 m thick) is considered to be of local provenance and forms a single unit of material derived from Proterozoic rocks of the Snow Lake area. The ice direction is roughly 190 to 210°. The 4 samples from Chisel Lake (90KDA 0011, 0015; 91KDA 0040, 0042) are from the C-horizon, which varies in depth from 0.30 to 0.80 meters.

Manitouwadge

Till samples were collected during a 1992 field excursion, primarily to the south and immediately down-ice from the Willroy and Geco VMS deposits (Fig. 2) Both deposits are hosted by the highly deformed (refolded synform), Archean Manitouwadge greenstone belt, which consists of a wide variety of rock types including metavolcanic, metasedimentary and metamorphosed Fe formation, and lies within the Wawa subprovince of the Archean Superior Province (Peterson and Zaleski, 1994; Zaleski and Peterson, 1993; Williams and Breaks, 1990; Zaleski *et al.*, 1994). The Geco Cu mine and several other previously-worked deposits lie south of the main belt of synvolcanic alteration and in most areas are associated with Fe formations. Intrusive rocks within the greenstone belt include foliated diorites to granites, gabbro, K-feldspar-megacrystic granodiorite and strongly foliated to massive pegmatites (Zaleski and Peterson, 1993; Zaleski *et al.*, 1994). Host rocks surrounding the Manitouwadge greenstone belt consist of granites and granite gneisses. The greenstone belt is host to 4 known VMS deposits, the largest of which is the Geco Cu–Zn–Ag deposit (Friesen *et al.*, 1982) and contains an ore grading of 1.9% Cu, 3.8% Zn, 1.7 ounces of Ag/ton, and minor amounts of Au, Cd, Bi and Pb (0.30%) (Williams *et al.*, 1990). Mineralization consists of deformed massive sulfides, predominantly pyrite–pyrrhotite–sphalerite–chalcopyrite which is spatially associated with banded ironstone horizons (Williams *et al.*, 1990; Williams and Breaks, 1989).

Glacial sediments in the Manitouwadge area are thought to have been deposited during the Late Wiconsinean, with striae measurements indicating that the predominant ice flow direction was toward 210–220° (Kristjansson and Geddes, 1985; Geddes and Bajc, 1985; Barnett *et al.*, 1991; Kettles, 1993a, 1993b). The till commonly forms a thin, discontinuous veneer (up to 1.5 m thick), but can exceed 10 m thickness in some places (Kristjansson and Geddes, 1985; Geddes and Bajc, 1985). Geochemical analysis of 286 till samples (Kettles and Murton, 1994) indicates the presence of local Precambrian lithologies and/or a large component of Paleozoic carbonate debris, transported more than 100 km from the Hudson and James Bay lowlands. In addition, high concentrations of Cu, Pb and Zn occur within the <63 and <2 μm fractions of till located near the main Manitouwadge VMS deposits (Kettles and Murton, 1994). MAN 128 is from the B/C horizon located at a depth of ~0.4 to 0.5 meters which contains some rusty brown mottles (Fe oxides) indicative of weathering. MAN 200 is a sample of olive–grey, C-horizon till taken at a depth of 0.60 to 0.65 meters.

ANALYTICAL METHODS

Approximately 1 g of till from the <63 μm fraction was sequentially leached according to the method briefly outlined in Table 1 (see Hall *et al.*, 1993, in press for details). Leachate solutions were subsequently evaporated to dryness and conditioned with 3 to 4 ml of 1N HBr acid. Lead was separated in HBr and HCl using a two-column (0.5 and 0.2 ml) extraction procedure (see Simonetti *et al.*, 1995 for details). Samples for Pb isotopic analyses were run on a single Re filament with silica gel and phosphoric acid using a Finnigan-MAT 261 solid-source mass spectrometer in the static mode. Blank levels for Pb in selective extraction reagents (Table 1) range from 0.001 to 0.004 ppm, whereas the total procedural Pb blank varies from 0.2 to 1.5 ng.

RESULTS

Distribution of Pb and other chalcophile elements

Elemental concentrations, obtained using atomic absorption spectrometry (AAS) at the Geological Survey of Canada, for all selective leachates are shown in Table 2, and abundances for various base metals (Cu, Ni, Pb and Zn), are plotted against their respective leachates (A to H) in Figs 3 and 4. Table 2 and Figs 3 and 4 show that the Pb contained within the 6 till samples occurs predominantly in 4 different forms: (1) water-soluble and exchangeable metal (adsorbed); (2) hydrous oxide of Fe or Mn (FeOH–MnOH); (3) crystalline FeO; (4) silicate and/or residual oxide. An extremely important finding is that *negligible* Pb is held in the sulfide form (leachates G, Table 2). Figure 3 shows that the till sample with the highest Pb concentration (88 ppm), 90KDA 0011 from Chisel Lake, has more than 50% of the Pb held as either an adsorbed metal (leachates A, B) or as an FeOH–MnOH (leachates C, D). In addition, "anomalous" samples 90KDA 0011 and 0015 from Chisel Lake and MAN 128 from Manitouwadge display a similar Pb distribution pattern to those for some "background" samples from the same deposit (Figs 3 and 4), although the latter plot at lower concentrations.

The distribution of the chalcophile elements Cu, Ni and Zn, typically abundant within VMS deposits, for the selective leachates are also shown in Figs 3 and 4. The distribution of these elements is similar to that of Pb, since they occur predominantly as either adsorbed metals, hydrous oxides of Fe and Mn, crystalline FeO, or silicates. A small proportion of the Cu, Ni and Zn occur as sulfides (Figs 3 and 4), which may suggest that sulfide minerals, such as chalcopyrite, and pyrrhotite, are present in trace amounts. A duplicate analysis of Chisel Lake sample 90KDA 0011 (Table 2) shows a mean reproducibility of approximately 2% for the quoted concentrations. In addition, shown in Table 3 are the mean and standard deviation values for various elements in control samples TILL-2 and LKSD-4 (from Hall *et al.*, in press). Abundances for control sample TILL-2, obtained during the course of this study, fall within the accepted standard deviations (Table 3).

Pb isotopic overprinting of some of the till samples (90KDA 0011, 90KDA 0015 and MAN 128) by the underlying ore deposit has been shown by Bell and Franklin (1993) and this occurs despite the lack of Pb in the sulfide form (Table 2). This indicates that a large component of the Pb which occurs as either an adsorbed metal (leachates A, B), hydrous oxide of Fe or Mn (leachates C, D), or crystalline FeO (leachates E, F) must have been derived from the ore deposit. It is highly probable that the dominant Pb–sulfide mineral associated with VMS deposits, galena (PbS), was

Table 1. Sequential extraction scheme (Hall *et al.*, 1993)

Extractant	Phases dissolved	Leachate symbol used
1 M NaOAc.HOAc 1 g sample/20 ml 2 × 6 hr constant shaking	Adsorbed metals, exchangeable, carbonates and some phosphates	**A, B**
0.25 M $NH_2OH.HCl$ in 0.25 M HCl 20 ml reagent, at 60°C; first leach for 2 hr, second for 0.5 hr	Amorphous oxyhydrides of Fe and Mn	**C, D**
1 M $NH_2OH.CHl$ in 25% HOAc 30 ml reagent, at 90°C; first leach for 3 hr, second leach for 1.5 hr	Crystalline Fe oxides (e.g., hematite, goethite, magnetite, maghemite, lepidocrocite)	**E, F**
$KClO_3/HCl$, 15 ml, for 0.5 hr with mixing; followed by 4M HNO_3 (10 ml) at 90°C	Sulphides and "less soluble" organic matter	**G**
HF–$HC1O_4$–HNO_3–HCl, 10 ml, to dryness	Silicates, residual crystalline fraction (refractory minerals could remain in a final residue)	**H**

Table 2. Elemental concentrations of selective extraction leachates from < 63 μm fraction of till samples

	Leachates								
	A	B	C	D	E	F	G	H	Total
Pb (ppm):									
90KDA 0011	37	5	24	1	6	-	-	15	88 (79)
90KDA 0011 Dup.	37	5	23	1	8	1	-	14	89
90KDA 0015	2	1	11	1	-	1	-	12	28 (26)
91KDA 0040	-	-	1	-	-	-	-	11	12 (11)
91KDA 0042	-	-	-	-	-	-	-	10	10 (12)
MAN 128	4	1	7	1	4	-	1	10	28 (29)
MAN 200	1	1	4	-	1	-	-	8	15 (11)
Blank*	-	-	0.5	-	1	-	-	-	1.5
Cu(ppm):									
90KDA 0011	8	2	84	11	47	5	14	31	202
90KDA 0011 Dup.	9	2	83	10	48	5	14	31	202
90KDA 0015	2	-	22	2	14	-	5	4	49
91KDA 0040	1	-	11	2	8	-	4	3	29
91KDA 0042	2	-	29	7	17	1	4	5	65
MAN 128	1	1	11	4	15	1	4	4	41
MAN 200	-	-	4	1	8	-	4	2	19
Blank*	-	-	-	-	-	-	1	-	1
Zn(ppm):									
90KDA 0011	2	1	189	37	130	10	30	64	463
90KDA 0011 Dup.	2	-	186	36	135	10	29	64	462
90KDA 0015	2	-	114	10	56	6	19	30	237
91KDA 0040	-	-	17	3	16	3	9	19	67
91KDA 0042	-	-	16	2	8	1	8	23	58
MAN 128	4	1	87	32	135	9	15	35	318
MAN 200	-	-	9	3	14	2	9	16	53
Blank*	-	-	-	-	-	-	4	-	4
Ni(ppm):									
90KDA 0011	-	-	8	1	8	-	4	9	30
90KDA 0011 Dup.	-	-	8	-	8	1	7	9	33
90KDA 0015	-	-	10	1	10	1	5	13	40
91KDA 0040	-	-	7	1	8	1	5	10	32
91KDA 0042	-	-	9	1	6	-	3	10	29
MAN 128	-	-	2	-	8	1	3	8	22
MAN 200	1	-	5	2	14	1	5	12	40
Blank*	1	-	-	-	-	-	1	1	3
Mn(ppm):									
90KDA 0011	2	-	35	4	29	5	11	191	277
90KDA 0011 Dup.	2	-	35	4	29	5	11	188	274
90KDA 0015	6	1	80	4	29	5	14	187	326
91KDA 0040	8	6	89	5	34	6	17	211	376
91KDA 0042	1	-	30	4	19	4	9	316	383
MAN 128	-	-	8	3	28	5	9	138	191
MAN 200	17	13	88	12	55	9	20	158	372
Blank*	-	-	-	-	-	-	-	-	-
Fe(ppm):									
90KDA 0011	48	28	5858	828	6925	1070	2975	16560	34292
90KDA 0011 Dup.	47	26	5865	780	6950	1140	2938	16940	34686
90KDA 0015	53	27	8400	1062	8300	985	2925	14160	35912
91KDA 0040	40	32	5588	885	7400	1070	3013	14460	32488
91KDA 0042	98	38	7005	1314	6750	805	2175	19800	37985
MAN 128	247	135	2258	477	4788	660	1475	7800	17840
MAN 200	106	63	5610	1143	7700	885	2413	10540	28460
Blank*	–	–	-	1	2.5	-	-	2.5	6
Co(ppm):									
90KDA 0011	-	-	3	-	1	-	-	4	8
90KDA 0011 Dup.	-	-	2	-	1	-	-	4	7
90KDA 0015	-	-	4	-	1	-	-	4	9
91KDA 0040	-	-	3	-	3	-	-	4	10
91KDA 0042	-	-	4	-	-	-	-	6	10
MAN 128	-	-	1	-	1	-	-	3	5
MAN 200	-	-	2	-	3	-	1	4	10
Blank*	-	-	-	-	-	-	0.5	-	0.5

Leachates: A—1st leachate for adsorbed/exchangeable metal; **B**—2nd leachate for adsorbed and exchangeable metal; **C**—1st leachate for hydrous oxides of Fe and Mn **(FeOH–MnOH)**; **D**—2nd leachate for hydrous oxides of Fe and Mn **(FeOH–MnOH)**; **E**—1st leachate for crystalline FeO; **F**—2nd leachate for crystalline FeO; **G**—sulphides; **H**—silicates and residual oxides. Value in bracket for Pb concentrations obtained by ICP analysis, and uncertainty is ± 10% of quoted value. Dup. = duplicate analysis; (-) = not detected; * = average values for two runs.

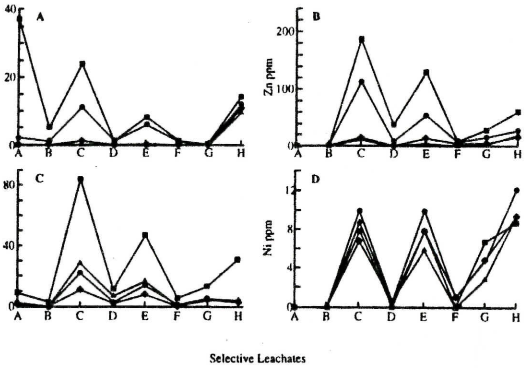

Fig. 3. Plots of elemental abundances vs selective leachates for till samples from Chisel Lake. Letters correspond to the following leachates: **A**—1st leachate for adsorbed and exchangeable metal; **B**—2nd leachate for adsorbed and exchangeable metal; **C**—1st leachate for hydrous oxides of Fe and Mn (FeOH–MnOH); **D**—2nd leachate for hydrous oxides of Fe and Mn (FeOH–MnOH); **E**—1st leachate for crystalline FeO; **F**—2nd leachate for crystalline FeO; **G**—sulfide leachate; **H**—silicate and/or residual oxide leachate. Solid square—90KDA 0011; Solid circle—90KDA 0015; Solid diamond-91KDA 0040; Solid triangle—91KDA 0042. A) Pb (ppm); B) Zn (ppm); C) Cu (ppm); D) Ni (ppm).

completely destroyed by glacial processes associated with till formation. The Pb isotopic ratios for the different Pb-bearing selective leachates will certainly provide much needed insight into the source of the Pb.

Pb isotopic ratios—Chisel Lake

Pb isotopic measurements for Pb-bearing selective leachates from Chisel Lake are listed in Table 4 and shown in Figs 5 and 6. Selective leachates A through F from anomalous samples 90KDA 0011 and 0015 contain relatively constant Pb isotopic ratios similar to those from the galena within the Chisel Lake VMS deposits (Fig. 5). In contrast, the silicate leachates (H) from both of these samples contain Pb isotopic ratios that are higher than those from the earlier leachates. The Pb isotopic ratios from total dissolution of the <63 μm fraction for both 90KDA 0011 and 0015 are intermediate between those obtained for the early leachates (adsorbed metal through to FeOH–MnOH, A to D), and those from the crystalline FeO (E) and silicate (H) leachates (Table 4). The Pb isotopic ratios for selective leachates from a separate, duplicate sequential leaching of 90KDA 0011 show excellent reproducibility, and, with one exception (silicate leachate-H), the duplicate analyses are the same order as duplicates on till (0.1%, 2σ level, Table 4).

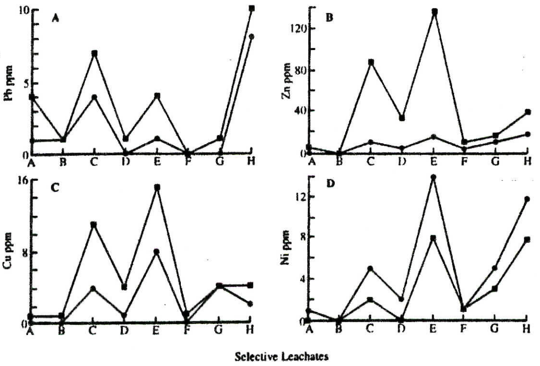

Fig. 4. Plots of elemental abundances vs selective leachates for Manitouwadge till samples. Letters representing selective leachates are as in Fig. 3 and Table 1. Solid square—MAN 128; Solid circle—MAN 200. A) Pb (ppm); B) Zn (ppm); C) Cu (ppm); D) Ni (ppm).

In contrast, the Pb isotopic composition for selective leachates from the 2 background till samples from Chisel Lake (91KDA 0040, 0042) differ from those obtained from the anomalous samples. Firstly, sample 91KDA 0042 contains Pb that is restricted mainly to the silicate minerals, whereas 91KDA 0040 contains Pb in both the first FeOH–MnOH (C) and silicate (H) leachates. All of these 3 leachates give Pb isotopic ratios that are much higher than the signature of the Chisel Lake galena. The highly radiogenic Pb isotopic composition ($^{206}Pb/^{204}Pb > 23.00$) for the FeOH–MnOH leachate (C) from sample 91KDA 0040 clearly shows that this Pb is derived from a different source to that found in the anomalous samples ($^{206}Pb/^{204}Pb$ range = 15.88 to 16.79). Pb in sample 91KDA 0040, was probably derived from the breakdown of rocks with much higher U/Pb ratios than VMS deposits such as those of the associated Proterozoic sequences. Another interesting feature is that the Pb isotopic ratios for the silicate leachates from both background samples approach the isotopic composition of the silicate leachates from the two anomalous samples (Fig. 5).

The $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ isotopic plot shown in Fig. 6A shows that analyses from the <63 μm fraction (84 in total) of till from Chisel Lake taken from Bell and Franklin (1993) form a linear array, with a slope of 0.122 ± 0.003 (MSWD = 9.3; corresponding to a date of about 2000 Ma), where the lower end is close to the isotopic signature of the ore deposit. Also shown for reference in Fig. 6 is the Stacey and Kramers (1975) growth curve which reflects the variation of Pb isotopic ratios throughout geologic time in the source region that generated most massive sulfide deposits. The Pb isotopic data from the Chisel Lake ores are close to the 2000 Ma point on the Stacey–Kramers growth curve (Bell and Franklin, 1993). The Pb isotopic ratios determined for selective leachates from the Chisel Lake samples also lie along this same linear array (Fig. 6A). The selective leachates from one of the background samples, 91KDA 0040, show a variation in Pb isotopic ratios that covers much of the range displayed by the 84 analyses of <63 μm fraction of till samples from Chisel Lake. Figures 5 and 6 show that the Pb isotopic ratios for the FeOH–MnOH leachate (C) from background sample 91KDA 0040 are the most radiogenic recorded in any of the size fractions (both <63 and

Table 3. Mean and standard deviation values in ppm for various elements in control samples TILL-2 and LKSD-4 (from Hall *et al.*, in press)

Sample	PHASE						
	AEC (Leach. **A** + **B**)	Am Fe ox (Leach. **C** + **D**)	Cry Fe ox (Leach. **E** + **F**)	Sulphides (Leach. **G**)	Silicates (Leach. **H**)	Total	Recommended[†]
Pb:							
TILL-2 this study	5	10	4	-	10	29	
TILL-2[‡]	4.8 ± 0.8	10.2 ± 0.4	< 1	< 1	8.0 ± 0.7	22.8 ± 1.4	31 ± 3
LKSD-4[*]	4.6 ± 0.8	16.0 ± 1.2	< 1	< 1	6.2 ± 3.3	84 ± 10	91 ± 6
Cu:							
TILL-2 this study	13	53	54	11	24	155	
TILL-2	12.2 ± 0.9	56.1 ± 1.9	46.6 ± 1.3	8.3 ± 2.2	22.4 ± 2.0	146 ± 3	150 ± 10
LKSD-4	< 1	6.8 ± 0.4	4.6 ± 0.9	11.4 ± 3.0	2 ± 0.4	32.2 ± 2.4	31 ± 4
Zn:							
TILL-2 this study	3	31	52	17	24	127	
TILL-2	3.0 ± 0.3	34.1 ± 1.0	44.9 ± 1.4	13.8 ± 2.0	24.0 ± 2.0	120 ± 3	130 ± 8
LKSD-4	9.8 ± 1.8	64.4 ± 5.1	16.2 ± 1.5	9.6 ± 0.5	14.8 ± 3.5	191 ± 10	194 ± 19
Ni:							
TILL-2 this study	-	9	20	6	11	46	
TILL-2	< 1	3.1 ± 1.0	14.6 ± 1.6	5.8 ± 2.1	8.5 ± 0.9	33.3 ± 2.5	32 ± 3
LKSD-4	< 1	10.2 ± 0.8	4.0 ± 1.0	4.8 ± 0.4	5.2 ± 1.3	30.6 ± 1.5	31 ± 5
Mn:							
TILL-2 this study	80	252	144	41	140	657	
TILL-2	86.8 ± 8.3	292 ± 11	125 ± 8	43.8 ± 4.0	145 ± 21	693 ± 40	780 ± 28
LKSD-4	16.0 ± 2.0	56.0 ± 6.0	42.2 ± 3.3	11.2 ± 1.7	83.4 ± 1.9	460 ± 39	500 ± 30
Fe:							
TILL-2 this study	339	8447	15890	4425	6240	35341	
TILL-2	403 ± 52	10190 ± 403	14866 ± 600	4131 ± 457	5821 ± 585	35403 ± 1036	37700 ± 1300
LKSD-4	126 ± 20	4610 ± 580	7591 ± 620	5397 ± 278	4963 ± 354	26182 ± 142	28000 ± 200
Co:							
TILL-2 this study	1	4	4	1	2	12	
TILL-2	1 ± 1	4.8 ± 0.5	4.8 ± 1.7	1 ± 1	3 ± 1	14.5 ± 1.4	15 ± 2

[†]: Recommended values for LKSD-4 from Lynch (1990) and for TILL-2 from Hall *et al.* (in press).

[‡]: Average value for 8 analyses.

[*]: Average value for 5 analyses. In addition, pyrophosphate extraction had been carried out on LKSD-4 prior to the sequential leach of Hall *et al.* (in press).
The total value includes this portion.

< 2 µm) of till samples from Chisel Lake analyzed to-date.

Pb isotopic ratios—Manitouwadge

Pb isotopic results for Pb-bearing selective leachates from anomalous sample MAN 128 and background sample MAN 200 are shown in Table 5 and Figs 7 and 8. The data exhibit the following features: (1) Pb isotope ratios for selective leachates A through to E from the anomalous sample, MAN 128, are constant and similar to the ratios obtained from the galena associated with the Manitouwadge VMS deposits (Fig. 7); (2) the Pb isotopic composition for the sulfide leachate (G) from sample MAN 128 is the most radiogenic of all its leachates, and is clearly quite different to that of the associated ore deposit (Fig. 7); (3) the selective leachates A, C and E from background sample MAN 200 contain Pb isotopic ratios that are relatively constant but significantly higher than those from MAN 128 (Fig. 7); (4) the silicate leachate (H) from MAN 200 contains an isotopic composition equivalent to that for the silicate leachate from MAN 128 (Fig. 7).

^{206}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb isotopic plot (Fig. 8A), shows that all the analyses from the < 63 µm fraction of the Manitouwadge tills plot along a linear array with a slope equivalent to a secondary isochron age of 2700 Ma (Bell and Card, in prep.), consistent with the ca. 2700 Ma age of the Geco and Willroy deposits. With the exception of the ^{208}Pb/^{204}Pb isotope ratio for sulfide leachate (G) from MAN 128, Pb isotope ratios from the selective leachates also plot along the same trends (Fig. 8). Figure 8 shows that most of the selective leachates (A to E) from anomalous sample MAN 128 fall closest to the analyses from the Manitouwadge ore (Bell and Card, in prep.), whereas all but one of those from background sample MAN 200 fall at the other end of the array, with very radiogenic Pb isotope ratios (^{206}Pb/^{204}Pb ~ 24.00).

Conventional leachates

During the development of the exploration technique using Pb isotopes as indicators of mineralization in glacial till, Bell and co-workers used an extraction technique that involved leaching of the till samples for

Table 4. Pb isotopic ratios for ore and selective Pb-bearing leachates for tills from Chisel Lake

	Measured†		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Ore*	15.42-15.46	15.16-15.22	35.00-35.17
90KDA 0011:			
<63 μm fraction*	**16.13**	**15.23**	**36.65**
A	15.88	15.24	35.37
A-*duplicate*	15.90	15.26	35.44
B	15.89	15.24	35.34
B-*duplicate*	15.89	15.22	35.35
C	15.94	15.24	35.40
C-*duplicate*	15.96	15.26	35.48
D	16.01	15.24	35.44
D-*duplicate*	16.02	15.28	35.57
E	16.05	15.26	35.52
E-*duplicate*	16.04	15.26	35.52
F	no signal		
F-*duplicate*	16.21	15.27	35.67
H	17.44	15.41	37.46
H-*duplicate*	17.22	15.40	37.35
90KDA 0015:			
<63 μm fraction*	**17.16**	**15.39**	**36.90**
A	16.70	15.33	35.85
B	16.75	15.32	35.82
C	16.79	15.37	35.94
D	16.79	15.32	35.90
F	17.53	15.40	36.65
H	17.39	15.40	37.61
91KDA 0040:			
<63 μm fraction*	**18.59**	**15.56**	**38.03**
C	23.03	16.08	40.37
H	17.65	15.46	38.22
91KDA 0042:			
<63 μm fraction*	**20.31**	**15.77**	**40.24**
H	19.02	15.65	39.82

†: Fractionation corrected ratios using a factor of 0.12% ±0.02 a.m.u. based on replicate analyses of NBS 982 Pb standard. *: Pb isotope ratios for ore and <63 μm fraction taken from Bell and Franklin (1993).

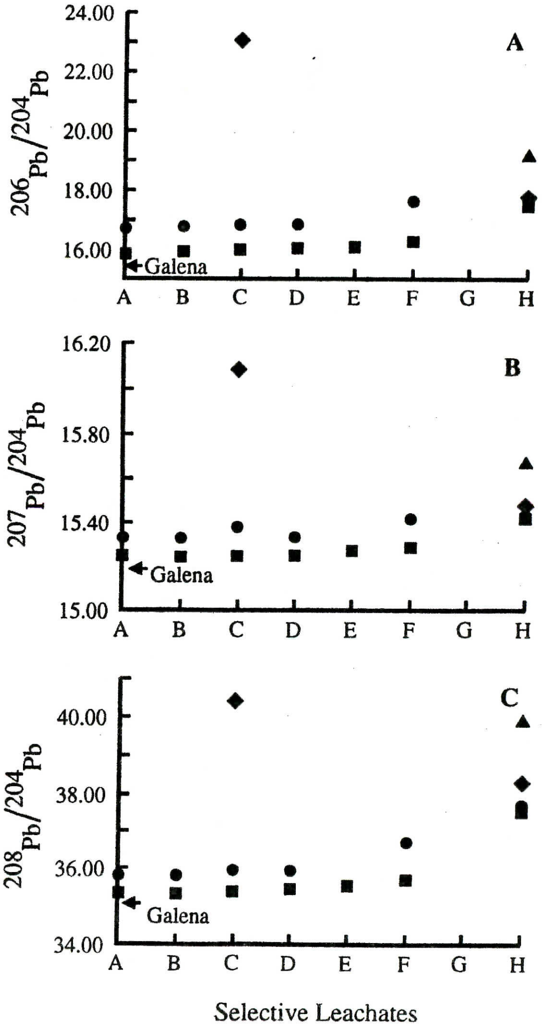

Fig. 5. Diagram showing Pb isotopic ratios for Pb-bearing selective leachates from Chisel Lake samples. Leachate letters and symbols as in Fig. 3. Pb isotopic ratios for galena taken from Bell and Franklin (1993). A) $^{206}Pb/^{204}Pb$ vs leachate; B) $^{207}Pb/^{204}Pb$ vs leachate; C) $^{208}Pb/^{204}Pb$ vs leachate.

about 2 h using 2.5N HCl. The results from the Pb isotope ratios of the leached Pb successfully delimited the mineralized areas, which were spatially similar to those that were found using complete dissolution of the samples with HF and HNO_3.

Conventional leaching experiments were conducted on all 6 till samples in order to measure their Pb isotopic composition and compare the results with those obtained from the selective leachates. 300 milligrams of till from the <63 μm fraction were immersed in approximately 5 ml of cold, double-distilled 2.5 M HCl for roughly 2 h, and occasionally shaken. The leachate solution was decanted, centrifuged, evaporated to dryness, and then conditioned with 1 N HBr. The residue sample was subsequently dissolved using a multi-acid procedure ($HF–HNO_3$ mixture and then 6 M HCl). A similar leaching technique was used by Gulson *et al.* (1992) to dissolve Fe and Mn coatings of stream pebbles, from the Mount Emmons area (Colorado), for Pb isotopic analysis in order to determine their feasibility as a guide to concealed mineralization.

Pb isotope ratios for the conventional leachates and residues are shown in Table 6. Figures 9 and 10 show that of the analyses from the total dissolution of the <63 μm fraction of tills from Chisel Lake (Bell and Franklin, 1993) and Manitouwadge (Bell and Card, in prep.) all but one plot between those obtained from their respective conventional leachate and residue. Anomalous samples 90KDA 0011, 0015, and MAN 128, have conventional leachates with Pb isotope ratios that are less radiogenic (i.e. more "ore-like") than the isotopic signature of the <63 μm fractions (Figs 9 and 10), and give Pb isotopic ratios similar to those obtained from the earlier selective leachates-adsorbed metal (A,B), FeOH–MnOH

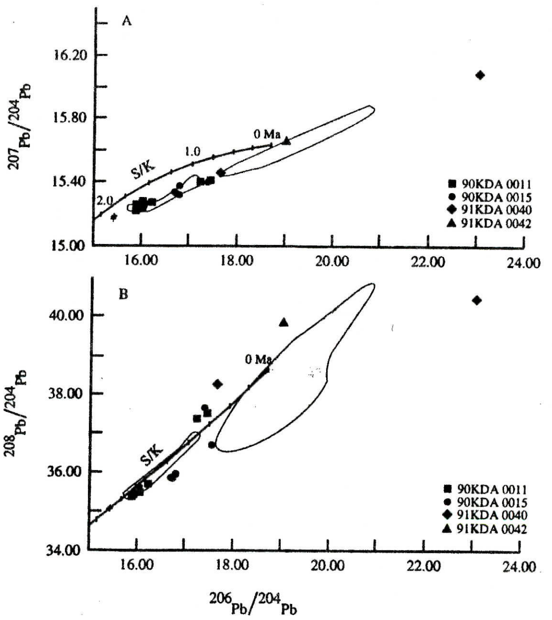

Fig. 6. Pb–Pb isotopic plots showing results for selective leachates from Chisel Lake samples. S/K = Stacey and Kramers (1975) Pb evolution curve; thicks along curve are at 0.25 Ga interval. Fields represent isotopic data from <63 µm fraction analyses (Bell and Franklin, 1993). + = galena analyses. A) $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$; B) $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$.

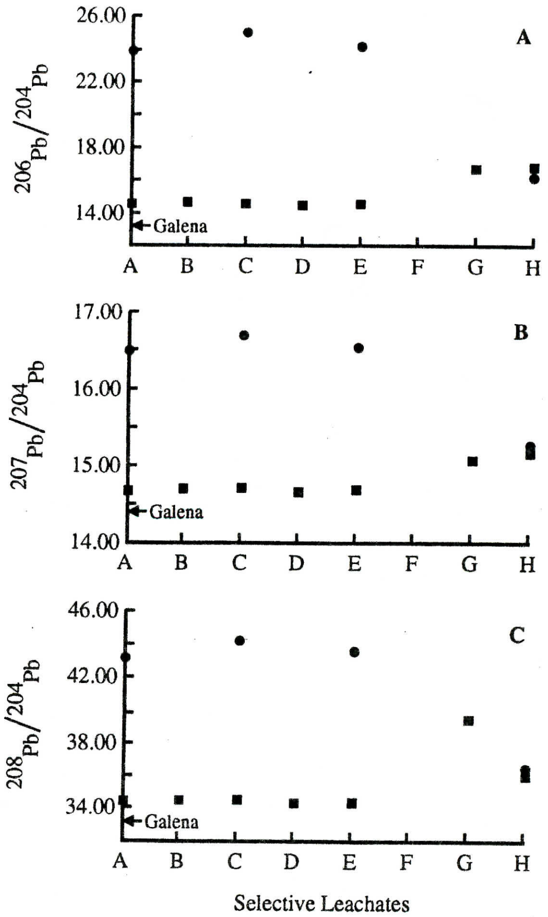

Fig. 7. Diagram showing Pb isotopic ratios for Pb-bearing selective leachates from Manitouwadge till samples. Leachate letters as in Fig. 3, and symbols as in Fig. 4. Pb isotopic ratios for galena taken from (Bell and Card, unpublished data). (A) $^{206}Pb/^{204}Pb$ vs leachate; (B) $^{207}Pb/^{204}Pb$ vs leachate; (C) $^{208}Pb/^{204}Pb$.

(C,D), or crystalline FeO leachates (E,F). The Pb isotopic composition for the residues from anomalous samples tend to approximate the ratios obtained from the silicate leachates for the same sample (Tables 4–6).

Similarly, the Pb isotopic composition for the conventional leachates from background samples (91KDA 0040, 0042, MAN 200) are also similar to those obtained from the early selective leachates (adsorbed metal, FeOH–MnOH, or crystalline oxide) from the same samples. The Pb isotopic ratios for the conventional leachates from the background samples, however, are much more radiogenic than values obtained from complete dissolution of the <63 µm fraction (Tables 4–6). Most of the Pb isotope ratios from the selective and conventional leachates seem to plot in the same fields defined by the results from completely digested <63 µm fraction from both deposits (Bell and Franklin, 1993; Bell and Card, in prep.).

Table 5. Pb isotopic ratios for ore and selective Pb-bearing leachates for tills from Manitouwadge

	Measured†		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Ore*	13.21-14.03	14.40-14.62	33.08-33.96
MAN 128:			
<63 µm fraction*	**14.99**	**14.84**	**34.94**
" duplicate	14.87	14.79	34.76
A	14.58	14.68	34.44
B	14.60	14.68	34.44
C	14.51	14.68	34.40
D	14.36	14.63	34.20
E	14.44	14.64	34.26
G	16.50	15.03	39.35
H	15.91	15.13	35.87
MAN 200:			
<63 µm fraction*	**20.05**	**15.82**	**39.69**
" duplicate	19.97	15.79	39.57
A	23.84	16.49	43.06
C	24.89	16.69	44.02
E	24.02	16.52	43.59
H	16.57	15.20	36.28

†: see Table 4 caption. *: Pb isotope ratios for ore and <63 µm fraction are taken from Bell and Card (in prep., unpublished data)

DISCUSSION

Selective leachates—weathering of till

Postglacial weathering of till typically occurs within the zone of oxidation above the groundwater or

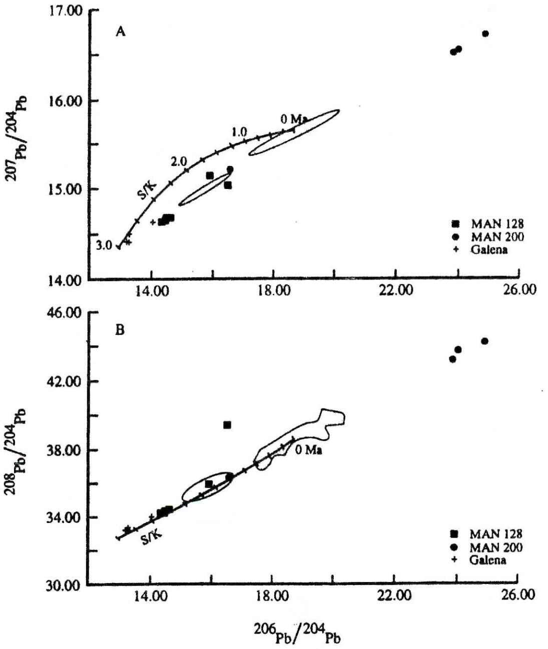

Fig. 8. Pb–Pb isotopic plot showing results for selective leachates of till samples from Manitouwadge. Fields represent data from <63 μm fraction analyses (Bell and Card, unpublished data). Other symbols as in Fig. 6. (A) $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$; (B) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$.

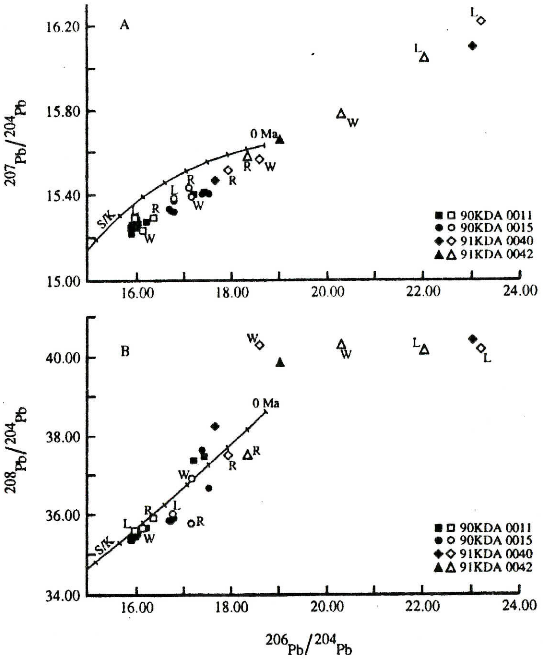

Fig. 9. Pb–Pb isotopic plot showing conventional leachate-residue (*open symbols*) results from Chisel Lake till samples. **L**—leachate; **W**—<63 μm fraction analyses (Bell and Franklin, 1993); **R**—residue. Corresponding filled symbols are selective leachate results from same sample. Other symbols as in Fig. 6. (A) $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$; (B) $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$.

permafrost table, and this process can alter drift geochemistry to considerable depth below the surface (Rencz and Shilts, 1980; Shilts, 1976, 1984; Peuraniemi, 1984; Shilts and Kettles, 1990). The depth of leaching and oxidation in till, however, is dependent on the original abundance of pyrite and other sulfides present in the oxidized zone (Levinson, 1980). Sulfide grains in till found within the zone of oxidation, in particular pyrite, are usually completely or partly altered to limonite (Shilts and Kettles, 1990), geothite (Nikkarinen *et al.*, 1984) or other secondary form of sulfide (Peuraniemi, 1984). Shilts and Kettles (1990) show that the upper 2 m of weathered till near Thetford Mines, Québec, is enriched (by a factor of 2 over the deeper sections of till) in goethite, leucoxene and other secondary minerals formed as a result of alteration and destruction of sulfide minerals, suggesting that they were created by weathering. Breakdown of the sulphide minerals can have taken place either prior to glaciation during weathering of the bedrock, during glaciation, or during post-glacial weathering of till. The effects of pre-glaciation weathering of sulfide minerals is difficult to evaluate due to the later superimposition of complex glacial processes and their correlated effects. Compared to sulfide minerals, pre-glacial, finer-grained(?) secondary minerals are less likely to have remained intact and preserve the Pb isotopic signature of the VMS deposit during till formation, assuming they were imparted with the isotopic signature of the ore deposit. Unfortunately, this scenario cannot be evaluated. Despite the alteration and weathering that occurs within the oxidized zones of till, geochemical profiles for the <63 μm

Table 6. Pb isotopic results from conventional leaching of Chisel Lake and Manitouwadge tills

	Measured†		
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Chisel Lake			
90KDA 0011:			
Leachate	15.96	15.29	35.58
Residue	16.36	15.29	35.91
90KDA 0015:			
Leachate	16.80	15.38	36.01
Residue	17.11	15.43	35.76
91KDA 0040:			
Leachate	23.21	16.20	40.83
Residue	17.94	15.51	37.74
91KDA 0042:			
Leachate	22.05	16.03	40.12
Residue	18.34	15.57	37.49
Manitouwadge			
MAN 128:			
Leachate	14.53	14.70	34.49
Residue	15.17	14.89	34.75
MAN 200:			
Leachate	24.67	16.62	43.80
Residue	17.77	15.40	36.67

†: see Table 4 caption.

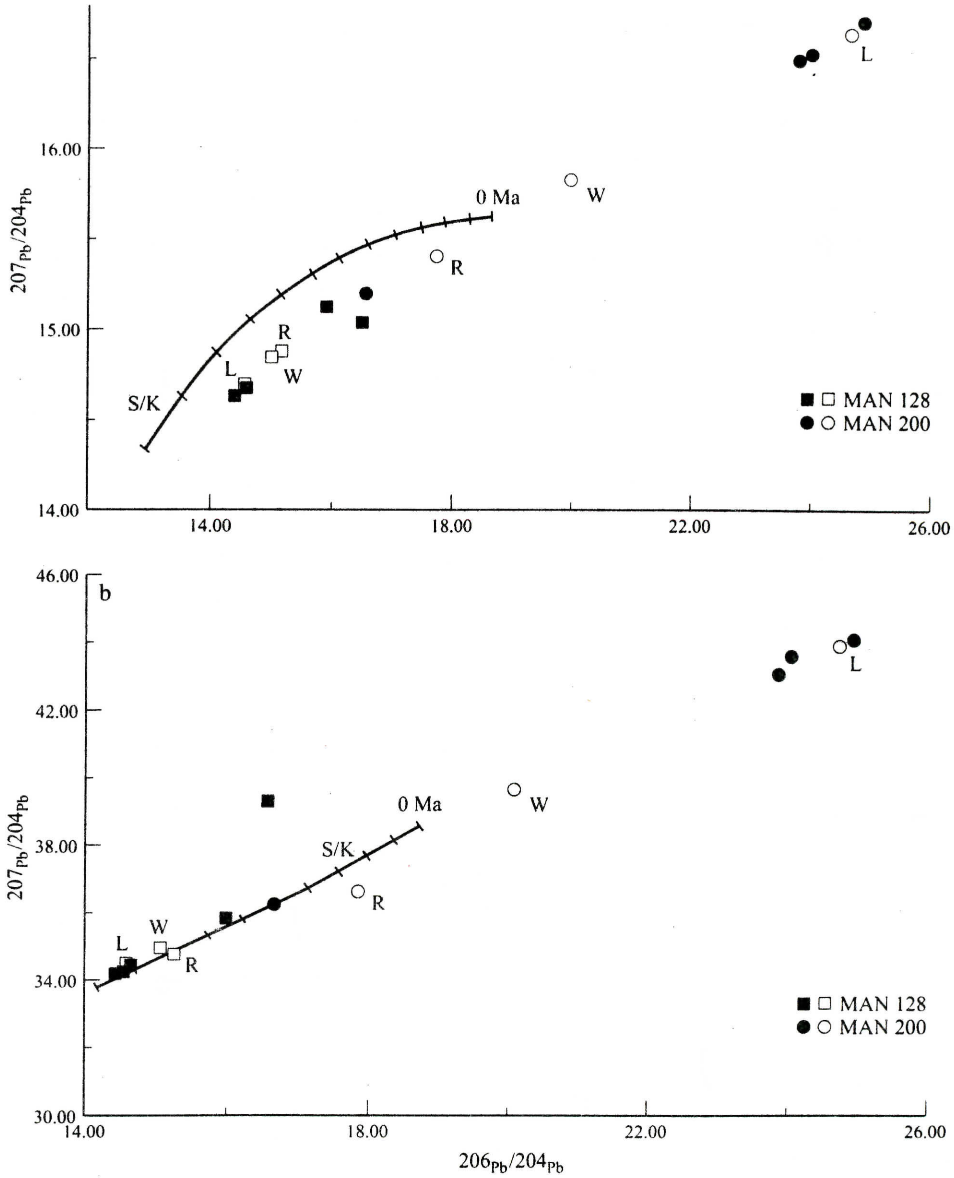

Fig. 10. Diagram showing Pb–Pb isotopic results from conventional leachate-residue (*open symbols*) from Manitouwadge till samples. L—leachate; W—<63 μm fraction analyses (Bell and Card, unpublished data); R—residue. Corresponding filled symbols are selective leachate results from same sample. Other symbols as in Fig. 6. (A) ^{206}Pb/^{204}Pb vs ^{207}Pb/^{204}Pb; (B) ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb.

grain size fraction show that the concentration of base metals is constant with depth (e.g. Shilts and Kettles, 1990), indicating that the trace metals are effectively scavenged and retained proximal to their site of destruction. Most of the Pb found in the 3 anomalous samples has to have been derived from the breakdown of the sulphide minerals along with the release of Pb into the natural system.

In the anomalous samples, Pb which occurs as crystalline FeO leachate (E, F) may represent Pb isotopic analysis of primary, more resistant FeO phases with low U/Pb (i.e. magnetite and hematite), usually associated with VMS deposits. The Pb abundances of magnetite and hematite, however, are much lower than those found in galena, which would mean that it would take large amounts of Fe oxides to swamp the isotopic signature of the galena. In addition, the crystalline FeO (E,F) and FeOH–MnOH leachates (C,D) contain high levels of Cu, Ni and Zn (Figs 3 and 4) suggesting sulfide minerals rather than magnetite and hematite which are not known to contain a large quantity of such elements. Although the Pb isotopic ratios for the selective leachates A to E from the anomalous samples are similar to the isotopic signature of the ore, they are not identical which indicates that a minor component of the Pb contained within these leachates was derived from a slightly more radiogenic source, possibly the surrounding volcanic rocks found within the host greenstone belt.

The sulfide leachate (G) from anomalous sample MAN 128 contains Pb isotope ratios that are quite different to those obtained from ore associated with the Manitouwadge VMS deposits (Fig. 7). The presence of sulfide-held Pb in selective leachates, therefore, should not automatically be attributed to glacial dispersal of sulfide minerals from proximal VMS deposits. One possible explanation for the origin of the sulfide-held Pb in sample MAN 128 is that it may represent a mixture of Pb from more than one source, and which is now contained in sulfide. Several Pb isotopic studies of sulfide minerals associated with VMS deposits (e.g. Red Lake, Gulson *et al.*, 1993; Beardmore-Geraldton, Simonetti, unpublished data), however, clearly show that sulfide minerals associated with VMS deposits, such as pyrite, chalcopyrite and pyrrhotite, have not evolved with the same, low time-integrated μ ($^{238}U/^{204}Pb$) value which characterizes galena (μ ~0) and as a result contain more variable and higher Pb isotopic ratios. The linear arrays in Pb–Pb isotope diagrams shown by the data from all of the selective leachates simply reflects the various Pb isotope ratios that are the result of differing μ (mu) values in the rocks that make up the host greenstone belt. Compared to silicate and other sulfide minerals, however, galena contains the mass balance of Pb within VMS deposits, and it is this feature which has guaranteed the successful application of Pb isotope ratios to till.

Pb concentrations and isotope composition for the selective leachates from the 3 background samples (91KDA 0040 and 0042, and MAN 200) show the following consistent features (Figs 5–10): (1) most of their Pb occurs in either silicates or residual oxides (leachate H); (2) the Pb isotopic composition for the silicate leachate is similar to that of the anomalous samples from the same deposit; (3) if present, the Pb isotopic signature for the adsorbed metal (A, B), FeOH–MnOH (C, D), or crystalline FeO (E, F) leachates are much more radiogenic than the same leachates from the anomalous samples. The highly radiogenic nature of these analyses (Figs 5 and 7) show that the background samples do not contain any Pb derived from the nearby VMS deposits as the result of glacial erosion and down ice sediment transport. Figures 1 and 2 confirm that samples 91KDA 0040 and 0042 and MAN 200 are either not directly down-ice from known ore deposits, or are too distal from them (>4 km), which may explain their lack of a VMS-like Pb isotopic signature. The Pb isotopic ratios for the silicate leachates (H) from both anomalous and background samples are similar and are less radiogenic than the average value for present-day continental crust (0 Ma point of Stacey and Kramers (1975) Pb evolution curve). Compared to the Pb isotope ratios of sulfides (e.g. galena) from the associated VMS deposits, the silicate leachates from both groups of till contain more radiogenic Pb isotope values, therefore, these leachates incorporate Pb from minerals with much higher time-integrated U/Pb ratios (μ values). Unlike the sulfide minerals, which have a higher specific gravity and are less-resistant to weathering, silicate components of the VMS terrains can be found at greater distances down-ice from the ore deposits.

All but one of the Pb isotopic measurements from the selective leachates ($n = 33$) plot along the linear arrays (Figs 6 and 8) defined by the analyses of the <63 μm fraction of till from both Chisel Lake and Manitouwadge. This feature further supports the mixing model proposed for till formation at Chisel Lake (Bell and Franklin, 1993) involving end-members with differing U/Pb, and is consistent with the interpretation of the Pb–Pb arrays as relict secondary isochrons (Bell and Franklin, 1993). Additional support for this interpretation is provided by the Pb isotope ratios from the conventional leachates and residues which also plot along the same linear arrays (Figs 9 and 10).

Conventional leachates—new exploration tool

Pb isotopic ratios for the conventional leachates from anomalous till samples are less radiogenic (i.e. more "ore-like") than analyses from the complete dissolution of the <63 μm fraction, whereas conventional leachates from background samples give Pb isotopic ratios that are more radiogenic, less "ore-like" than the <63 μm fraction. In addition, conventional leachates for all samples contain Pb isotopic ratios (Table 6) that are similar to those obtained from the earlier selective leachates (adsorbed metal to FeOH–MnOH, A to C); whereas Pb isotopic ratios from the residues give isotopic ratios that are closer to those obtained from the silicate leachates (Tables 4–6). The difference in Pb isotopic ratios shown by the conventional leachate and residue for an individual sample, however, is not as large as that obtained from the selective leachates. With the exception of Fig. 9B, the Pb isotopic ratios for the conventional leachates and residues plot on the linear arrays defined by those from the selective leachates. One possible explanation for the scatter of the data points in Fig. 9B is sample heterogeneity since isotope results from conventional leaching (and residue), and whole rock analyses (Bell and Franklin, 1993; Bell and Card, in prep.) were obtained from separate aliquots of the same sample powder. Alternatively, the scatter may be attributed, in part, to a real variation in Th/U ratio in the Chisel Lake deposit and associated volcanic rocks, a feature that is supported by the large variation in $^{208}Pb/^{204}Pb$ ratio for a given $^{206}Pb/^{204}Pb$ value (Fig. 6B). However, since the Pb isotopic results from the conventional leachates approximate those obtained from the selective leachates, the former could be used as a first-order approximation to sequential leaching. A conventional leaching approach instead of total dissolution of a particular grain size fraction of till would have resulted in a bimodal distribution of points rather than linear arrays in Pb–Pb isotopic plots (Figs 6 and 8). Conventional leachates from anomalous till samples would give "ore-like" Pb isotopic ratios, whereas those from background samples would give higher isotope ratios than the former (Figs 9 and 10), providing greater resolution between target areas. This greater difference in the Pb isotopic composition for conventional leachates between anomalous and background till samples would greatly facilitate selection of potential sites for further mineral exploration. The conventional leaching method, however, must be tested on additional till deposits surrounding VMS deposits.

CONCLUSIONS

Selective leachates for tills from Chisel Lake and Manitouwadge show similar results in that chalcophile elements such as Cu, Ni, Pb, and Zn (typically concentrated in VMS deposits), are bound as either adsorbed/exchangeable metals, hydroxides of Fe or Mn, crystalline Fe oxides, or silicates. Despite the proximity of some of the till samples to VMS deposits, a very small proportion of these chalcophile elements are held in the sulfide form. Lead isotopic ratios for Pb-bearing selective leachates from anomalous till samples suggest that the Pb and other chalcophile elements held as either an adsorbed/exchangeable metal, hydrous oxide of Fe or Mn, or crystalline Fe oxide were most probably derived from the breakdown of original sulfide minerals during glaciation. In contrast, Pb within the same leachates from background samples give isotopic compositions that are significantly more radiogenic than those from anomalous samples, which clearly suggests that this Pb does not originate from the associated VMS deposits. It is also interesting to note that Pb from natural sources can be relatively mobile, and that such Pb can be scavenged from solution in the natural environment and concentrated. In addition, only Pb isotopic ratios from till can accurately provide interpretations into the origin of the Pb (and other chalcophile elements), and that the latter can be at odds with interpretations based solely on elemental distribution patterns obtained from selective leachates.

We propose that conventional leaching rather than total dissolution of a particular grain size of till samples be conducted for mineral exploration purposes, since the former can be done more quickly and cheaply and the latter type of analysis tends to mask or reduce the "ore-like" Pb isotopic component within anomalous samples.

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REFERENCES

Antropova L. V., Goldberg I. S., Voroshilov N. A. and Ryss Ju. S. (1992) New methods of regional exploration for blind mineralization: application in the USSR. *J. Geochem. Explor.* **43**, 157–166.

Bailes A. H. (1992) Wekusko Lake (North) Project (MTS 63J/13SW), *Manitoba Energy and Mines, Mineral Division, Report of Activities*, pp. 56–64.

Bailes A. H. and Galley A. G. (1989) Geological setting of and hydrothermal alteration below the Chisel Lake massive Zn–Cu sulphide deposit, *Manitoba Energy and Mines, Minerals Division, Report of Field Activities*, pp. 31–45.

Barnett P. J., Henry A. P. and Babuin D. (1991) Quarternary geology of Ontario, east-central sheet, *Ontario Geol. Surv.*, Map 2555.

Bell K. and Franklin J. M. (1993) Application of lead isotopes to mineral exploration in glaciated terrains. *Geology* **21**, 1143–1146.

Bell K. and Murton J. B. (1995) A new indicator of glacial dispersal: lead isotopes. *Quaternary Science Reviews* **14**, 275–287.

Chao T. T. (1984) Use of partial dissolution techniques in geochemical exploration. *J. Geochem. Explor.* **20**, 101–135.

Friesen R. G., Pierce G. A. and Weeks R. M. (1982) Geology of the Geco base metal deposit. *Geol. Assoc. of Canada Special Paper* **25**, 343–363.

Galley A. G., Bailes A. H., Syme E. C., Bleeker W., Mackek J. J. and Gordon T. M. (1990) Geology and mineral deposits of the Flin Flon and Thompson belts, Manitoba (8th International Association for the Genesis of Ore deposits Symposium field trip guidebook no. 10). *Geol. Surv. Canada, Open file* **2165**, 136.

Geddes R. S. and Bajc A. F. (1985) Quaternary geology of the White Lake (Hemlo area), District of Thunder Bay, *Ontario Geol. Survey*, Map, **P. 2849**.

Gulson B. L. (1986) Lead isotopes in mineral exploration. *Developments in Economic Geology* **23**, 245.

Gulson B. L., Church S. E., Mizon K. J. and Meier A. L. (1992) Lead isotopes in iron and manganese oxide coatings and their use as an exploration guide for concealed mineralization. *Applied Geochemistry* **7**, 495–511.

Gulson B. L., Mizon K. J. and Atkinson B. T. (1993) Source and timing of gold and other mineralization in the Red Lake area, northwestern Ontario, based on lead-isotope investigations. *Can. J. Earth Sci.* **30**, 2366–2379.

Hall G. E. M., Vaive J. E., Beer R. and Hoashi M. Selective leaches *revisited*, with emphasis on the amorphous Fe oxyhydroxide phase extraction, *J. Geochem. Explor.*, (in press).

Hall G. E. M., Vaive J. E. and Kaszycki C. (1993) The diagnostic capabilities of selective leaching. *Explore* **80**, 3–9.

Hawkes H. E. and Webb J. S. (1962) *Geochemistry in Mineral Exploration*, Harper and Row.

Jenne E. A. (1962) Controls on Mn, Fe, Co, Ni and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Advances in Chemistry Series, Am. Chem. Soc.* **73**, 337–388.

Kettles I. M. (1993a) Reconnaissance geochemical data for till samples from the Manitouwadge area, Ontario. *Geol. Surv. Canada, Open file* **2616**, 197.

Kettles I. M. (1993b) Till geochemistry in the Manitouwadge area, Ontario. *Current Research, Geol. Surv. Canada, Paper* **93-1E**, 165–173.

Kettles I. M. and Murton J. B. (1994) Till composition in the vicinity of the Manitouwadge greenstone belt, Ontario. *Geol. Surv. Canada, Curr. Res.* **1994-C**, 249–257.

Kristjansson F. J. and Geddes R. S. (1985) Quaternary geology of the Manitouwadge area, Ontario. *Curr. Res. Geol. Surv. Canada* **93-1E**, 165–173.

Levinson A. A. (1980) *Introduction to Exploration Geochemistry, 2nd edition*, Applied Publishing, Wilmette, Illinois, p. 924.

Lynch J. J. (1990) Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4. *Geostand. Newsl.* **14**, 153–167.

Nikkarinen M., Kallio E., Lestinen P. and Ayras M. (1984) Mode of occurrence of Cu and Zn in till over three mineralized areas in Finland. *J. Geochem. Explor.* **21**, 239–247.

Peterson V. L. and Zaleski E. (1994) Structure and tectonics of the Manitouwadge greenstone belt and Wawa-Quetico subprovince boundary, Superior Province, northwestern Ontario. *Current Research, Geol. Surv. Canada* **1994-C**, 237–247.

Peuraniemi V. (1984) Weathering of sulfide minerals in till in some mineralized areas in Finland, In: Prospecting in Areas of Glaciated Terrain, *Inst. Min. Metall.*, pp. 127–135, London.

Rencz A. N. and Shilts W. W. (1980) Nickel in soils and vegetation of glaciated terrains, In *Nickel in the Environment*, (ed. Nriagu, J. O.), John Wiley and Sons, Inc., pp. 151–188.

Shilts W. W. (1976) Glacial till and mineral exploration, In *Glacial Till*, (ed. Legett, R. F.), Special Publication 12, Royal Society of Canada, pp. 205–233.

Shilts W. W. (1984) Till geochemistry in Finland and Canada. *J. Geochem. Explor.* **21**, 95–117.

Shilts W. W. and Kettles I. M. (1990) Geochemical/mineralogical profiles through fresh and weathered till, In *Handbook of Glacial Indicator Tracing*, (eds Kujansuu, R. and Saarnisto, M.), pp. 187–216, Balkema, Rotterdam.

Simonetti A., Bell K. and Viladkar S. G. (1995) Isotopic data from the Amba Dongar carbonatite complex, west-central India: Evidence for an enriched mantle source. *Chem. Geol.* **122**, 185–198.

Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.

Williams H. R. and Breaks F. W. (1989) Geological studies in the Manitouwadge-Hornpayne area. *Ontario Geol. Surv. Misc. Paper* **146**, 79–91.

Williams H. R. and Breaks F. W. (1990) Geology of the Manitouwadge-Hornpayne area; *Ontario Geol. Surv. Open file*, Map **142**.

Williams H. R., Breaks F. W., Schnieders B. R., Smyk M. C., Charlton S. G. and Lockwood H. C. (1990) Field Guide to the Manitouwadge area, In *Mineral Deposits in the western Superior Province, Ontario*, Open file 2164, pp. 7–25, Geol. Surv. Canada.

Zaleski E. and Peterson V. L. (1993) Lithotectonic setting of mineralization in the Manitouwadge greenstone belt, Ontario: preliminary results. *Curr. Res. Geol. Surv. Canada* **93-1C**, 307–317.

Zaleski E., Peterson V. L. and van Breemen O. (1994) Geological, geochemical and age constraints on base metal mineralization in the Manitouwadge greenstone belt, northwestern Ontario, *Current Research, Geol. Surv. Canada*, **1994-C**.

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Application of a Sequential Extraction Scheme to Ten Geological Certified Reference Materials for the Determination of 20 Elements*

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Methods are described for a sequential extraction scheme to dissolve selectively elements bound in soils and sediments in the following nominal forms: (1) adsorbed, exchangeable, carbonate (AEC); (2) amorphous iron oxyhydroxide (am Fe ox), including manganese oxides; (3) crystalline iron oxides (cry Fe ox); (4) organics and sulfides; and (5) residual (mainly silicates). This scheme has been applied in triplicate to a suite of ten international CRMs, *i.e.*, soils SRM 2709–2711 and the SO-1–4 series, marine mud MAG-1, lake sediment LKSD-4 and the till sample TILL-2. Elements determined comprise: As (by HG–quartz tube AAS, HG–QTAAS); Be, Ca, Co, Cr, Cu, Ni, P, Ti and V (by ICP-AES); Mn, Fe and Zn (by FAAS); and Cd, Ce, La, Li, Tl, Pb and U (by ICP-MS). The precision obtained is excellent, generally in the range 2–10% RSD, at concentrations 10 × higher than detection limits. Most results for the element concentrations summed over the five phases agree, within statistical uncertainties, with the recommended total values for the CRMs. Those where recoveries are significantly below 90% are for elements such as Cr and V, which are known to be present in refractory minerals and would require fusion for complete dissolution. The results presented herein for samples SO-1–4 and MAG-1 do not agree well with those recently published using a scheme purported to dissolve similar phases. This highlights the need to be more definitive in describing the nature and extent of the phases actually extracted so that comparisons can be made between different laboratories and studies.

Keywords: *Selective extraction; leach; speciation; soil; geological; standard reference material*

Selective dissolution techniques are currently of renewed interest in exploration geochemistry, and recently have been re-examined and further developed at the Geological Survey of Canada (GSC).[1,2] The identification of the main binding sites of trace metals in surficial media not only helps in the understanding of geochemical processes but also allows one to predict the potential for remobilization, to determine the bioavailability of an element and to discriminate between sources (*e.g.*, atmospheric deposition *versus* hydromorphic transport *versus* clastic dispersion). The measurement of speciation is a much more challenging task than the determination of total content. A sequential extraction scheme consists of a series of successive chemical treatments of a sample, each being more drastic in action or of a different nature than the previous one. The order in which the extractants are used is critical and could well depend upon sample type and overall composition, and the objectives of the project. It must be recognized that the results obtained are '*operationally defined*', *i.e.*, selectivity is not 100% and is dependent upon such factors as the chemicals employed, the time and nature of contact, sample to volume ratio, *etc.* Results will also be dependent on the grain-size fraction chosen for analysis and whether coarser grains have been made finer by ball-milling, thus increasing exposure to attack. Published schemes include those of Sondag,[3] Chao[4] and Cardoso Fonseca and Martin,[5] designed for application in exploration geochemistry, and that of Tessier *et al.*,[6] applied mostly in environmental studies. The scheme adopted in the present work was devised by examining the strengths and weaknesses of the 'specific' reagents commonly employed, with consideration given to the variety of sample types (*e.g.*, lake and stream sediments, B-horizon soils) to be analysed and the objectives of the projects undertaken.[2] Of particular importance in exploration geochemistry is that portion of element bound to phases which have a high capacity to scavenge or adsorb labile elements; such phases include amorphous manganese oxide, amorphous iron oxyhydroxide and the 'soluble organic' component of humus (fulvic and humic complexes).

The water-soluble fraction of a soil or sediment is the first to be brought into solution in any sequential scheme. This fraction is usually negligible, except in areas where evaporites are present. Exchangeable metals, those held through electrostatic attraction on exchange sites on the surface and interface of negatively charged complexes of soils, also generally constitute a small proportion and can be replaced by neutral salts such as $MgCl_2$ or ammonium acetate ($CH_3CO_2NH_4$). It was decided to group exchangeable and adsorbed metals with those coprecipitated with carbonates and to extract this component (labelled here as AEC) with sodium acetate (CH_3CO_2Na), buffered at pH 5. Also extracted together, in the next step, are the hydrous oxides of Mn and Fe, the well known 'sinks' in the surficial environment for heavy metals. Scavenging by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: coprecipitation; adsorption; surface complex formation; ion exchange; and penetration of the lattice. These mechanisms and their interrelations have been discussed by Chao and Theobald;[7] clearly, predominant forms will depend upon the element in question and the physico-chemical conditions prevailing. Amorphous iron oxyhydroxide [$Fe(OH)_3.nH_2O$] is chemically more reactive than crystalline forms and it is on this basis that they are separated. Both Fe and Mn form mixed oxides, owing to their similar chemical properties and ionic radii. The relative importance of iron and manganese oxides as scavengers will depend upon such conditions as existing pH–Eh values, degree of oxide crystallinity, their abundances and presence of organic matter; it is impossible to generalize. Therefore, it was decided to group the extraction of manganese oxides together with that of amorphous iron oxyhydroxides. Chao and Zhou[8] compared the speci-

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ficity of different reagents in the extraction of amorphous iron oxyhydroxides from soils and sediments. They demonstrated that, after 30–60 min in 0.25 mol l^{-1} $NH_2OH.HCl$ in 0.25 mol l^{-1} HCl at 70 °C, further dissolution of the test amorphous iron oxides was minimal, while $<1\%$ of the crystalline iron oxides was dissolved except for one magnetite (*ca.* 2%). This extraction was chosen for the amorphous iron oxyhydroxide phase (am Fe ox), operating at a temperature of 60 °C to minimize dissolution of crystalline iron oxide. Research at the GSC with this leach led to a lowering of the strength of HCl to 0.05 mol l^{-1}, in order to minimize dissolution of monosulfides such as sphalerite (ZnS) and galena (PbS).[2] (Soluble organics such as humic and fulvic complexes will dissolve significantly in this leach and, if desired, can be removed by extraction with 0.1 mol l^{-1} $Na_4P_2O_7$ solution first.) Hydroxylamine hydrochloride under stronger reducing conditions was selected for the next phase (cry Fe ox), after the method originally designed by Chester and Hughes for the partitioning of trace elements in pelagic sediments.[9] This extractant consists of 1 mol l^{-1} $NH_2OH.HCl$ in 25% CH_3CO_2H and is carried out at 90 °C.

Metals bound to organic matter and sulfides are next in the sequence of most selective extraction schemes, assuming that these forms have not been previously dissolved to any significant degree. The type of action on the sample changes from reducing to oxidizing at this point. The highly oxidizing attack recommended by Chao and Sanzalone was chosen for the present work, being much more efficient than *aqua regia* or H_2O_2–HNO_3: digestion with $KClO_3$ and HCl followed by 4 mol l^{-1} HNO_3 with gentle boiling.[10] Finally, the common mixed acid attack of HCl–HF–$HClO_4$–HNO_3 is used in the proposed scheme to dissolve silicates and resistant mineral species from the residue. In some cases, where refractory primary minerals such as tourmaline, barite, beryl, chromite and sphenes are present, a small residue still persists.

Evidence for increased efficiency of extraction with fresh reagent, such as $NH_2OH.HCl$ solution, added to the sample has been presented and discussed by Kersten and Forstner.[11] In the present scheme, each of the first three leaches in the sequence is repeated as significant proportions (up to 40%) of elements (*e.g.*, Zn, Cu and Fe) were found to be further extracted by this second application.[2]

The present paper reports the application of this sequential extraction scheme to a suite of CRMs. There is now a momentum amongst agencies mandated to provide standards to certify these CRMs for partial or specific element concentrations in addition to total. For example, NIST is providing an addendum to its certificates for the soils SRM 2709–2711 where preliminary 'leach' data are given. The leach employed by the participating laboratories is that specified in Method 3050 of the US Environmental Protection Agency's (EPA) recommended methods list and is based on HNO_3–H_2O_2, an oxidizing attack which is not very specific. These soils were included in the present study. With a slightly different approach than that of NIST, the European Commission's Measurements and Testing Programme (formally known as the BCR) launched an action recently to harmonize these sequential extraction schemes and to certify soil and sediment reference materials for specific classifications of elements.[12,13] While adequate agreement amongst laboratories can be obtained by adhering strictly to the recommended protocols, the three phases therein defined are vague (1, exchangeable, water and acid soluble; 2, reducible; and 3, oxidizable) and therefore limited in their usefulness for interpretative purposes. One could easily argue, for example, that the protocol of digestion in 0.1 mol l^{-1} $NH_2OH.HCl$ solution at 20 °C is by no means effective for quantitative dissolution of iron oxyhydroxides, species which should fall into the 'reducible' category.

The analytical techniques employed in the present work were selected for compatibility for particular elements in these various extractants and include: HG quartz tube AAS (HG-QTAAS); ICP-AES; and ICP-MS. Elements determined were: As by HG-QTAAS; Be, Ca, Co, Cr, Cu, Ni, P, Ti and V by ICP-AES; Mn, Fe and Zn by FAAS; Cd, Ce, La, Li, Tl, Pb and U by ICP-MS.

EXPERIMENTAL

Reagents

All reagents used in this project were Baker (Phillipsburg, NJ, USA) 'analysed-reagent' grade. Standard solutions employed for calibration in the measurement techniques were purchased from High Purity Standards (Charleston, SC, USA). Distilled, de-ionized water was used throughout. Most of the leaches were performed in 'Falcon' poly(propylene) centrifuge tubes (Becton Dickinson, Lincoln Park, NJ, USA) and the Teflon centrifuge tubes employed in the later stages of the procedure were purchased from Nalgene (Rochester, NY, USA).

Instrumentation and Operating Conditions

A Perkin-Elmer Model 3030, in the air–acetylene mode, was employed for measurements by FAAS. The elements Fe, Mn and Zn were measured at 248.8, 279.5 and 213.9 nm, respectively. A Perkin-Elmer Model 5000, with an electrically heated quartz cell (at 800 °C) for atomization, was used for measurement of As at 193.7 nm by HG-QTAAS. The hydride generator was of GSC design. The 4 mol l^{-1} HCl containing the analyte was pumped at 2 ml min^{-1} to mix with 2% $NaBH_4$ solution at 0.6 ml min^{-1}. A 48 s wash with 4 mol l^{-1} HCl was carried out between samples aspirated for 12 s. A conventional gas–liquid separator was employed.

The ICP-AES analysis for Be, Ca, Co, Cr, Cu, Ni, P, Ti and V was carried out using a Jobin-Yvon sequential Model 38 spectrometer. Operating conditions are given in Table 1; background correction on one or both sides of the analyte peak was employed where necessary.

The ICP-MS analysis was carried out using a VG PlasmaQuad 2+ (Winsford, Cheshire, UK). The operating conditions are given in Table 2. Corrections were made for spectral interferences of Sn and MoO on ^{114}Cd by monitoring ^{118}Sn and ^{198}Mo. All analyte solutions derived from the five extractions described below were diluted 50-fold in 1% HNO_3 just prior to nebulization. Calibration solutions were run after every eight samples; internal standards were not employed. Periodically, measurement by standard additions was carried out to confirm the absence of non-spectral matrix interferences.

For all analytical techniques, calibration solutions were prepared by spiking, with known amounts of analytes, 'blank'

Table 1 ICP-AES operating conditions

Torch	Demountable
Nebulizer	Concentric
Spray chamber	Scott, double pass
Rf power	1.15 kW
Reflected power	<1 W
Outer gas flow rate	13 l min^{-1}
Aerosol gas flow rate	0.3 l min^{-1}
Intermediate gas flow rate	0.8 l min^{-1}
Sample uptake rate	1 ml min^{-1}
Measurement parameters—	
Integration time	1.5 s per peak (3 points per peak, 0.5 s each)
Number of readings	3
Lines measured	Be, 313.0; Ca, 422.7; Co, 228.6; Cr, 267.7; Cu, 324.7; Ni, 231.6; P, 213.6; Ti, 337.3; V, 311.1 nm

Table 2 ICP-MS operating conditions

Torch	Standard, short
Nebulizer	Concentric
Spray chamber	Scott, double pass, 0 °C
Rf power	1.35 kW
Reflected power	<1 W
Outer gas flow rate	12 l min^{-1}
Aerosol gas flow rate	0.9 l min^{-1}
Intermediate gas flow rate	0.8 l min^{-1}
Sampler	1 mm, Ni
Skimmer	1 mm, Ni
Measurement parameters—	
Dwell time	320 µs
Channels per m/z	20
Sweep time	0.5 s
Integration time	20 s
Number of readings	3
Scan regions	5.6–8.4 (^{7}Li) 90.6–129.4 (^{114}Cd) 138.6–239.4 (^{139}La, ^{140}Ce, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U)

solutions of the particular extractants and the appropriate dilutions made.

Sequential Leach Procedure

A suite of ten certified reference samples (soils, a lake sediment and a marine basin sediment) was taken through the sequential extraction scheme in triplicate. Samples were taken from their bottles 'as received' from suppliers; they were not dried further. These CRMs are described in Table 3. The sequential procedure is shown schematically in Fig. 1. Extractions were carried out in air rather than under nitrogen as these samples were not anoxic and therefore changes in element distribution by air oxidation were not of concern. The procedure is as follows.

AEC phase

(1) To 1 g of sample in a 50 ml screw-cap centrifuge tube, add 20 ml of 1.0 mol l^{-1} CH_3CO_2Na solution (at pH 5) and cap.

(2) Vortex the contents for 5–10 s and place in a horizontal shaker for 6 h.

(3) Centrifuge for 10 min at 2800 rev min^{-1} and decant the supernatant liquid into a labelled test-tube. Rinse the residue with 5 ml of water, vortex and centrifuge again; do this twice and add the supernatant rinses to the test-tube. Make up to the 30.0 ml mark and analyse.

(4) Carry out a second 20 ml 1 mol l^{-1} CH_3CO_2Na solution leach of the residue, repeating steps 2 and 3.

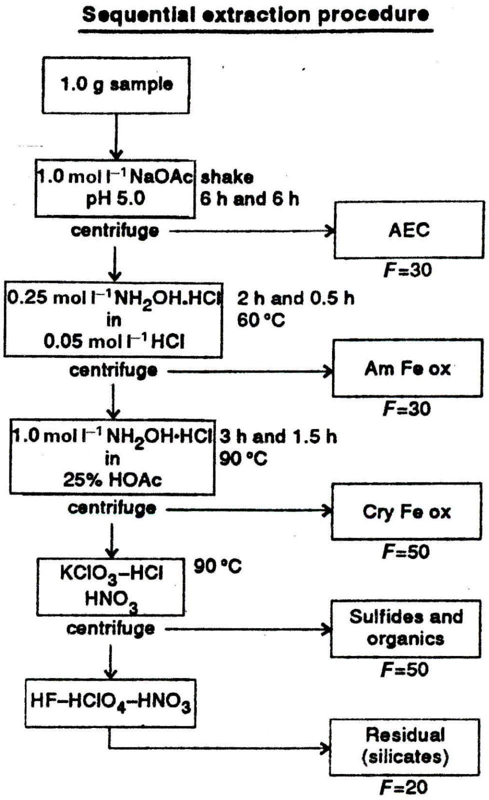

Fig. 1 Schematic diagram of the sequential extraction procedure. F is the initial dilution factor (*e.g.*, $F = 30$ represents 1 g of sample diluted to 30 ml)

Am Fe ox phase

(5) To the residue from step 4, add 20 ml of 0.25 mol l^{-1} $NH_2OH.HCl$ in 0.05 mol l^{-1} HCl, cap and vortex for 5–10 s.

(6) Place in a water-bath at 60 °C for 2 h with the cap loosened. Every 30 min, cap tightly and vortex the contents.

(7) Centrifuge for 10 min and decant the supernatant liquid into a labelled test-tube. Rinse the residue with 5 ml of water, vortex and centrifuge again; do this twice and add the supernatant rinses to the test-tube. Make up to the 30.0 ml mark and analyse.

(8) Carry out a second 0.25 mol l^{-1} $NH_2OH.HCl$ solution leach of the residue but heat for only 30 min.

Cry Fe ox phase

(9) To the residue from step 8, add 30 ml of 1.0 mol l^{-1} $NH_2OH.HCl$ solution in 25% CH_3CO_2H, cap and vortex for 5–10 s.

Table 3 Certified reference materials under investigation

CRM	Description	Source
SRM 2709	San Joaquin Soil [Soil (background) from San Joaquin Valley]	NIST
SRM 2710	Montana Soil Highly Elevated Traces (highly contaminated Montana soil)	NIST
SRM 2711	Montana Soil Moderately Elevated Traces	NIST
SO-1	Regosolic C-horizon soil	CCRMP*
SO-2	Podzolic B-horizon soil	CCRMP
SO-3	Calcareous C-horizon soil	CCRMP
SO-4	Chernozemic A-horizon soil	CCRMP
MAG-1	Marine mud (bottom sediment)	United States Geological Survey
LKSD-4	Composite centre lake sediment	CCRMP
TILL-2	Till from New Brunswick	CCRMP

* Canadian Certified Reference Materials Project.

(10) Place in a water bath at 90 °C for 3 h with the cap on tightly. Vortex the contents every 20 min.

(11) Centrifuge for 10 min and decant the supernatant liquid into a labelled test-tube. Rinse the residue with 10 ml of 25% CH_3CO_2H, water, vortex and centrifuge again; do this twice and add the supernatant rinses to the test-tube. Make up to the 50.0 ml mark and analyse.

(12) Carry out a second 1.0 mol l^{-1} $NH_2OH.HCl$ solution leach of the residue but heat for only 1.5 h.

Organics and sulfides phase

(13) To the residue from step 12, add 750 mg of $KClO_3$ and 5 ml of 12 mol l^{-1} HCl. Cap and vortex (care, as frothing can occur). Add a further 10 ml of HCl, cap and vortex.

(14) After 30 min, add 15 ml of water, cap, vortex and centrifuge for 10 min. Decant the supernatant liquid into a labelled test-tube.

(15) To the residue, add 10 ml of 4 mol l^{-1} HNO_3, cap and vortex. Place in a water-bath at 90 °C for 20 min. After digestion, transfer all of the contents to a Teflon pressure tube.

(16) Vortex and centrifuge for 10 min. Decant the supernatant liquid into the previous labelled test-tube, in effect mixing the $KClO_3$–HCl extractant with this HNO_3 leachate.

(17) Rinse the residue with 5 ml of water, vortex and centrifuge again; do this twice and add the supernatant rinses to the test-tube. Make up to 50.0 ml and analyse.

Silicates and residual oxides phase

(18) To the residue, add 2 ml of 16 mol l^{-1} HNO_3 and place in a dry heating block on a hot-plate at 200 °C. Heat to reduce the volume to ≈0.5 ml.

(19) After cooling, add 2 ml of 12 mol l^{-1} HCl and heat for 20 min at 90 °C in the water-bath.

(20) After cooling, add 10 ml of the acid mixture (all concentrated) [HF (5 ml)–$HClO_4$ (3 ml–HNO_3 (2 ml)] and cap tightly. Heat for 1 h at 90 °C in the water-bath.

(21) Transfer the contents to a Teflon beaker, rinsing with water for complete transfer. Evaporate at ≈70 °C overnight and raise the heat to ≈120 °C in the last stage to achieve incipient dryness.

(22) Add 1 ml of 12 mol l^{-1} HCl and 3 ml of 16 mol l^{-1} HNO_3 and swirl the contents. Add 3 ml of water and warm gently for 5–10 min. Transfer the contents to a calibrated test-tube, rinsing with water. Make up to 20.0 ml and analyse.

Analysis for As by ICP-MS was precluded, owing to significant spectral interference of ArCl on monisotopic ^{75}As created by the variable amounts of Cl present in the different sample solutions. Hence, HG-QTAAS was used to determine As. The procedure routinely employed at the GSC to separate As (and other hydride forming elements) from potential transition metal interferences was applied here, *i.e.*, coprecipitation with $La(OH)_3$. Two ml of sample solution resulting from the five extractions above were taken and the following reagents added: 3 ml of 1% $La(NO_3)_3$ and 8 ml of 1+1 NH_4OH solution. After sitting overnight, the solution was centrifuged at 2800 rev min^{-1} for 4 min and the supernatant decanted. The residue was dissolved in 7.5 ml of 4 mol l^{-1} HCl, to which were added 750 µl of a 1+1 solution of 10% KI and 10% ascorbic acid, for prereduction of As^{V} to As^{III}. After 30 min, the solution was made up to 10.0 ml with 4 mol l^{-1} HCl, ready for analysis by HG-QTAAS.

RESULTS AND DISCUSSION

The sequential leach results are presented in Tables 4–23, in the form of the mean and standard deviation obtained for three separate 1 g samples of each CRM, accompanied by the recommended (denoted by an asterisk), proposed or information value (shown in parentheses) for total concentration compiled by Govindaraju.[14] The uncertainties associated with these mean recommended values were obtained from original compilations of CRM data and from accompanying certificates:[15–18] *i.e.*, certificates for SRMs 2709–2711; Gladney and Roelandts[15] for SO-1–SO-4; Gladney and Roelandts[16] for MAG-1; Lynch[17,18] for LKSD-4; and Lynch[18] for TILL-2. In summing the individual phase results for 'total' element concentration, raw data were used rather than data truncated at the detection limit. A 3σ instrumental detection limit was used, based on aspiration of the appropriate blank solution for each extraction.

Perhaps the most striking feature of the results is the excellent precision evident throughout, regardless of the significant number of manipulations involved in the sequential procedure. Most values for precision associated with the 'total' element result are in the range 1–5% RSD. Exceptions arise where concentrations are close to instrumental detection limit, as is the case for Be below 0.2 mg kg^{-1} (ppm) (Table 5), Co below 5 mg kg^{-1} (Table 9), Ni below 5 mg kg^{-1} (Table 16) and Tl below 50 µg kg^{-1} (ppb) (Table 20). The only surprising, poor result for precision is that of Ca in the AEC phase of SO-3 (Table 6), at 18% RSD, perhaps reflecting heterogeneity in this calcareous C-horizon soil. The five leaches of this procedure do not appear to differ in their inherent reproducibility.

Accuracy is almost impossible to assess in the present absence of CRMs certified for their phase-selective elemental compositions. However, comparison of the summed result with recommended values provides some estimate of overall accuracy. It is shown in Tables 4–23 that these two values agree within the respective standard deviations in the vast majority of cases. Exceptions to this, where recovery of the element is below 90% of the recommended value, are: As in SRM 2711 (87% of recommended value), SO-4 (85%) and LKSD-4 (76%); Be in LKSD-4 (66%) and TILL-2 (77%); Co in SO-2 (87%); Fe in SO-2 (87%); La in SO-4 (77%); Mn in SO-3 (83%), SO-4 (88%) and MAG-1 (86%); P in SRM 2709 (84%); Ti in SO-4 (82%); and Cr, U and V in various samples. The reason for these apparently low recoveries could well be that these elements are bound in resistant minerals in these samples and a fusion would be required to effect complete dissolution. Such minerals include chromite, spinel, beryl, zircon and tourmaline, known for hosting the elements listed above.

In these CRMs, the silicate phase dominates as the principal residence of Be, Ce (except in SO-1 and LKSD-4), Cr (except in SO-1), La (except in SO-1 and LKSD-4), Li (except in SO-1 and SO-3), Ti, Tl, U (except in SRM 2710 and LKSD-4) and V (except in SO-1 and SO-2). As expected, Ca is found predominantly in the AEC phase, except for SRM 2710, SO-1, SO-2 and TILL-2 where the silicate phase contains the majority of Ca. In most samples, the am Fe ox and cry Fe ox phases contain the greatest percentage of the Fe, Co, Cu, Ni, P and Zn contents. Arsenic and Pb are distributed amongst all phases without obvious bias, whereas Cd and Mn are held mostly in labile forms, in the first two phases extracted. These trends confirm the general observation made by Lynch in certification studies, that elements such as Cd, Co, Cu, Ni, Pb and Zn are efficiently extracted from lake sediments LKSD 1–4 and soils using only a hot *aqua regia* or HNO_3–$HClO_4$ attack.[17,18] It is interesting that the dominance in the silicate phase (as opposed to more soluble phases) of Co in SRM 2711, Ni in SRM 2710 and Pb in SRM 2709 is also reflected in results reported by Kane *et al.*[19] These workers found that EPA Method 3050 (digestion in H_2O_2–HNO_3) resulted in complete recovery of Co in SRM 2709 and SRM 2710, Ni in SRM 2709 and SRM 2711 and Pb in SRM 2710 and SRM 2711 but low recoveries

Table 4 Results (mean ± s in mg kg^{-1}) for As: application of sequential leach procedure to CRMs in triplicate. Literature sources for this and all subsequent tables: (1) certificates for SRMs 2709–2711; (2) Gladney and Roelandts[15] for SO 1–4; (3) Gladney and Roelandts[16] for MAG-1; (4) Lynch[17] and Lynch[18] for LKSD-4; and (5) Lynch[18] for TILL-2

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature
SRM 2709	1.24±0.03	1.20±0.01	9.51±0.05	4.13±0.17	1.58±0.07	17.3±0.2	17.7±0.8*
SRM 2710	56.5±0.57	403±18	108±2.0	18.3±0.65	14.8±0.32	631±17	626±38*
SRM 2711	28.6±1.23	32.1±0.49	22.6±0.45	5.34±0.06	3.42±0.02	91.6±2.0	105±8*
SO-1	0.105±0.009	0.119±0.004	0.705±0.028	0.714±0.034	0.473±0.023	2.12±0.04	2.0±0.2*
SO-2	0.184±0.001	0.294±0.004	0.342±0.011	0.148±0.10	0.212±0.013	1.18±0.007	1.17±0.13*
SO-3	0.134±0.005	0.207±0.003	1.43±0.02	0.333±0.006	0.370±0.022	2.38±0.05	2.51±0.13*
SO-4	0.400±0.026	0.555±0.003	3.07±0.01	0.799±0.040	1.45±0.05	6.31±0.05	7.40±0.22*
MAG-1	0.778±0.015	0.719±0.013	1.33±0.05	2.63±0.03	3.49±0.03	8.93±0.09	9.2±1.2
LKSD-4	0.961±0.052	2.72±0.05	4.67±0.06	2.83±0.05	0.897±0.087	12.1±0.17	16±1*
TILL-2	0.096±0.013	1.42±0.04	16.5±0.5	4.75±0.03	2.88±0.11	25.5±0.44	26±2

* Recommended value.

Table 5 Results for Be (mean ± s in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	0.06±0.01	0.34±0.01	<0.05	0.20±0.13	3.81±0.03	4.44±0.16	—
SRM 2710	0.20±0.01	0.39±0.02	0.05±0.07	<0.05	1.32±0.05	1.92±0.14	—
SRM 2711	<0.05	0.41±0.02	0.09±0.07	0.09±0.01	1.32±0.03	2.08±0.20	—
SO-1	0.05±0.01	0.25±0.01	0.05±0.04	0.35±0.13	1.09±0.05	1.75±0.08	1.98±0.29
SO-2	0.06±0.01	0.19±0.08	0.05±0.01	0.08±0.11	1.69±0.08	2.07±0.15	2.0±0.3*
SO-3	<0.05	0.11±0.11	<0.05	<0.05	0.49±0.01	0.63±0.12	0.81±0.15
SO-4	<0.05	0.28±0.12	0.14±0.01	<0.05	0.71±0.01	1.14±0.12	1.26±0.14*
MAG-1	0.08±0.01	0.45±0.01	0.27±0.07	0.16±0.01	1.86±0.08	2.83±0.11	3.2±0.4*
LKSD-4	0.07±0.01	0.06±0.04	0.14±0.12	<0.05	0.38±0.01	0.66±0.11	1.0±0.03*
TILL-2	0.19±0.01	0.24±0.01	0.43±0.01	0.10±0.01	2.13±0.03	3.09±0.03	4.0±0.5

* Recommended value.
† See Table 4 for relevant references.

Table 6 Results for Ca (mean ± s in %): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	1.237±0.001	0.067±0.001	0.025±0.001	0.025±0.001	0.556±0.033	1.911±0.039	1.89±0.05*
SRM 2710	0.276±0.013	0.081±0.004	0.039±0.000	0.036±0.002	0.801±0.043	1.234±0.061	1.25±0.3*
SRM 2711	1.819±0.074	0.188±0.012	0.028±0.001	0.038±0.001	0.844±0.030	2.919±0.077	2.88±0.08*
SO-1	0.256±0.004	0.109±0.003	0.059±0.001	0.136±0.001	1.214±0.096	1.775±0.098	1.76±0.10*
SO-2	0.013±0.001	0.251±0.001	0.105±0.001	0.035±0.001	1.653±0.032	2.058±0.030	1.98±0.10*
SO-3	9.198±1.666	3.455±0.045	1.251±0.106	0.029±0.001	0.473±0.015	14.41±1.78	14.8±1.0*
SO-4	0.522±0.002	0.093±0.001	0.011±0.001	0.019±0.002	0.516±0.008	1.163±0.004	1.11±0.09*
MAG-1	0.648±0.050	0.066±0.001	0.023±0.001	0.038±0.001	0.253±0.010	1.031±0.057	0.98±0.07*
LKSD-4	0.680±0.044	0.095±0.002	0.022±0.001	0.021±0.002	0.518±0.013	1.338±0.058	1.29±0.14*
TILL-2	0.030±0.001	0.039±0.001	0.021±0.001	0.039±0.001	0.825±0.033	0.956±0.032	0.91±0.05

* Recommended value.
† See Table 4 for relevant references.

Table 7 Results for Cd (mean ± s in µg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	158±10	84±3	111±14	14±3	34±6	401±27	380±10*
SRM 2710	14352±288	2424±144	453±24	2458±119	555±36	20243±445	21800±200*
SRM 2711	31201±924	4331±263	1222±30	483±15	188±15	37426±779	41700±250*
SO-1	24±6	34±4	35±20	37±52	<10	125±9	130±40
SO-2	25±8	39±10	18±7	<10	105±6	188±16	130±40
SO-3	83±7	<15	<15	<10	9±3	115±21	120±30
SO-4	102±7	179±18	58±6	<10	34±8	373±21	340±60
MAG-1	155±10	15±2	<15	<10	<10	200±2	202±29*
LKSD-4	1081±45	801±55	57±1	<10	19±4	1968±19	1900±500
TILL-2	69±14	93±7	167±6	17±5	20±4	366±30	300±200

* Recommended value.
† See Table 4 for relevant references.

for these elements in the third member of this series, in keeping with the present findings. NIST soil SRM 2710 is contaminated with high concentrations of Cu, Mn, Pb and Zn originating from flooding of nearby settling ponds containing effluent from the Anaconda processing plant in Butte, MT, USA. Thus the highest concentrations of these elements should exist in the first two labile phases (rather than in crystalline forms) of the sequential leach procedure. This is borne out in Tables 11, 15, 18 and 23 where it is evident that these first two phases account for 82, 50, 88 and 51%, respectively, of the total Cu, Mn, Pb and Zn in this soil.

The distributions of elements in the marine mud MAG-1 and in the soil SO series, found in the present study, are in sharp contrast to those reported by Li *et al.*[20] using the scheme

Table 8 Results for Ce (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	4.11±0.10	7.76±0.29	8.31±0.31	6.16±0.23	23.2±0.85	49.3±0.64	42
SRM 2710	5.27±0.18	9.80±0.43	10.7±0.43	4.83±0.16	33.7±0.98	64.3±0.88	57
SRM 2711	5.72±0.43	11.3±0.08	9.18±0.01	8.40±0.23	45.3±0.22	79.9±0.32	69
SO-1	13.6±0.16	29.6±1.90	39.5±0.57	11.8±0.44	11.1±0.17	106±0.9	102±10*
SO-2	4.55±0.07	29.5±0.16	33.1±0.32	3.68±0.09	55.2±2.96	126±3.0	112±8*
SO-3	7.43±0.21	3.20±0.20	6.48±0.12	2.95±0.13	12.0±0.24	32.0±0.41	34±2*
SO-4	0.36±0.03	6.53±0.12	11.4±0.28	5.81±0.03	35.8±0.20	59.9±0.10	54±1*
MAG-1	5.72±0.05	15.3±0.24	15.8±0.47	12.2±0.25	45.0±1.80	94.1±2.12	88±9*
LKSD-4	3.00±0.01	7.96±0.48	22.4±0.57	2.53±0.11	9.43±0.17	45.3±0.44	48±6*
TILL-2	3.65±0.02	9.92±0.13	13.3±0.10	15.2±0.14	78.4±3.40	121±3.3	98±7

* Recommended value.

† See Table 4 for relevant references.

Table 9 Results for Co (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	0.70±0.06	6.01±0.13	4.03±0.12	1.02±0.49	2.46±0.30	14.22±0.88	13.4±0.7*
SRM 2710	0.43±0.15	3.53±0.40	1.17±0.61	2.49±0.64	2.41±0.93	10.03±0.95	10
SRM 2711	2.42±0.18	2.25±0.25	2.21±0.91	1.23±0.57	2.57±0.19	10.88±0.58	10
SO-1	<0.25	9.6±0.81	8.78±1.06	4.62±1.07	5.77±0.47	28.9±2.89	29±2*
SO-2	<0.25	0.46±0.08	0.80±0.55	<0.25	5.3±0.46	6.6±0.80	7.6±0.6*
SO-3	0.58±0.12	<0.25	1.96±0.16	<0.25	3.03±0.07	5.57±0.31	5.0±0.8
SO-4	<0.25	7.09±0.10	2.26±0.11	<0.25	1.06±0.59	10.6±0.68	10.4±1.4*
MAG-1	0.98±0.14	5.86±0.46	3.99±1.24	4.56±0.60	4.69±0.96	20.1±2.14	20.4±1.6*
LKSD-4	2.24±0.05	1.83±0.13	3.56±0.90	0.81±0.21	1.88±0.87	10.3±0.85	11±1*
TILL-2	0.85±0.05	4.59±0.46	4.01±0.84	2.29±0.88	2.27±1.02	14.0±1.25	15±2

* Recommended value.

† See Table 4 for relevant references.

Table 10 Results for Cr (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	1.04±0.17	6.41±0.22	27.5±0.63	10.9±0.29	55.7±2.08	101±1.33	130±4*
SRM 2710	0.44±0.06	1.14±0.22	4.51±0.11	5.60±0.40	15.9±0.56	27.7±1.10	39
SRM 2711	<0.25	0.78±0.06	5.73±0.07	3.90±0.03	24.9±0.69	35.3±0.60	47
SO-1	<0.25	9.49±0.70	59.4±2.20	47.5±0.49	45.0±2.70	161±4.83	170±22*
SO-2	<0.25	0.71±0.16	1.85±0.05	0.51±0.01	5.20±0.31	8.37±0.61	12.3±1.3*
SO-3	0.64±0.17	<0.25	5.10±0.37	1.75±0.10	13.3±0.21	20.9±0.62	27±4*
SO-4	<0.25	0.56±0.04	5.80±0.11	4.19±0.04	31.1±0.53	41.6±0.56	64±9*
MAG-1	0.66±0.03	3.45±0.23	19.5±0.92	12.5±0.49	51.8±1.90	88.9±2.26	97±8*
LKSD-4	0.89±0.14	<0.25	6.64±0.18	6.08±0.22	12.6±0.38	26.2±0.26	33±6*
TILL-2	0.64±0.01	2.96±0.15	14.5±0.30	8.60±0.17	30.5±0.47	57.2±0.36	67±11

* Recommended value.

† See Table 4 for relevant references.

Table 11 Results for Cu (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	<0.50	4.08±0.17	22.7±0.35	3.98±0.22	3.79±0.80	34.7±1.0	34.6±0.7*
SRM 2710	1501±43	925±58	400±3.8	96.5±0.80	40.9±1.46	2964±12	2950±130*
SRM 2711	15.5±0.92	33.9±1.48	36.8±1.33	22.2±0.42	5.26±0.20	115±1	114±2*
SO-1	1.57±0.01	13.1±0.75	29.2±0.21	11.5±0.41	5.67±0.61	61.1±1.0	61±5*
SO-2	<0.50	1.44±0.05	2.61±0.10	0.88±0.07	3.11±1.02	8.03±0.50	8±3
SO-3	<0.50	<0.50	9.84±0.66	1.66±0.10	2.73±0.05	14.7±0.60	17±2*
SO-4	<0.50	0.88±0.01	9.99±0.56	4.61±0.09	7.37±1.25	22.9±0.83	21±2*
MAG-1	<0.50	2.21±0.52	11.1±0.24	13.1±0.81	4.35±0.35	30.8±1.02	30±3*
LKSD-4	<0.50	1.50±0.07	12.9±0.29	13.4±0.20	3.05±0.09	30.8±0.37	31±4*
TILL-2	11.8±0.27	26.1±0.41	81.6±0.30	15.5±0.25	21.0±0.40	156±0.78	150±10

* Recommended value.

† See Table 4 for relevant references.

described by Tessier *et al.*[6] That protocol is designed to extract the following nominal classifications of element form: (1) exchangeable; (2) bound to carbonate and adsorbed; (3) bound to iron–manganese oxides; (4) bound to organic matter and sulfides; and (5) residual. The first two phases, equivalent to AEC in the present scheme, are interpreted as being relatively unstable under natural conditions (*e.g.*, elements in the first phase are loosely termed 'bioavailable') whereas the last three are considered as residence sites where elements are strongly bound and retained. Amorphous and crystalline iron and manganese oxides are not differentiated in the scheme of Tessier *et al.* and are interpreted by Li *et al.* as both reporting to the 'iron–manganese oxide' phase (3) extracted by 0.04 mol l^{-1} $NH_2OH.HCl$ in 25% CH_3CO_2H at 96 °C. Some of the

Table 12 Results for Fe (mean ± s in %): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	0.006±0.001	0.524±0.055	1.70±0.124	0.421±0.007	0.802±0.008	3.441±0.010	3.49±0.11*
SRM 2710	0.009±0.000	0.942±0.025	0.733±0.004	0.511±0.004	0.861±0.019	3.072±0.024	3.37±0.10*
SRM 2711	0.004±0.002	0.408±0.013	0.762±0.046	0.400±0.008	0.988±0.011	2.610±0.003	2.88±0.06*
SO-1	0.030±0.000	0.624±0.026	1.875±0.025	1.836±0.029	1.151±0.027	5.669±0.067	5.99±0.22*
SO-2	0.148±0.002	0.785±0.007	1.238±0.012	0.178±0.015	2.424±0.072	4.775±0.079	5.51±0.21*
SO-3	0.032±0.004	0.283±0.000	0.668±0.005	0.101±0.005	0.454±0.013	1.541±0.019	1.55±0.07*
SO-4	0.001±0.000	0.443±0.003	0.984±0.006	0.159±0.022	0.665±0.010	2.254±0.014	2.35±0.10*
MAG-1	0.001±0.000	0.647±0.009	1.45±0.054	1.03±0.037	1.196±0.249	4.327±0.062	4.75±0.21*
LKSD-4	0.026±0.000	0.656±0.008	1.08±0.008	0.546±0.010	0.444±0.005	2.749±0.003	2.85±0.2*
TILL-2	0.019±0.000	0.762±0.013	1.757±0.016	0.643±0.019	0.528±0.003	3.711±0.123	3.84±0.17

* Recommended value.
† See Table 4 for relevant references.

Table 13 Results for La (mean ± s in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	1.77±0.07	3.48±0.17	4.09±0.13	3.12±0.09	7.92±0.32	20.4±0.43	23
SRM 2710	2.81±0.11	4.92±0.17	5.72±0.23	2.95±0.06	9.41±0.27	25.8±0.23	34
SRM 2711	2.76±0.22	5.78±0.02	4.70±0.01	4.46±0.03	18.0±0.38	35.7±0.37	40
SO-1	16.2±0.19	11.2±0.53	13.6±0.13	7.02±0.31	5.58±0.05	53.6±0.25	54±2*
SO-2	1.79±0.04	11.1±0.03	8.02±0.16	1.87±0.03	21.6±1.19	44.4±1.13	46.5±0.7*
SO-3	4.02±0.18	1.18±0.04	2.44±0.06	1.50±0.05	6.19±0.17	15.3±0.40	16.9±1.3*
SO-4	0.15±0.02	3.87±0.04	4.68±0.18	2.81±0.05	10.2±0.18	21.8±0.12	28.2±1.7*
MAG-1	2.90±0.01	7.35±0.12	6.60±0.23	5.82±0.09	17.9±0.40	40.6±0.54	43±4*
LKSD-4	1.86±0.02	6.39±0.37	10.5±0.37	1.22±0.06	4.70±0.05	24.7±0.18	26±2*
TILL-2	2.03±0.02	3.75±0.03	2.83±0.07	7.95±0.12	28.4±1.57	44.9±1.48	44±4

* Recommended value.
† See Table 4 for relevant references.

Table 14 Results for Li (mean ± s in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	2.04±0.14	5.44±0.18	14.84±0.09	4.39±0.06	28.9±1.49	55.7±1.7	—
SRM 2710	1.06±0.09	1.93±0.02	7.92±0.10	6.19±0.21	21.5±0.29	38.6±0.56	—
SRM 2711	0.42±0.01	1.55±0.03	5.50±0.09	2.41±0.04	16.4±0.27	26.3±0.31	—
SO-1	1.08±0.02	4.72±0.12	17.7±0.19	11.7±0.45	11.2±0.33	46.4±0.07	48±2*
SO-2	<0.02	0.25±0.03	2.27±0.03	0.21±0.03	7.81±0.11	10.6±0.08	9±2
SO-3	0.61±0.01	0.56±0.00	4.71±0.03	0.83±0.08	4.58±0.05	11.4±0.09	9±3
SO-4	0.14±0.02	0.88±0.02	4.22±0.19	0.94±0.01	14.7±0.10	20.9±0.30	17±4
MAG-1	2.60±0.00	8.02±0.20	24.7±0.85	9.25±0.67	32.0±0.26	76.7±0.71	79±4*
LKSD-4	0.13±0.00	0.54±0.00	4.50±0.10	1.77±0.09	4.85±0.09	11.8±0.08	12±2*
TILL-2	0.16±0.01	2.01±0.07	17.8±0.29	8.09±0.25	20.0±0.63	48.1±0.68	47±4

* Recommended value.
† See Table 4 for relevant references.

Table 15 Results for Mn (mean ± s in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	135±4	166±2	103±2	25±1	63±1	492±5	534±17*
SRM 2710	1005±7	4522±15	1525±6	165±2	1851±25	9068±40	10100±400*
SRM 2711	236±4	124±2	58±1	23±1	129±1	570±6	638±28*
SO-1	30±1	280±9	159±1	138±7	173±3	780±5	851±40*
SO-2	17±1	63±1	58±2	6±0	509±10	652±11	666±40*
SO-3	229±10	84±1	52±1	7±0	78±2	450±10	542±30*
SO-4	123±2	315±2	39±1	6±0	58±1	542±2	619±30*
MAG-1	135±2	143±2	181±9	82±4	112±1	654±8	758±70*
LKSD-4	223±2	62±1	68±1	17±1	84±1	453±3	464±30*
TILL-2	70±1	253±3	156±2	64±1	158±2	701±3	780±28

* Recommended value.
† See Table 4 for relevant references.

differences in the results from these two schemes are illustrated in Fig. 2. The concentrations of elements reporting to phases (1) and (2) in Li *et al.* have been added together and represented by AEC, whereas phase (3) has been labelled as equivalent to am Fe ox, in contrast to their interpretation but more in keeping with applications described by Tessier *et al.*[21] The contrast in results is alarming. In general, Li *et al.* found a much higher percentage of element in the 'residual' phase, usually taken to mean silicates and, to a lesser extent, resistant sulfides and refractory organics.[6] The postulation that the predominant form of elements such as Zn and Cu in these soils is in the silicate phase rather than bound as oxides, oxyhydroxides, carbonates, adsorbed on iron, manganese or aluminium oxides or with organic substances (as complexes,

Table 16 Results for Ni (mean $\pm s$ in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	AM Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	4.01±0.23	26.1±0.51	39.4±1.02	7.85±0.26	12.8±0.56	90.1±1.02	88±5*
SRM 2710	<1.0	1.50±0.25	2.53±0.09	3.59±0.13	4.35±0.19	12.8±0.53	14.3±1.0*
SRM 2711	1.12±0.65	5.09±0.38	6.30±0.32	2.75±0.17	4.79±0.16	21.0±0.46	20.6±1.1*
SO-1	<1.0	9.5±0.81	35.9±2.28	25.2±0.20	23.8±1.41	95±2.66	92±12*
SO-2	<1.0	<1.0	<1.0	0.96±0.68	2.53±0.34	4.82±1.12	8±2
SO-3	<1.0	<1.0	5.17±0.08	1.68±0.19	4.36±0.65	13.1±0.76	14±5
SO-4	<1.0	8.6±0.34	8.30±0.53	1.99±0.04	6.35±0.37	25.3±0.73	24±4
MAG-1	3.40±0.20	11.6±0.74	19.0±0.93	9.49±0.57	10.8±0.50	54.3±1.36	53±8*
LKSD-4	4.85±0.11	9.2±0.50	8.85±1.23	6.04±0.25	5.38±0.16	34.4±1.36	31±5*
TILL-2	<1.0	3.28±0.24	16.7±0.36	8.80±0.17	7.51±0.28	35.6±0.51	32±3

* Recommended value.
† See Table 4 for relevant references.

Table 17 Results for P (mean $\pm s$ in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	<10	281±11	169±7	<10	61±3	519±15	620±50*
SRM 2710	13±1	748±64	109±1	<10	124±7	996±69	1060±150*
SRM 2711	31±4	650±42	75±5	<10	83±6	840±32	860±70*
SO-1	<10	303±29	268±29	<10	37±2	608±44	654±80*
SO-2	108±2	1470±53	1566±4	<10	39±4	3184±52	3008±200*
SO-3	<10	124±19	275±23	<10	<10	399±9	479±70*
SO-4	<10	204±8	178±36	222±7	226±5	840±54	872±70*
MAG-1	52±2	319±27	82±12	46±8	159±2	660±28	710±90*
LKSD-4	31±3	455±6	483±9	216±13	223±16	1410±3	1438±130*
TILL-2	<10	126±31	296±25	<10	188±4	611±53	750±80

* Recommended value.
† See Table 4 for relevant references.

Table 18 Results for Pb (mean $\pm s$ in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	1.00±0.11	4.68±0.32	6.70±0.12	0.653±0.048	7.17±0.67	20.2±0.98	18.9±0.15*
SRM 2710	2797±7.0	2021±5.0	359±7.3	63.0±1.16	217±2.38	5457±8.6	5532±80*
SRM 2711	843±6.2	235±2.9	48.2±1.94	3.68±0.08	13.4±0.40	1144±8.5	1162±31*
SO-1	0.352±0.017	3.79±0.30	5.42±0.55	0.820±0.066	8.23±0.12	18.7±0.48	20±3*
SO-2	1.02±0.03	2.38±0.03	2.01±0.04	0.109±0.017	13.1±0.51	18.7±0.40	20±2*
SO-3	2.96±0.19	1.32±0.05	4.45±0.07	0.285±0.090	3.82±0.12	12.8±0.12	13±3
SO-4	0.163±0.004	4.90±0.16	4.18±0.07	0.237±0.020	5.68±0.09	15.1±0.14	14±2*
MAG-1	10.0±0.25	7.28±0.27	4.23±0.16	0.847±0.050	6.45±0.17	28.9±0.38	24±3*
LKSD-4	43.9±0.67	32.6±0.64	12.4±0.39	0.436±0.029	3.58±0.11	92.9±0.84	91±6*
TILL-2	4.03±0.04	8.88±0.02	8.38±0.06	1.64±0.02	9.54±0.19	32.5±0.15	31±3

* Recommended value.
† See Table 4 for relevant references.

Table 19 Results for Ti (mean $\pm s$ in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	<0.5	0.64±0.05	16.4±2.2	186±1.9	3329±52	3533±52	3420±240*
SRM 2710	<0.5	3.44±0.04	35.5±0.5	525±4.3	2321±75	2885±78	2830±100*
SRM 2711	<0.5	0.78±0.23	15.1±0.2	182±3	2748±48	2946±46	3060±230*
SO-1	<0.5	7.06±0.51	165±2	2533±71	2870±145	5577±196	5211±200*
SO-2	8.05±0.09	8.59±0.13	124±0.7	116±4.7	8661±395	8919±399	8565±500*
SO-3	1.45±2.05	<0.5	43.3±1.5	82.3±3.3	1686±52	1813±59	1976±200*
SO-4	<0.5	<0.5	8.07±0.14	79.6±1.1	2767±3.3	2854±4	3474±240*
MAG-1	<0.5	2.30±0.10	41.2±2.1	353±2.0	4178±182	4576±185	4498±400*
LKSD-4	1.70±0.19	1.19±0.19	45.8±0.9	391±8	1476±41	1916±33	2156±470*
TILL-2	2.67±0.11	13.4±0.1	217±6	616±13.0	4088±247	4938±247	5300±190

* Recommended value.
† See Table 4 for relevant references.

chelates) is in conflict with the soil science literature.[22] Besides occurring in a chelated form in organic-rich upper horizon soils, Fe occurs largely as oxides and hydroxides (*e.g.*, as goethite, FeO_2H; lepidocrocite, FeO_2H; ferrihydrite, $Fe_2O_3.nH_2O$; hematite, Fe_2O_3; and maghemite, Fe_2O_3). It is likely that much of this Fe is reporting to the final fifth step (residual) under the conditions employed by Li *et al.* This was found to be the case in a study by Kheboian and Bauer[23] who examined the procedure of Tessier *et al.* and found, for example, goethite to be little dissolved until the final step. The present scheme generally extracts a greater percentage of element reporting to the organic–sulfide phase than does the phase (4) extraction in the work of Li *et al.*, reflecting the stronger oxidizing action of the $KClO_3$–HCl–HNO_3 attack. In fact,

Table 20 Results for Tl (mean ± *s* in µg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	7±1	65±3	119±12	82±7	407±3	685±24	740±50*
SRM 2710	146±6	117±10	238±5	159±11	615±18	1275±28	1300
SRM 2711	177±14	368±8	651±41	213±13	883±38	2292±16	2470±150*
SO-1	<5	25±8	141±17	181±26	255±11	606±20	(640)‡
SO-2	13±2	41±20	<10	<10	406±15	475±36	(580)
SO-3	5±2	21±12	37±18	14±5	152±2	229±14	(180)
SO-4	<5	20±1	109±8	26±1	310±4	468±6	(260)
MAG-1	12±1	17±3	124±9	49±4	532±7	735±13	(590)
LKSD-4	174±7	142±10	56±9	37±4	174±9	583±15	
TILL-2	21±2	49±6	116±6	79±7	646±26	910±11	

* Recommended value.
† See Table 4 for relevant references.
‡ Values in parentheses are proposed or for information.

Table 21 Results for U (mean ± *s* in µg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	428±36	97±12	508±13	239±2	1594±91	2866±150	3000
SRM 2710	10800±399	1898±79	5701±101	2511±83	2840±25	23749±396	25000
SRM 2711	134±3	48±3	336±9	323±35	1682±116	2523±84	2600
SO-1	359±27	175±11	330±18	222±10	492±16	1579±52	1710±40*
SO-2	90±16	57±1	184±8	43±12	301±16	675±19	980±50*
SO-3	129±15	42±2	129±5	52±5	597±14	949±31	1110±20*
SO-4	123±21	24±2	140±13	335±19	1232±22	1853±51	2380±70*
MAG-1	543±27	65±6	484±20	292±33	1316±7	2700±25	2700±300*
LKSD-4	19650±179	448±22	4719±77	5162±77	590±17	30569±153	31000±1800*
TILL-2	602±35	215±21	1088±26	589±34	2232±28	4726±50	5700±400

* Recommended value.
† See Table 4 for relevant references.

Table 22 Results for V (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	<0.5	15.5±0.29	25.9±0.41	8.12±0.15	55.5±2.04	105±1.9	112±5*
SRM 2710	<0.5	18.3±1.3	12.4±0.14	7.80±0.22	27.9±1.43	66.5±2.6	76.6±2.3*
SRM 2711	<0.5	6.90±0.41	14.5±0.37	6.46±0.05	40.1±1.4	67.9±1.4	81.6±2.9*
SO-1	<0.5	24.2±1.2	39.9±1.4	21.0±0.7	29.2±2.0	114±3.0	133±4*
SO-2	<0.5	5.39±0.36	14.1±0.31	2.47±0.26	7.23±1.35	29.2±2.1	57±4*
SO-3	<0.5	1.80±0.08	6.64±0.25	1.35±0.09	15.1±0.43	24.8±0.8	36±4*
SO-4	<0.5	5.58±0.02	12.5±0.10	3.89±0.03	46.9±1.34	68.9±1.4	85±5*
MAG-1	0.72±0.15	18.5±0.86	25.7±1.62	15.8±0.49	60.5±2.8	121±3.2	140±6*
LKSD-4	1.07±0.13	6.65±0.19	14.8±0.27	3.17±0.07	14.4±0.20	40.2±0.28	49±8*
TILL-2	<0.5	4.94±0.29	19.9±0.21	6.53±0.16	33.8±3.0	65.3±3.2	77±10

* Recommended value.
† See Table 4 for relevant references.

Table 23 Results for Zn (mean ± *s* in mg kg^{-1}): application of sequential leach procedure to CRMs in triplicate

CRM	AEC	Am Fe ox	Cry Fe ox	Organic–sulfide	Silicate	Sum	Literature value†
SRM 2709	3±0	18±1	56±1	14±1	15±1	107±2	106±3*
SRM 2710	1481±5	1743±26	1467±17	1043±16	556±3	6291±23	6952±91*
SRM 2711	45±1	99±1	88±1	58±1	32±1	322±3	350.4±4.8*
SO-1	1±0	20±1	54±1	43±1	17±0	135±1	144±8*
SO-2	5±0	5±0	35±1	5±0	58±2	107±3	115±6*
SO-3	8±1	4±0	26±1	3±0	6±0	48±1	48.3±1.8*
SO-4	2±0	14±0	44±0	10±0	18±1	89±2	94±4*
MAG-1	3±0	28±1	53±2	24±1	18±1	126±1	130±6*
LKSD-4	68±1	50±1	40±1	14±0	11±1	183±2	194±19*
TILL-2	3±0	12±1	66±1	22±0	15±2	118±1	130±8

* Recommended value.
† See Table 4 for relevant references.

elements bound in humic and fulvic forms will dissolve to a considerable degree in both the am Fe ox and iron–manganese oxide leaches of both methods.[2] Note also in Fig. 2, the contrasting distribution in P in SO-1 evident in the two methods; this behaviour is repeated in the other four soils common to both studies. Crystalline forms of phosphate minerals rarely occur in soils but many varieties of metastable and metamorphous phosphates are abundant and should be dissolved prior to the last mixed acid attack.[22] Li *et al.* dried their test suite of samples at 105 °C prior to application of the sequential extraction, an action which could easily lead to redistribution of elements to more crystalline forms and which nullifies the purpose of selective leaching.[11] Further investigation is needed to clarify whether drying at such a high

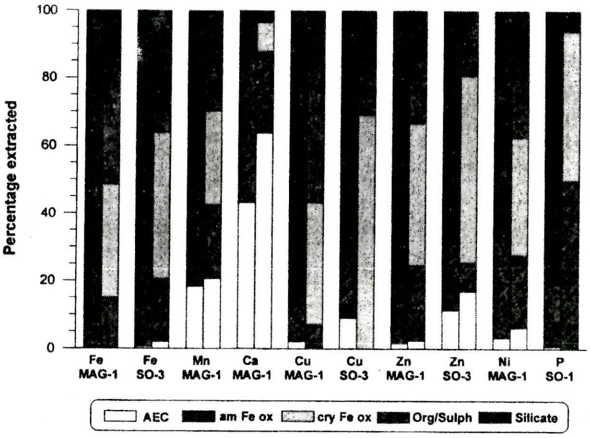

Fig. 2 Bar charts showing the comparison of results using the present method and that of Li *et al.*[20] The first bar of each pair represents the results of Li *et al.* and the second represents the present work

temperature could sufficiently explain the differences found in these two studies. However, previous studies have shown that, although drying oxic samples at elevated temperatures (50–100 °C) does have a significant redistribution effect on element associations, it is unlikely to explain differences of this magnitude under discussion (Fig. 2).[11,24]

The comparison of results shown in the present paper suggests that further research (mineralogical and chemical) is needed to improve the understanding of the capabilities and limitations of these leaches. The final goal of such work is to provide an arsenal of thoroughly examined selective leaches some or all of which would be used in a particular sequence to quantify the form(s) of an element for the objectives at hand.

CONCLUSIONS

Excellent precision, mostly in the range 2–10% RSD at levels a decade higher than detection limits, is achievable by this sequential extraction scheme. Somewhat inferior precision would be expected for samples other than CRMs which would probably not undergo such rigorous blending and homogenizing protocols during preparation. Determination of elements such as Co, Cu, Ni and V would benefit from the use of a more sensitive technique such as ICP-MS rather than ICP-AES, but matrix effects would require careful evaluation. Further research is needed to facilitate the comparison of results obtained by different selective extraction schemes, and in so doing, geochemists and analysts should strive to be more, rather than less definitive, in the phases described and 'specifically' extracted. Detailed mineralogical studies are required together with chemical analysis, to assess the true degree of specificity of each step and to obviate the inherent weaknesses of testing with synthetic compounds and phases. Assignment of very broad categories to phases of a sequential scheme, in order to standardize protocols for comparison purposes, defeats the purpose of applying selective leaches and indeed, can lead to misinterpretation.

REFERENCES

1 Hall, G. E. M., Vaive, J. E., and MacLaurin, A. I., *J. Geochem. Explor.*, 1996, **50**, issue 1.
2 Hall, G. E. M., Vaive, J. E., Beer, R., and Hoashi, M., *Geol. Surv. Can. Bull. 426*, 1996, p. 169.
3 Sondag, F., *J. Geochem. Explor.*, 1981, **15**, 645.
4 Chao, T. T., *J. Geochem. Explor.*, 1984, **20**, 101.
5 Cardoso Fonseca, E., and Martin, H., *J. Geochem. Explor.*, 1986, **26**, 231.
6 Tessier, A., Campbell, P. G. C., and Bisson, M., *Anal. Chem.*, 1979, **51**, 844.
7 Chao, T. T., and Theobald, P. K., *Econ. Geol.*, 1976, **71**, 1560.
8 Chao, T. T., and Zhou, L., *J. Soil Sci. Soc., Am. Proc.*, 1983, **47**, 225.
9 Chester, R., and Hughes, M. J., *Chem. Geol.*, 1967, **2**, 249.
10 Chao, T. T., and Sanzalone, R. F., *J. Res. U.S. Geol. Surv.*, 1977, **5**, 409.
11 Kersten, M., and Forstner, U., in *Trace Element Speciation: Analytical Methods and Problems*, ed. Batley, G., CRC Press, Boca Raton, 1989, p. 245.
12 Quevauviller, P., Rauret, G., Muntau, H., Ure, A. M., Rubio, R., López-Sánchez, J. F., Fiedler, H. D., and Griepink, B., *Fresenius' J. Anal. Chem.*, 1994, **349**, 808.
13 Fiedler, H. D., López-Sánchez, J. F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A. M., and Muntau, H., *Analyst*, 1994, **119**, 1109.
14 Govindaraju, K., *Geostand. Newsl.*, 1994, **18**, 158.
15 Gladney, E. S., and Roelandts, I., *Geostand. Newsl.*, 1989, **13**, 217.
16 Gladney, E. S., and Roelandts, I., *Geostand. Newsl.*, 1988, **12**, 253.
17 Lynch, J. J., *Geostand. Newsl.*, 1990, **14**, 153.
18 Lynch, J. J., personal communication.
19 Kane, J. S., Wilson, S. A., Lipinski, J., and Butler, L., *Am. Environ. Lab.*, 1993, **6**, 14.
20 Li, X., Coles, B., Ramsey, M. H., and Thornton, I., *Chem. Geol.*, 1995, **124**, 109.
21 Tessier, A., Rapin, F., and Carignan, R., *Geochim. Cosmochim. Acta*, 1984, **49**, 183.
22 Kabata-Pendias, A., and Pendias, H., *Trace Elements in Soils and Plants*, CRC Press, Boca Raton, 1985.
23 Kheboian, C., and Bauer, C. F., *Anal. Chem.*, 1987, **59**, 1417.
24 Thomson, E. A., Luoma, S. N., Cain, D. J., and Johansson, C., *Water, Air Soil Pollut.*, 1980, **14**, 215.

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COMPARISON OF TWO REAGENTS, SODIUM PYROPHOSPHATE AND SODIUM HYDROXIDE, IN THE EXTRACTION OF LABILE METAL ORGANIC COMPLEXES

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Abstract. The international reference lake sediment, LKSD-4, was used to compare Hg, organic C and Zn extracted from its 'soluble organic' phase by two commonly used reagents: 0.1 M $Na_4P_2O_7$ solution at pH 10 and 0.5 M NaOH solution at pH 12. While recoveries of Hg and Zn by 0.1 M $Na_4P_2O_7$ are not affected by changes in sample weight to reagent volume ratio (W/V) or contact time, those by NaOH show a marked dependency. In general, the NaOH leach extracts more organic C and Hg from LKSD-4 but less Zn. Over the range of conditions studied, the NaOH-based method extracted 4.7-9.8% C, 27-103 ng g^{-1} Hg and 19-69 µg g^{-1} Zn from LKSD-4, compared to 2.3-2.8% C, 17-24 ng g^{-1} Hg and 64-72 µg g^{-1} Zn by the $Na_4P_2O_7$ leach. Clearly, different groups of organic substances are being dissolved by these two reagents and therefore a comparison of data from different laboratories becomes meaningless. This paper suggests that more research is needed into the exact nature of metal-organic associations extracted by selective leaches and into associated artifacts of extraction such as readsorption phenomena.

Keywords: selective leach; organic; humic; fulvic; analysis; mercury; zinc

1. Introduction

The efficiency of sodium pyrophosphate solution in extracting metals bound to humic and fulvic complexes in humus, soil and sediment samples has been studied recently at the Geological Survey of Canada (Hall *et al.*, 1995; Hall *et al.*, 1996). This work was stimulated by interest amongst the mineral exploration community in distinguishing that portion of metal held in a relatively labile form, in the surficial environment, from that portion present in mineralogical structures such as crystalline oxides or silicates (e.g. Antropova *et al.*, 1992). The high scavenging capacity of humic and fulvic complexes is usually attributed to their carboxylic acid functional groups, with contributions from other groups such as -NH_2 (amine) and -SH (thiol). As metals can be adsorbed, complexed or chelated by these organic substances, design of a phase-specific leach is challenging. Oxidative destruction of the organic matter, by reagents such as H_2O_2 or NaOCl, is undesirable as other phases such as sulphides and Mn oxides may also be dissolved and precipitation can occur at high pH. Dissolution of organic matter by sodium pyrophosphate, $Na_4P_2O_7$, has been adopted by soil scientists (e.g. McKeague, 1968; Bascomb and Thanigasalam, 1978; Jeanroy and Guillet, 1981) and, moreover, the ratio of C in humic to C in fulvic components of the extract has been used to classify A and B horizons. The normal procedure employed by soil scientists is that described by McKeague *et al.* (1971) where 1 g of sample is stirred for 16 h in 100 ml of 0.1 M $Na_4P_2O_7$ at room temperature. Application of this procedure to 70 soil and sediment samples and the international lake sediment reference material, LKSD-4, demonstrated that the commonly used period of 16 h for the 0.1 M $Na_4P_2O_7$ leach could be shortened to 1 h without significant decrease in extraction efficiency (<5%); indeed, the shorter contact time is of benefit to elements such as Ni which are prone to readsorption (Hall *et al.*, 1996). Analyses of 28 1-g samples of LKSD-4 over a two year period

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demonstrated relative standard deviations in the range 2-6% for elements such as Zn, Pb, Cu, Fe, Mn and C.

While the $Na_4P_2O_7$ leach is being adopted widely in exploration geochemistry, th NaOH reagent remains that suggested by the International Humic Substances Society (Kersten and Forstner, 1989) and is prominent in environmental studies in sediment analys (e.g. Dmytriw *et al.*, 1995). Kersten and Forstner (1989) warn against the use of NaOH fo two main reasons: it causes unacceptable dissolution of clay minerals; and metals tend to hydrolyze and readsorb onto reactive surface sites following removal of their organic coatings. This paper compares the efficacy of extraction of Hg, Zn and C bound to `soluble organic matter in the geological reference material (GRM), LKSD-4, using these two popular leach solutions, 0.1 M $Na_4P_2O_7$ and 0.5 M NaOH.

2. Methods

The GRM, LKSD-4 (from the Canadian Certified Reference Materials Project, CCRMP), was used to study the effects of (a) the ratio of sample weight to volume of reagent and (b) contact time in both the 0.1 M $Na_4P_2O_7$ (at pH 10) and 0.5 M NaOH (at pH 12) leaches. This GRM contains 17.7% C, 190 ng g^{-1} total Hg and 194 µg g^{-1} Zn (Lynch, 1990). Each test was performed in triplicate. In the first half of the study, contact times of 1 h ($Na_4P_2O_7$) and 18 h (NaOH) were used, 18 h having being recommended by Schnitzer and Skinner (1968) in the development of the NaOH procedure. Ratios of sample weight:reagent volum examined were 0.005, 0.01, 0.02, 0.04 and 0.1 g ml^{-1}, the minimum sample weight taken being 0.25 g. The NaOH leach was carried out under N_2 (to minimise auto-oxidation and hydrolysis) and constant shaking was employed for both leaches.

Contact times of 1, 2, 3, 4 and 18 h were tested, using two ratios of sample weight:reagent volume: 0.005 and 0.01 for the $Na_4P_2O_7$ procedure; and 0.04 and 0.06 for th NaOH extraction. These ratios reflect those commonly used in the literature. Each solution was centrifuged at 2800 rpm for 10-15 min for separation from the residue prior to analysis.

Each leach solution was diluted with water and, for Hg determination, the solution immediately made 4 M in HCl and 0.5% in BrCl (to maintain Hg in solution as Hg^{2+}). The dilution factor was variable, the criterion being that the final solution contained less than 40 ng l^{-1} Hg, the uppermost calibration standard. Mercury was determined in the resulting solutions by ICP-MS with $NaBH_4$ as reductant in-line to form Hg^0 vapour which was swept into the central channel of the ICP torch (for details, see Hall and Pelchat, 1997). Zinc was determined by flame AAS at 213.9 nm. Organic C in solution was determined using the Schimadzu Model 5000 TOC instrument, based on combustion at 680 °C and non-dispersive infra-red detection.

3. Results and Discussion

The influence of changing the sample weight to reagent volume ratio on the extraction of Hg and organic C in LKSD-4 is illustrated in Fig. 1 for both methods. Change in this ratio, from 0.005 to 0.1, has little effect on the Hg or C concentrations extracted by $Na_4P_2O_7$ which are about 18 ng g^{-1} and 2.5%, respectively (Fig. 1a). However, there is a marked increase in Hg (exponential?) extracted by NaOH solution when the sample weight:reagent volume ratio decreases below 0.04, resulting in a maximum average Hg concentration of 102 ng g^{-1} as compared to a minimum of 55 ng g^{-1} (Fig. 1b). This increase is not evident in the behaviour of C which is constant at about 8.4% except for the increase to 9.8% at the minimum sample weight:volume ratio of 0.005. Clearly, a much greater component of the organic C is being extracted by the NaOH leach (8.4 vs. 2.5% C) but the lack of coherence between the Hg and C graphs for this leach suggests that much of the corresponding Hg is not associated with organics. The results for Zn are presented in Fig. 2.

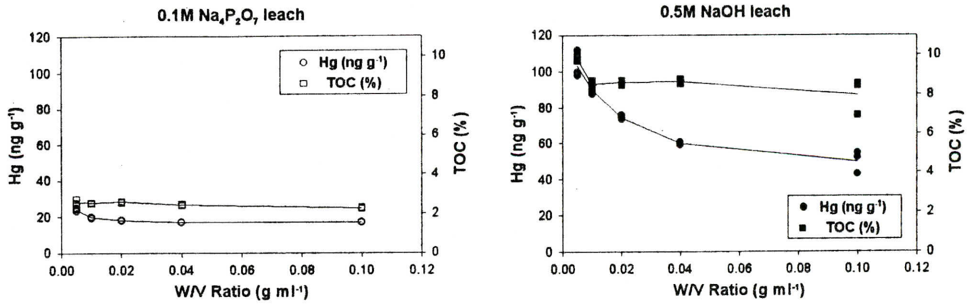

Fig. 1 Effect of sample weight to reagent volume ratio (W/V) on Hg and organic C extracted from LKSD-4 by (a) 0.1 M $Na_4P_2O_7$ and (b) 0.5 M NaOH solutions.

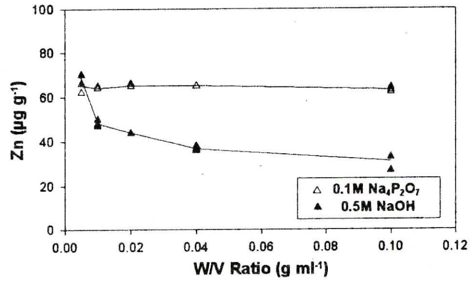

Fig. 2 Effect of sample weight to reagent volume ratio (W/V) on Zn extracted from LKSD-4 by 0.1 M $Na_4P_2O_7$ and 0.5 M NaOH solutions.

Note the plateau again evident for the $Na_4P_2O_7$ graph and a sharp increase in Zn extracted by NaOH at the minimum sample:volume ratio which coincides with the increase in C. Here we see the converse in trends: Zn in the 'labile organic' component of LKSD-4 is about 65 µg g^{-1} by the $Na_4P_2O_7$ extractant, whereas it ranges from a low of only 31 µg g^{-1} to 69 µg g^{-1} using NaOH. The Hg and Zn graphs suggest that more than one 'phase' is being dissolved by NaOH and that readsorption could be occurring. If 0.1 M $Na_4P_2O_7$ is extracting the humic and fulvic component of LKSD-4 with adequate specificity (as indicated by McKeague, 1968; McKeague *et al.*, 1971; Bascomb and Thanigasalam, 1978), then the 0.5 M NaOH leach is over-estimating the associated labile Hg and under-estimating Zn. Clearly it is undesirable to select conditions of extraction where slight deviations cause major changes i recovery, as would be the case when operating below a ratio of 0.04 in Fig. 1b (see Dmytri *et al.*, 1995).

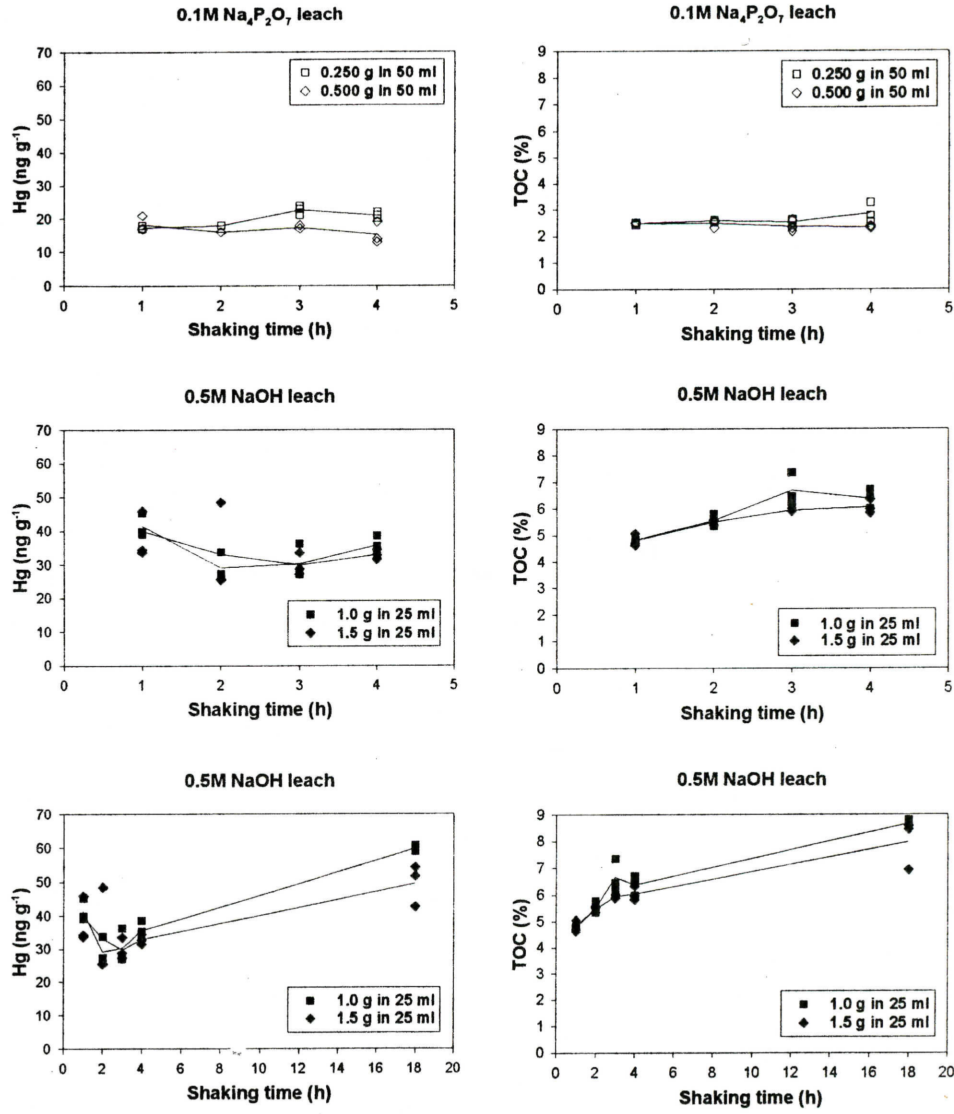

Fig. 3 Effect of contact time on Hg and organic C extracted from LKSD-4 by (a) 0.1 M $Na_4P_2O_7$ and (b)-(c) 0.5 NaOH solutions.

Contact time has a slight effect on the extraction of Hg and C by 0.1 M $Na_4P_2O_7$ at the lower sample weight of 0.25 g of LKSD-4 which may be a reflection of heterogeneityand noisier measurements at the lower concentrations (Fig. 3a). Extraction of Hg and C by 0.5M NaOH differs over the 4 h period examined: Hg concentrations fall at hour 2 and 3 compared to that at hour 1 and rise again slowly whereas C concentration increases continuously with time from 1 h on (Figs. 3b, c). Triplicate analyses indicate inferior reproducibility by the NaOH leach (Fig. 3).

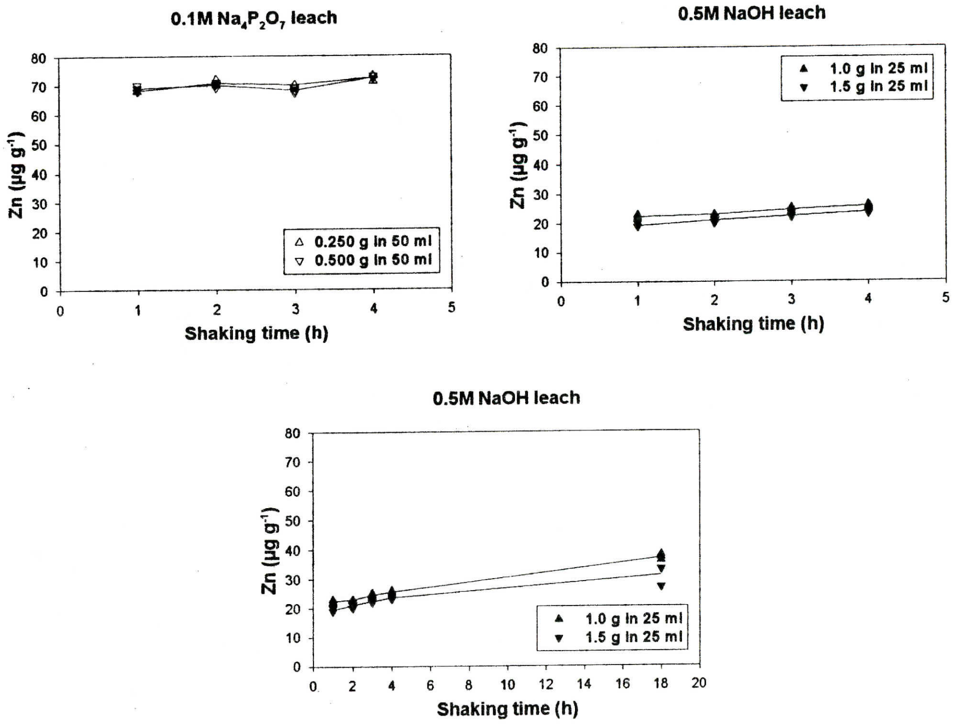

Fig. 4 Effect of contact time on Zn extracted from LKSD-4 by 0.1 M $Na_4P_2O_7$ and 0.5 M NaOH solutions.

The effect of contact time on Zn extraction by both methods is shown in Fig. 4: Zn levels are unchanged (70±2 µg g^{-1}) with time using $Na_4P_2O_7$ but increase gradually with NaOH reagent, from 24-26 µg g^{-1} at 1 h to a concentration of 30-37 µg g^{-1} at 18 h.

Relatively little is known about the extent to which the organic matter extracted by 0.5 M NaOH differs from that dissolved by 0.1 M $Na_4P_2O_7$. In a comparison of the two reagents applied to several different soil types, Schnitzer and Schuppli (1989a) found there to be a tendency for the humic acids derived from the 0.1 M $Na_4P_2O_7$ leach to be more aromatic and of higher molecular weight but did not find the significant difference in recoveries of organic C we find in LKSD-4 (2.5 vs. 8.4% C). They recommended the 0.1 M $Na_4P_2O_7$ leach as an attractive alternative to 0.5 NaOH as the probabilities for auto-oxidation and hydrolysis are greatly diminished. A sequential extraction procedure then developed by Schnitzer and Schuppli (1989b), to define various organic fractions in soil, placed 0.1 M $Na_4P_2O_7$ before 0.5 M NaOH to specifically dissolve organic matter complexed to metals and clays as opposed to “free” organic matter including less decomposed material which would finally be leached with the latter reagent. In outlining knowledge gaps yet to be addressed, Schnitzer (1991) calls for future research into metal, clay and humic sustance (humic acids, fulvic acids and humin) interactions. Given the complexity of these interactions (via adsorption, chelation and complexation) and the range of chemical structures involved (e.g. aliphatic-, aromatic-, phenolic-, carbohydrate-C), the classification of the ‘soluble’ or ‘poorly soluble organic’ phases liberated in commonly use ‘selective’ leaches is very oversimplified. It is hardly surprising, therefore, that dissimilar metal concentrations are obtained by the application of these different reagents. Further attention should be given to exactly what group(s) of metal-organic substances are of interest, to, for example, distinguish between diagenesis in a sediment core and a process taking place prior to deposition.

4. Conclusion

The 0.1 M $Na_4P_2O_7$ leach at pH 10, designed to dissolve the ‘soluble organic’ phase of a so or sediment, shows minimal change in the amount of organic C, Hg or Zn leached from LKSD-4 when parameters of sample weight to reagent volume (W/V) and contact time are altered. This is in contrast to the 0.5 M NaOH leach at pH 12, where there appears to be an exponential increase in Hg (and Zn) extracted with decrease in W/V which does not correspond to the behaviour of organic C. Contact time has a less dramatic effect on recoveries by NaOH which are seen to increase generally with time for all three elements, though Hg does show a slight decrease initially after 1 h. Thus, the ratio of W/V selected in the NaOH procedure will have a significant effect on the results. Over the range of conditions studied, the NaOH-based method extracted 4.7-9.8% C and 27-103 ng g^{-1} Hg from LKSD-4, compared to 2.3-2.8% C and 17-24 ng g^{-1} Hg by the $Na_4P_2O_7$ leach. Unlike Hg, extraction of Zn by the $Na_4P_2O_7$ leach was consistently higher, at 64-72 µg g^{-1} over this range, compared to 19-69 µg g^{-1} by NaOH. Clearly the two reagents are extracting differen groups of organic substances and results for both cannot be equated to the same nominal phase.

References

Antropova, L.V., Goldberg, I.S., Voroshilov, N.A., and Ryss, Ju.S.: 1992, *J. Geochem. Explor.* **43**, 157-166.
Bascomb, C.L. and Thanigasalam, K.: 1978, *J.Soil Sci.* **29**, 382-387.
Dmytriw, R., Mucci, A., Lucotte, M., and Pichet, P.: 1995, *Water Air Soil Pollut.* **80**, 1099-1103.
Hall, G.E.M., MacLaurin, A.I, and Vaive, J.E.: 1995, *J. Geochem. Explor.* **54**, 27-38.
Hall, G.E.M., Vaive, J.E., and MacLaurin, A.I.: 1996, *J. Geochem. Explor.* **56**, 23-36.
Hall, G.E.M. and Pelchat, J.C.: 1997, *J. Anal. At. Spectrom.* **12**, *page info coming (Jan issue)*

Jeanroy, E. and Guillet, B.: 1981, *Geoderma* **26**, 95-105.
Kersten, M. and Forstner, U.: 1989, *Trace Element Speciation: Analytical Methods and Problems*, G. Batley [ed], CRC Press, 245-317.
Lynch, J.J.: 1990, *Geostand. Newsl.* **14**, 153-167.
McKeague, J.A.: 1968, *Can. J. Soil Sci.* **48**, 27-35.
McKeague, J.A., Brydon, J.E., and Miles, N.M.: 1971, *Soil Sci. Soc. Amer. Proc.* **35**, 33-38.
Schnitzer, M.: 1991, *Soil Sci.* **151**, 41-58.
Schnitzer, M. and Schuppli, P.: 1989a, *Can. J. Soil Sci.* **69**, 253-262.
Schnitzer, M. and Schuppli, P.: 1989b, *Soil Sci. Soc. Am. J.* **53**, 1418-1424.
Schnitzer, M. and Skinner, S.I.M.: 1968, *Soil Sci.* **105**, 392-396.

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Assessment of the 1 M NH_4NO_3 extraction protocol to identify mobile forms of Cd in soils

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Abstract

Extraction of soils by leaching 20 g in 50 ml of unbuffered 1 M NH_4NO_3 for 2 h has become the standard German protocol (DIN 19730) to estimate mobile and potentially hazardous forms of trace elements. This protocol was examined using soil controls of chernozem and podzol character collected in the Canadian Prairies and Ontario. It was found that this procedure was not robust with respect to change in sample weight per unit volume of reagent or to contact time. A 3- to 15-fold increase in Cd extracted was produced by decreasing sample weight from 10 g to 1 g in 50 ml of reagent. This change in extractable-Cd was more pronounced with increasing pH of the soil, ranging from 5.2 to 8.1 amongst the control samples. Leach period was less significant in determining results but longer time (1–3 h) generally produced lower extractable-Cd, suggesting readsorption. Lack of stability of Cd in this reagent was further demonstrated by spiking experiments where Cd was added at the beginning of the leach. Recoveries of Cd at 50 and 200 ppb were below 20% for soils of pH 6.1 and 6.9. Such severe adsorption of Cd was not encountered with another unbuffered reagent, 1 M NH_4Cl, operating at a similar initial pH of 5. Cadmium levels extracted from soils by NH_4Cl and 0.1 M $Na_4P_2O_7$ were comparable and could be used to predict uptake in durum wheat on the Canadian Prairies, whereas data by the 1 M NH_4NO_3 leach were generally near the detection limit of 0.1 ppb (ng g^{-1}) Cd. Readsorption of Cd and lack of equilibrium in the 1 M NH_4NO_3 extraction could lead to underestimation of plant-available Cd in neutral and alkaline soils.

Keywords: ammonium nitrate; extraction; soil; cadmium; DIN 19730

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1. Introduction

There is global concern for the negative effects on human health and ecosystems of excessive amounts of heavy metals such as Cd (Chaney, 1997). The search for sound protocols designed to predict 'bioavailable' forms of toxic metals such as Cd in soils is evident in the focus of recent international meetings such as the 'Cadmium Workshop' (Sources of Cadmium in the Environment) held in Sweden in 1996 and hosted by member countries of the Organisation for Economic and Cooperative Development (OECD).

A procedure to determine mobile concentrations of trace elements (viz. Ag, As, Bi, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, U, V and Zn) in soils was adopted in 1995 in Germany, to be used for risk assessment, for limiting agricultural use and as a tool to identify soils with high amounts of leach-

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able elements (DIN 19730, 1995; Prüeß, 1998). This protocol, known as 'DIN 19730', is based on extraction of 20 g of air-dried soil in 50 ml of 1 M NH_4NO_3 for 2 h at room temperature. Application of this leach in Germany has been used to derive background, action and threshold values for mobile trace elements in soils (Prüeß, 1992). For example, the 'action value' for NH_4NO_3-extractable Cd is set at 20 ppb (ng g^{-1}), a soil concentration below which critical element concentrations in plants should not be exceeded in 95% of the cases. The corresponding threshold value for limiting agricultural use is 40 ppb NH_4NO_3-extractable Cd for food plants (e.g. broccoli, wheat, spinach). Adoption of this protocol by other countries, such as those within the European Community or even internationally, has been proposed (Anderson et al., 1994).

This procedure (DIN 19730) is based on work by Symeonides and McRae (1977) in their assessment of plant-available Cd in soils. They compared the extraction efficiencies of seven reagents (e.g. NH_4OAc, AcOH, EDTA) used to recover Cd which had been added to 25 samples of various surface soils collected in Kent, England. Results were then plotted against the Cd found in dry radish tops grown in these soils and soil extraction by 1 M NH_4NO_3 showed the best correlation, with a coefficient of 0.97. The pH of the soils ranged from 4.9 to 8.0; Cd was added at unnaturally high levels, as $CdCl_2$, equivalent to 50 and 100 ppm in the dried soil. Ammonium acetate, buffered at pH 7, showed the next best correlation coefficient, at 0.50, with Cd extracted in the range 8–78 ppm (cf. 0.6–66 ppm in 1 M NH_4NO_3). Symeonides and McRae (1977) argue that the best correlation with crop response would be expected with an unbuffered reagent such as 1 M NH_4NO_3 so that extraction takes place near the pH of the soil encountered by the root system. The only significant difference found by altering conditions of soil weight : extractant volume and equilibration time was that less Cd was extracted by longer shaking (e.g. 18 h) which suggested readsorption. They recommended a 1-h equilibration, with agitation, of a 10-g sample in 100 ml of 1 M NH_4NO_3.

Later work by Stuanes et al. (1984) advocated the use of 1 M NH_4NO_3 to provide data on exchangeable elements, exchangeable acidity, exchangeable Al, cation exchange capacity and base saturation of the soil. They found results by this reagent to be identical to those produced using 1 M KCl and 1 M NH_4Cl for the purpose of evaluation of soil status. Furthermore, there were no differences in the amounts of Na, K, Mg and Ca extracted by 1 M NH_4NO_3 and NH_4OAc at pH 7 from the various acidic soils investigated. Ammonium nitrate was preferred over the Cl-based reagents as the latter posed problems in the analytical techniques employed. In their development of a sensitive ICP–MS-based method to determine As and Se in soils, Anderson et al. (1994) analysed three standard reference samples (soil GXR-5, sediment MESS-1 and coal fly ash NIST 1633a) for both total and NH_4NO_3-extractable As and Se. Although total concentrations were as high as 132 ppm in As and 10.6 ppm in Se in NIST 1633a, extractable-As and Se were found to be below the detection limits of 5 and 10 ppb, respectively, in all three samples.

Garrett and colleagues (Garrett et al., 1998; R.G. Garrett, pers. commun., 1997) have studied different extractants applied to soils collected in the Canadian Prairies (Garrett, 1994) in an attempt to estimate that amount of Cd which would be phyto-available to various cultivars of durum wheat. The reagents tested comprise: 0.1 M $Na_4P_2O_7$ (McKeague, 1968; Hall et al., 1996); 0.005 M DTPA (Lindsay and Norvell, 1978); 1 M NH_4Cl (Krishnamurti et al., 1995); and 1 M NH_4NO_3. It was during this study that problems with the NH_4NO_3 extraction became apparent; this paper documents those limitations.

2. Experimental

Six soil control reference materials (CRMs) were prepared: three (CR-Ap, MO-1 and MO-7) were collected on the Canadian Prairies and another three (HIG-1, FOR-1 and ROS-1) in Ontario (Table 1). These bulk samples were air-dried, coarse material removed by hand and finally they were screened to pass a 2-mm sieve. With the exception of a small split which was ball-milled for total metal determination (by HF–$HClO_4$–HNO_3), they were used 'as is' for the extraction experiments.

All reagents used in this project were Baker (Phillipsburg, NJ, USA) 'analysed reagent' grade. Standard solutions employed for calibration in the measurement techniques were purchased from High

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Table 1
Description of soil CRMs used in the study; all had been air-dried and screened to pass a 2-mm sieve

Soil CRM	Description	pH [a]	Total Cd (ppb)
CR-Ap	Ploughed horizon, dark brown chernozem	6.4	322 ± 8 ($n = 3$)
MO-1	Ploughed horizon, black chernozem	6.4	1600
MO-7	C-horizon, black chernozem	8.1	2400
HIG-1	Ploughed horizon, melanic brunisol	6.9	428 ± 5 ($n = 3$)
FOR-1	A-horizon forest, humo-ferric podsol	5.2	198 ± 7 ($n = 3$)
ROS-1	Ploughed horizon, melanic brunisol	6.1	199 ± 8 ($n = 3$)

[a] Measured in 0.01 M $CaCl_2$ according to Peech, 1995.

Purity Standards (Charleston, SC, USA). Distilled deionized water was used throughout. Ultrex nitric acid, at 1%, was used to dilute leachates prior to analysis by ICP–MS.

Initial results showed that the reagent, 1 M NH_4NO_3, contained high concentrations of the trace elements of interest and therefore required cleaning. This procedure comprised passing the reagent through a column of Chelex-100 resin (100–200 mesh) in the NH_4 state. If necessary, the pH of the reagent was then adjusted to 4.7 (that before contact with Chelex resin) and this solution was used throughout the study.

The ICP–MS analysis was carried out using the VG PlasmaQuad II+ (Winsford, Cheshire, UK). In addition to Cd, measured at m/z 114 and 118, analysis was also carried out at m/z: 63 for Cu; 57 for Fe; 55 for Mn; 208 for Pb; and 66 for Zn. Corrections were made for spectral interferences of Sn and MoO on ^{114}Cd by monitoring ^{118}Sn and ^{198}Mo. All analyte solutions were diluted at least 10-fold in 1% HNO_3 just prior to nebulisation ICP–MS. Calibration solutions were run after every eight samples; internal standards were not employed. Periodically, measurement by standard additions was carried out to confirm the absence of non-spectral matrix interferences.

The effects of changing leach time and sample weight : reagent volume from those stipulated in the DIN 19730 procedure were investigated using the six soil CRMs. All tests were carried out in triplicate for each CRM. The basic procedure is as follows.

(1) Weigh 20 g of <2 mm dried sample into a 250-ml high-density polyethylene bottle. Add 50 ml of 1 M NH_4NO_3 and cap. Place on a horizontal reciprocating shaker at 180 cycles min^{-1} for 2 h. [These ratios and times were changed to evaluate their effects.]

(2) Pour into centrifuge tube and spin at 2800 rpm for 10 min.

(3) Decant and filter through 0.45-μm Millipore filter paper (type HAWP) under vacuum.

(4) Dilute filtrate 10-fold with 1% HNO_3 prior to analysis by ICP–MS (overall dilution factor 25).

The detection limit for Cd under these experimental conditions was 0.1 ppb in the original sample.

The three Ontario CRMs were used to measure the recovery of Cd added at equivalent concentrations of 5, 50 and 200 ppb (ng g^{-1}) at the beginning of the DIN 1 M NH_4NO_3 procedure. A set of spiked blank solutions was also carried through the procedure to test for any Cd lost to the walls of the vessels. This experiment was repeated for two other extractions: 0.1 M $Na_4P_2O_7$, as described by Hall et al. (1996); and 1 M NH_4Cl, as described by Krishnamurti et al. (1995). Cadmium was added as $CdCl_2$ in solution for the 1 M NH_4Cl leach, whereas the standard stock solution in 2% HNO_3 was used for spiking in the other two leaches.

3. Results and discussion

Initial indication of readsorption occurring in the NH_4NO_3 leach was given by comparison of blank reagent values (prior to cleaning with Chelex-100) for Cd, Cu, Fe, Mn, Pb and Zn with element concentrations in the leachates of the suite of CRMs. For example, the data presented in Table 2 show that, although the reagent blank (1 M NH_4NO_3) contains 9 μg l^{-1} Pb, levels of Pb found in the leachates of the CRMs are much lower, in the range 0.2 to 2 μg l^{-1}. Similarly, the blank concentration of Fe (6.4 μg l^{-1}) is higher than that in any of the CRMs (<4 μg l^{-1}). Hence, contact of the NH_4NO_3 reagent with the soils

Table 2
Element concentrations (in µg l^{-1}) in 1 M NH_4NO_3 leachates of soil CRMs (5 g/50 ml)

Medium	Cd	Cu	Fe	Mn	Pb	Zn
1 M NH_4NO_3 [a]	0.21 ± 0.01	3.0 ± 0.2	6.4 ± 0.2	15.0 ± 0.4	9.0 ± 0.5	5.7
CRMs	0.29–0.55	0.5–4.9	<1–4.0	1–650	0.2–2.0	3.3

[a] Six processed blanks.

is effectively cleaning it for these elements! The concentration of Cd in the CRMs is just above that of the blank reagent. All further work carried out with NH_4NO_3, which had been cleaned by passing the solution through a column of Chelex-100, showed blank analyte concentrations below detection limits.

Precision was acceptable throughout, with RSDs of triplicate analyses averaging 10% except at levels of Cd extracted below 1 ppb where analytical variability was dominant, and at sample weights of 1 g where sampling variability was dominant. Fig. 1 shows the effect of leaching time on the extraction of Cd from 5 and 10 g weights of the three Prairie CRMs. Leaching time appears to have little effect on MO-1, but the other two show varying decreases in Cd extracted over 3 h compared to 2 or 1 h. More significant is the difference in results obtained at the two sample weights taken. For example, 2.8 ± 0.3 ppb Cd is leached from 5 g of MO-7 in 1 h compared to only 0.48 ± 0.08 ppb from 10 g. The equivalent values for CR-Ap are 2.0 ± 0.2 ppb and 0.8 ± 0.1 ppb, respectively. These data could be even lower if the ratio of 20 g to 50 ml specified in DIN 19730 had been implemented. Results for 5 and 10 g of MO-1 are similar at 1 h extraction but diverge at longer leaching times, with decreases in Cd for the 10-g aliquot suggestive of readsorption. Manganese determined in these solutions of CR-Ap showed different behaviour to that of Cd, with consistent *increa* extraction with time and a greater amount extr in the 10-g sample (Fig. 2).

In another set of experiments with the F CRMs, even lower weights of 1 and 2.5 g leached for 1 and 3 h (Fig. 3). By lowerin absolute amount of sample from 10 g to 1 g in of NH_4NO_3, a 3- to 15-fold increase in Cd extr in 1 h is obtained, the greatest difference bein MO-7 (0.48 ± 0.08 to 7.3 ± 2.3 ppb) and the for MO-1 (2.1 ± 0.2 to 7.2 ± 2.3 ppb Cd). Soil is the most alkaline of the three (pH 8.1 compa 6.4, Table 1). Similar patterns are evident for th data set (Figs. 1 and 3). The anomalous behavi MO-1 in that *more* Cd is leached from a 1-g sa in 3 h (9.4 ± 0.6 ppb) compared to 1 h (7.2 ppb) may not be significant in view of the dev

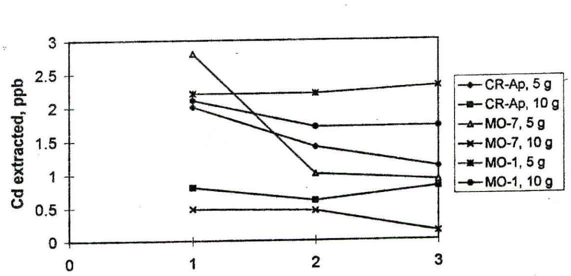

Fig. 1. Effect of contact time on Cd extracted by 50 ml of 1 M NH_4NO_3 leach of 5 and 10 g sample weights of Prairie CRMs.

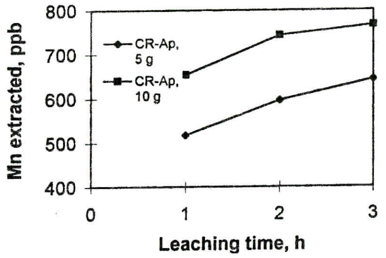

Fig. 2. Effect of contact time on Mn extracted by 50 ml NH₄NO₃ leach of 5 and 10 g sample weights of soil CR-

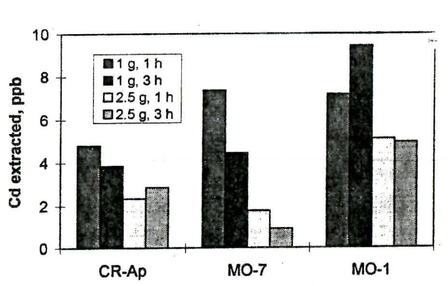

Fig. 3. Effects of contact time and sample weight in extrac Cd by 50 ml of 1 M NH_4NO_3 leach on Prairie CRMs.

	Zn
) ± 0.5	5.7 ± 0.5
2–2.0	3.3–15

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nts with the Prairie
of 1 and 2.5 g were
3). By lowering the
m 10 g to 1 g in 50 ml
crease in Cd extracted
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2.3 ppb) and the least
3 ppb Cd). Soil MO-7
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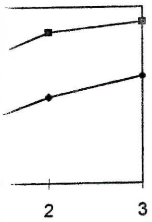
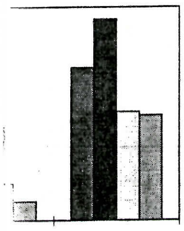


extracted by 50 ml of 1 M
weights of soil CR-Ap.



ple weight in extraction of
n Prairie CRMs:

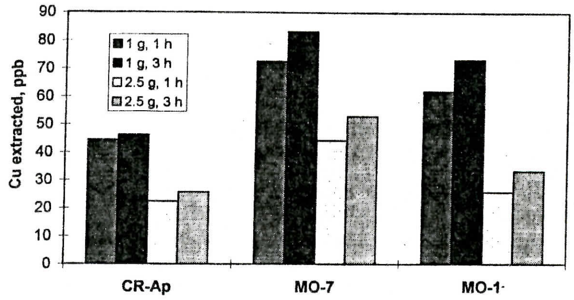


Fig. 4. Effects of contact time and sample weight in extraction of Cu by 50 ml of 1 M NH_4NO_3 leach on Prairie CRMs.

in results at the 1-g weight. Copper, measured in these solutions, shows similar behaviour to Cd in that much more is leached using the 1-g aliquot rather than 2.5 g (Fig. 4). For example, 62 ± 1 ppb Cu is extracted from 1 g of MO-1 in 1 h compared to 26 ± 1 ppb from 2.5 g. Slightly more Cu is leached from all three CRMs at greater equilibration times.

The effect of sample weight and contact time in leaching Cd from the more acidic Ontario CRMs is shown in Fig. 5. Decrease in Cd recovered with increase in sample weight taken is again evident. For example, the amount of Cd extracted by 25 ml of NH_4NO_3 in 2 h decreases from 4.0 ± 0.1 ppb Cd at 2 g of HIG-1 to 2.1 ± 0.1 ppb at 10 g (the ratio used in the DIN protocol). This sample, with the most 'total' Cd (428 ppb) and the highest pH (6.9) of the three, shows the least NH_4NO_3-extractable Cd. Conversely, the most acidic soil (pH of 5.2), FOR-1, exhibits the greatest amount of extractable Cd. The pH of the solutions following application of the DIN protocol were 5.8, 4.9 and 4.0 for HIG-1, ROS-1 and FOR-1, respectively. Time of leaching, at 1 or 2 h, had little influence on Cd results.

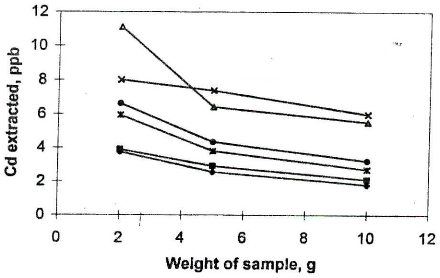


Fig. 5. Effects of contact time and sample weight in extraction of Cd by 25 ml of 1 M NH_4NO_3 leach on Ontario CRMs.

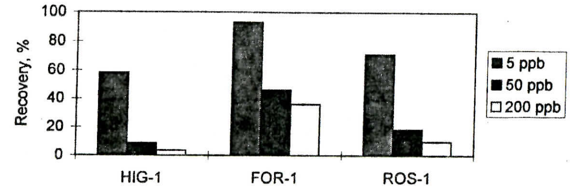


Fig. 6. Recovery of Cd added at 5, 50 and 200 ppb to Ontario CRMs leached according to DIN 19730.

The Ontario CRMs were used to study the recovery of Cd, added in nitrate form, after carrying out the 2-h leach at 10 g in 25 ml of reagent. Blank reagent solutions which had also been spiked showed complete recoveries of added Cd. The results for the CRMs, shown in Fig. 6, demonstrate similar patterns to those of Fig. 5 in that recoveries of Cd are highest for the most acidic soil, FOR-1. The degree of adsorption of Cd added at levels equivalent to 50 and 200 ppb in the soil is high, at values greater than 80% in ROS-1 (soil pH of 6.1) and HIG-1 (pH of 6.9). Even FOR-1, with a soil pH of 5.2, shows adsorption of greater than 50% at these Cd levels. Measurement of Pb in these solutions, spiked at the same concentrations as Cd, indicated 0% recovery throughout. In contrast, a similar experiment, carried out in 0.1 M $Na_4P_2O_7$ at 2.5 g of sample in 50 ml for 1 h, exhibited full recoveries for all spike additions of Cd. Results of the same experiment carried out for the 1 M NH_4Cl leach (16 h, 5 g of sample in 30 ml) showed reasonable recoveries of about 80% or more at the 5 ppb spike level (Fig. 7). Table 3 compares the amounts of Cd extracted by these three leaches.

The much lower extraction efficiency of NH_4NO_3 compared to that of $Na_4P_2O_7$ or NH_4Cl, shown in Table 3, is also reflected in results for about 130 Prairie soil samples (R.G. Garrett, pers. commun.,

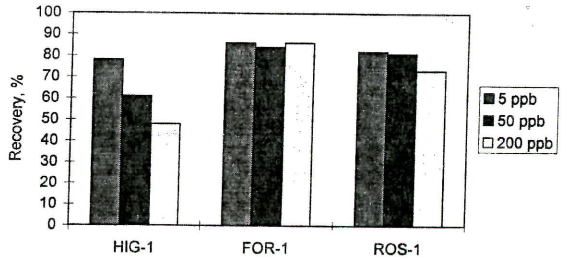


Fig. 7. Recovery of Cd added at 5, 50 and 200 ppb to Ontario CRMs leached in 1 M NH_4Cl.

Table 3
Concentrations of Cd (in ppb) leached from triplicate samples of CRMs by 1 M NH_4NO_3, 1 M NH_4Cl and 0.1 M $Na_4P_2O_7$

CRM	NH_4NO_3	NH_4Cl	0.1 M $Na_4P_2O_7$
HIG-1	2.1 ± 0.05	91 ± 2	136 ± 2
FOR-1	5.96 ± 0.34	25 ± 1	19 ± 1
ROS-1	3.2 ± 0.1	51 ± 2	56 ± 2

1997). Most of the values for Cd by the NH_4NO_3 extraction were below the detection limit of 0.1 ppb, consistent with those soils of pH greater than about 7.4. Results rose to several ppb when the pH of the soil decreased to the range 5.5–6.5. However, concentrations of Cd extracted in 0.1 M $Na_4P_2O_7$ ranged from 5 to 500 ppb, with levels of Cd generally slightly lower by the NH_4Cl extraction. More importantly, in a subset of 34 paired soil and wheat samples, a high degree of fit (ca. 75%) has been found between the $Na_4P_2O_7$-extractable Cd (including the extractable organic carbon) and the Cd present in durum wheat (Garrett et al., 1998). No such modelling was afforded by the NH_4NO_3 data as most were below the detection limit. The comparison of data for seven Prairie wheat/soil sites, shown in Table 4, demonstrates the dependency of results by the NH_4NO_3 leach on the pH of the soil. Neither the Cd in the durum wheat nor that extracted from the soil by $Na_4P_2O_7$ exhibits such pH dependency. The soil, E, whose wheat contains the greatest amount of Cd in this set (204 ppb) is extremely low in NH_4NO_3-extractable Cd (0.2 ppb). The most acidic soil in this set, A at a pH of 4.6, contains the highest amount of NH_4NO_3-extractable Cd (19.3 ppb), close to the German action level, but its wheat Cd concentration is lower than that of soil E.

4. Conclusion

The quest for a single robust soil leach to pred
metal availability to plants will probably never su
ceed. The action of metal uptake by plants is high
complex, dependent on many parameters such
species, soil biogeochemistry and local pH–Eh co
ditions. Most of the numerous empirical extracti
methods designed to predict availability are based
displacement of loosely held ('adsorbed, exchang
able') metals by competing ions (see review
Kennedy et al., 1997). Dissolution of 'phases' su
as carbonate, hydrous oxides and the humic a
fulvic component tends to reveal that proportion
metal which was free or labile but is not necessar
available subsequent to this mode of fixation. T
advantage of selecting a weak reagent such as 1
NH_4NO_3 is attributed to the fact that it does r
radically change the soil pH and indeed, the resu
shown here have demonstrated major soil pH contr
in Cd released by this leach. However, pH is on
one soil characteristic which effects uptake of
and its relative role is controversial (see literatu
cited in Kabata-Pendias and Pendias, 1984). The e
tractant, 1 M NH_4Cl, is also unbuffered, its resu
reflecting to a degree the soil pH; however, it do
not create the unstable environment for leached
that NH_4NO_3 does. The strong dependency of
leached by 1 M NH_4NO_3, on sample weight p
unit volume indicates that soil–extractant equili
rium has not been reached at higher sample weigh
certainly not at the low ratio of 1 : 2.5 specified
the DIN 19730 protocol. A 15-fold increase in
extracted by a 10-fold reduction in sample weight,
demonstrated here, makes this procedure unaccep
able. These data show that use of the 1 M NH_4N
extraction will underestimate mobility of Cd in ne

Table 4
Comparison of Cd concentrations in durum wheat and parent soil extractions using NH_4NO_3 and $Na_4P_2O_7$

Prairie soil, pH	Cd in wheat (ppb)	NH_4NO_3–Cd (ppb)	$Na_4P_2O_7$–Cd (ppb)
A, 4.6	157	19.3	325
B, 6.0	138	2.9	194
C, 6.6	28	0.7	64
D, 7.1	126	0.3	91
E, 7.2	204	0.2	145
F, 7.6	138	<0.1	52
G, 8.0	21	<0.1	31

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in sample weight, as
procedure unaccept-
of the 1 M NH_4NO_3
obility of Cd in neu-

tral to alkaline soils such as those present in the Canadian Prairies.

References

Anderson, S.T.G., Robert, R.V.D., Farrer, H.N., 1994. Determination of total and leachable arsenic and selenium in soils by continuous hydride generation inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 9, 1107–1110.

Chaney, R.L., 1997. Soil cadmium as a threat to human health. In: Iskander, I.K., Hardy, S.E., Chang, A.C., Pierzynski, G.M. (Eds.), Extended Abstracts of the Fourth International Conference on Biogeochemistry of Trace Elements, pp. 671–672.

DIN 19730, 1995. Extraktion von Spurenelementen mit Ammoniumnitratlosung. Deutches Institut für Normung Hrsg., Berlin, 9 pp.

Garrett, R.G., 1994. The distribution of cadmium in A horizon soils of the Prairies in Canada and adjoining United States. Geol. Surv. Can. Pap. 94-1A, 73–82.

Garrett, R.G., MacLaurin, A.I., Gawalko, E.J., Tkachuk, R.T., Hall, G.E.M., 1998. A prediction model for estimating the cadmium of Durum wheat from soil chemistry. J. Geochem. Explor. 64, 101–110 (this issue).

Hall, G.E.M., Vaive, J.E., MacLaurin, A.I., 1996. Analytical aspects of the application of sodium pyrophosphate reagent in the specific extraction of the labile organic component of humus and soils. J. Geochem. Explor. 56, 23–36.

Kabata-Pendias, A., Pendias, H., 1984. Trace Elements in Soils and Plants. CRC Press, Boca Raton, 114 pp.

Kennedy, V.H., Sanchez, A.L., Oughton, D.H., Rowland, A.P., 1997. Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils to root uptake. Analyst 122, 89R–100R.

Krishnamurti, G.S.R., Huang, P.M., van Rees, K.C.J., Kozak, L.M., Rostad, H.P.W., 1995. A new soil test for the determination of plant-available cadmium in soils. Commun. Soil. Sci. Plant Anal. 26, 2857–2867.

Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Sci. Soc. Am. J. 42, 421–428.

McKeague, J.A., 1968. Humic–fulvic acid ratio, Al, Fe and C in pyrophosphate extracts as criteria of A and B horizons. Can. J. Soil Sci. 48, 27–35.

Peech, M., 1965. Hydrogen-ion activity. In: Black, C.A. (Ed.), Methods of Soil Analysis, American Society of Agronomy, Soil Science, Society of America, Madison, pp. 914–926.

Prüeß, A., 1992. Vorsorgewerte und Prufwertre fur mobile und mobilisierbare, potentiell okotoxische Spurenelemente in Boden. Verlag Ulrich E. Grauer, Wendlingen, Stuttgart, 145 pp.

Prüeß, A., 1998. Action values for mobile (NH_4NO_3-extractable) trace elements in soils based on the German national standard DIN 19730. In: Proceedings of the Third International Conference on Biogeochemistry of Trace Elements, 1995, Paris (in press).

Stuanes, A.O., Ogner, G., Opem, M., 1984. Ammonium nitrate as extractant for soil exchangeable cations, exchangeable acidity and aluminium. Commun. Soil Sci. Plant Anal. 15, 773–778.

Symeonides, C., McRae, S.G., 1977. The assessment of plant-available cadmium in soils. J. Environ. Qual. 6, 120–123.

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Mobile Metal Ions in the A horizons of soils

Mobile Metal Ions in the A Horizons of Soils

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Short Course Notes 19th IGES Vancouver, April 1999

NON-SELECTIVE EXTRACTION

Non-selective extraction is based on the notion that by providing an extractant with a sufficiently strong ligand (for a particular metal) then a proportion of that metal will be removed from the soil. Metal will tend to be removed from those sites within the soil which become energetically unfavourable compared to the complexed state of the metal in solution, irrespective of the specific chemical or physical nature of the component of the soil to which it was formerly attached. Metals within the soil are thus classified as 'bound' or unremovable, and 'unbound' or extractable on this basis. These terms are operationally defined (by the strength of the ligand). Figure 1 depicts this in a pictorial representation of a soil particle for the case of Cu.

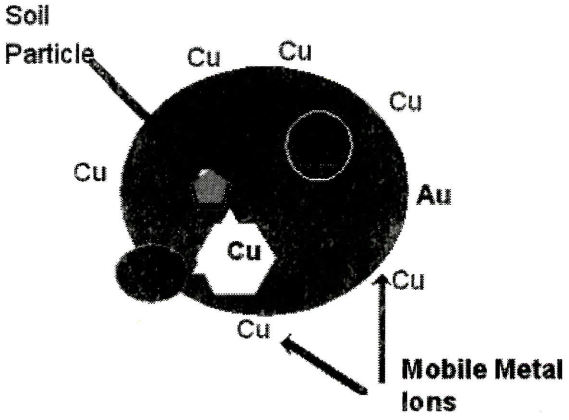

Figure 1. Bound and unbound metals in a soil.

Examples of non-selective extractants with a single complexing ligand include BLEG (Bulk-Leach Extractable Gold) which uses cyanide for Au, and Deep Leach and Regoleach which use weak mineral acids for a range of metals. There are a number of problems however which can arise when a single ligand such is used as the complexing ligand for a range of metals. There are environments (e.g. acid or strongly reducing) where a strong ligand such as cyanide ion is potentially chemically compromised. Whilst it is possible to initially extract many metals (in fact a significant proportion of the periodic table) with the chloride ion e.g. from dilute HCl, the ligand strength may not be sufficient to retain all elements initially extracted in solution through the course of the analysis. This latter problem which simply occurs because chloride is not the optimum ligand for a number of metals, is referred to as re-adsorption. A related problem with the reproducibility of extraction and analysis can occur when a single ligand is deployed to ensure extraction and solution retention of a number of metals from a number of different samples. This can arise from competition from other metals for the available ligand.

MOBILE METAL ION (MMI) EXTRACTION

By providing an extractant solution with a number of optimum ligands (at least one for each metal), a number of these problems can be overcome. Thus the MMI-A extractant solution consists of a number of water-soluble organic and inorganic components, which provide ligands for the optimum dissolution of base metals Cu, Pb, Zn, and Cd. This is a weak acid.

Figure 2 shows pictorially how the ligand L in MMI-A specific for Cu, attaches and complexes with the Cu ion in solution, ensuring its solubility.

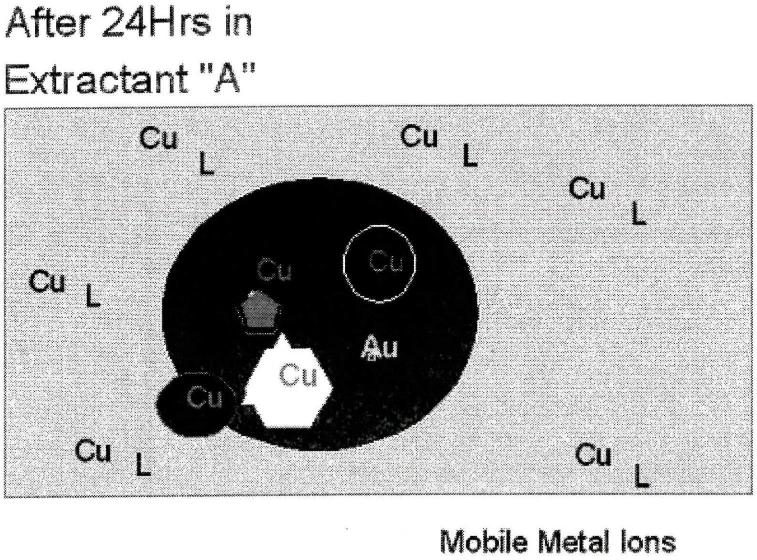

Figure 2 Schematic model of Mobile Metal Ions being leached from a soil particle by the chemical action of a weak digestant.

Similarly, MMI-B contains a number of ligands in a weak base suitable for optimum extraction of Au, Ag, Ni, Co, and Pd from soils. Note that in each case, it is the specific intention to minimize attack on the substrate, and to release a significant, but minor proportion of the total metal, usually between 5% and 50%. This not only ensures compliance with the adsorption isotherm requirements above, but also, as we will see, ensures some very significant improvements in background and signal to noise ratio. Table 1 shows the range of MMI extractions currently available, or currently under investigation.

Table 1. Range of MMI extractions currently available, or currently under investigation.

Extractant	**Target**	**Elements**
MMI-A	Base Metals	Cu, Pb, Zn, Cd
MMI-B	Precious Metals	Au, Ag, Ni, Co, Pd (Pt)
MMI-C	Base Metals (high carbonates)	Cu, Pb, Zn, Cd
MMI-D	Kimberlites (diamonds)	Ni, Nb, Cr, Mg, Pd, Mn
MMI-E	Majors, lithogeochem	Ti, Fe, Si, Mg, Ca, Th, Zr, Sc
MMI-F	Pathfinders	As, Sb, Mo, W
MMI-G	Granophiles (Pegmatophiles)	U, Pb, Th, Sn, Li, Ta

It is implicit in the MMI approach, that the number of elements in the extraction suite is limited, in order to optimise the extraction efficiency for each metal contained in the suite. As shown in the above table, the extractants are therefore designed for complexing a particular (limited) suite of elements, and are designed for a particular geological target or targets.

STANDARD REFERENCE MATERIALS, REPRODUCIBILITY

In any geochemical survey, it is important to maintain a check sample program independent from that undertaken by the laboratory. One standard reference material and one duplicate sample should be inserted within each sequence of 50 samples to monitor precision and accuracy. QC samples should be inserted as part of the numbering sequence but not essential. It is essential to know to what degree of precision, the duplicates and standards should replicate.

In any analysis scheme, and particularly for partial digestion methods such as MMI, there are a number of possible sources of error, each of which contribute to the error or non-reproducibility. Error can arise at the extraction stage as well as the instrument reading stage. In a comprehensive survey of the sources of error in the MMI technique, and the errors introduced at a number of stages, were investigated. A summary of the outcomes is shown in Table 2.

Table 2. MMI-A and B Analysis - Reproduciblity Summary.

Category	Results (C of V or R squared)	Conclusions
1. Spiked solutions. 1000ppb solutions of Cu, Pb, Zn and Ni. 100ppb solutions of Au, Ag, Cd, Co and Pd, in MMI-A & MMI-B.	Cu 4.2% Pb 3.3% Zn 5.2% Ni 5.6% Cd 3.0% Au 3.2% Ag 4.1% Co 6.7% Pd 5.2%	ICP-MS is reproducible ICP-MS is accurate MMI-A is suitable analyte MMI-B is suitable analyte
2. Splits of a single homogenized bulk sample. Same ICP, same digest, same day. (Wamtech data base, n=6.)	Cu 10.6% Pb 10.6% Zn 2.1% Ni 7.4% Cd 2.3% Au 5.9% Ag 4.5% Co 23.0% Pd 4.2%	Average C of V 7.8% Zn the best Co the worst Reflects intra-batch ICP variation.
3. Splits of a single homogenized bulk sample (HBS). Same ICP & lab over a period of time. (Wamtech data base, n=11-16.)	Cu 15.5% Pb 19.4% Zn 15.3% Ni 10.0% Cd 21.7% Au 5.7% Ag 6.9% Co 24.6% Pd 8.5%	Average C of V 14.2% Au the best Co the worst Reflects lab, digest and time variations.
4. Splits from a non-homogenized sample, same digests, same labs for MMI. (Replicate analysis set of 12 samples sent to 2 labs.)	Cu 18% Cu 21% Pb 22% Pb 25% Zn 8% Zn 20% Cd 11 % Cd 16%	Average C of V's 14.8%, 21% Laboratory difference Similar to HBS. Little intra-sample variation. Homogenize standards.
5. Same as above for conventional analysis comparison.	Cu 15.3% Pb 13.6% Zn 13.3% Cd 14.9%	Average C of V 14.3%. Basis for comparison
6. Replicate samples, different sites, same lab, same digest.	Regression Analysis (R^2) Au = 0.998 Ag = 0.999 Ni = 0.982 Co = 0.986 Pd = 0.988	c.f. Eggo, R^2=0.97 for ICPMS Good linear discrimination over a wide range.
7. Replicate samples, different sites, different labs, different digests.	Regression Analysis (R^2) Au = 0.993 Ag = 0.998 Ni = 0.957 Co = 0.865 Pd = 0.901	c.f. Eggo, R^2=0.97 for ICPMS Use same laboratory whenever possible.
8. Different samples from 1-5m radius of anomalous (A) and background (B) site. (Wamtech MG data, n=26.)	Anomalous site Background Au Mean 3.3ppb 0.4ppb Au C of V 13.6% 24.9% Ag Mean 13.6ppb 1.8ppb Ag C of V 15% 23.9%	Small site sampling variation. Percentage increases as values approach L.D.L. of instrument.
9. Different samples from same sites after an elapsed (rainfall) period.	Au=3.7ppb(15.7%) Ag=10.2ppb(17.2%) X-Y scatter plots for Cu, Cd, Ni and Au from Nepean East	Anomalies and backgrounds maintained across significant rainfall events.
10. Different samples composited. Compare analysis with arithmetic mean. (Wamtech data, n=6)	Average variation from arithmetic mean: Ni 11.2% Au 8.5% Ag 19.8% Co 9.8%	Compositing samples is an option.

Whilst the coefficients of variation in general increase from the first (top) category to lower in the table as the number of analytical steps increases, the absolute values are very comparable to those involved in any geochemical analysis. It is of interest that not all elements have identical C of Vs; in general Co has higher values than (say) Au, for which the procedures and the ICP-MS are very suitable. All regression curves (categories 6 and 7) were very linear, proving the technique is suitable over a wide analytical range.

In summary the conclusions of this study were:

(1) that ICP-MS is a very suitable instrument for analysis of MMI extracts;
(2) that MMI extracts A and B are suitable analytes;
(3) coefficients of variation are comparable with those of conventional (total) digestion on bulk homogenized samples;
(4) samples for a survey should be submitted as a single batch if possible;
(5) the same laboratory should be used wherever possible;
(6) lateral variation of mobile elements at a sample site is very small;
(7) vertical differentiation of both mobile and total metal at a sample site is of greater concern;
(8) for this reason samples should be 500 g or less, and selected from 5-15 cm below surface;
(9) rainfall has a minimal effect on mobile metal ion values; and
(10)compositing of samples is a viable option.

MOBILE ION SIGNATURES IN THE A HORIZON

Analysis of vertical profiles conducted early in research programs (for example as shown in Figure 3), indicated that a significant proportion of the mobile form of each metal is located in the upper (A horizon) part of the soil. In some cases, as in that shown in Figure 3, the A horizon is exotic.

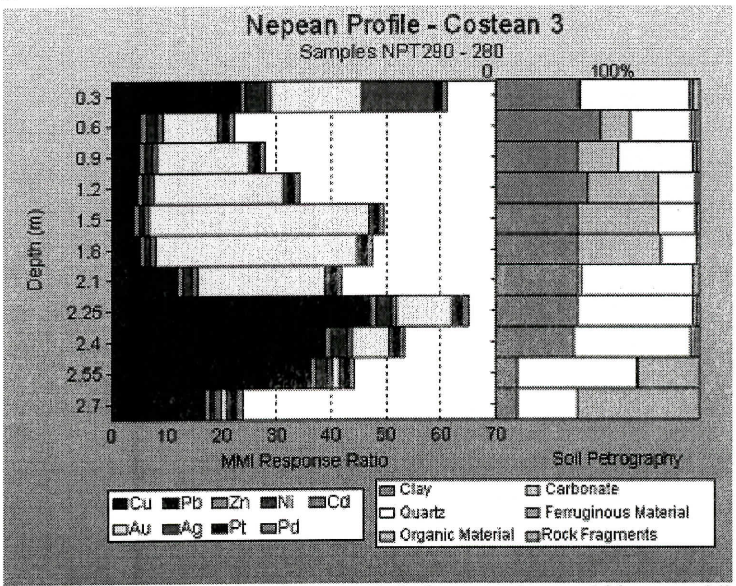

Figure 3. MMI analysis of various metals in a costean at Nepean Ni mine.

A large number of laboratory experiments were then carried out to elucidate the mechanism of this transfer of metal within the solum (the A & B soil horizons). Included in these were experiments which showed that capillary rise and evaporation are extremely important in the formation and preservation of the mobile ion signals in the A horizon. The results of one of these experiments are shown in Figure 4.

In this particular experiment, a self-watering flower pot containing barren silica sand has had a pregnant solution containing 1ppm of Cu, Pb and Cd placed in the well beneath the pot. Within one week measureable concentrations of Cu and Cd (measured in an MMI-A extract) are evident in the near-surface, some 15cm above the lower well. The concentration for Pb (less mobile) increases above background several days later. It is evident that processes involving mobile metal ions are rapid, and that processes in the solum are dynamic.

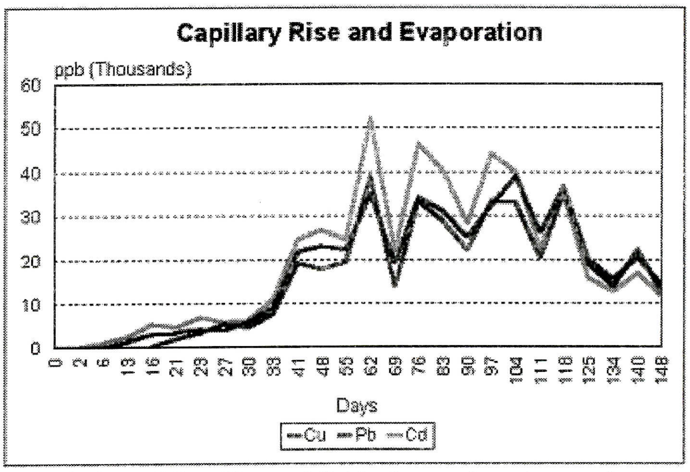

Figure 4. Accumulation of Cu, Pb, and Cd in the surface layer of coarse silica sand.

Sampling for MMI is normally recommended at a depth of 5-15cm, to ensure that it is the A horizon which is sampled, and to minimise contamination from sticks, leaves, etc. The soil is roughly sieved, e.g. to 3-4mm.

CARBONATES

The strong dependence of solubilities of base metals on pH is well known. Soils which contain appreciable concentrations of carbonate require special attention because of this. Whilst leachants such as MMI-B which are basic are relatively unaffected, mild acid leachants such as MMI-A have to be monitored carefully in that there is likely to be a soil-carbonate concentration beyond which they may not be expected to operate. Firstly however, and as illustrated in Figure 5, there is a significant pH difference between the natural pH of a soil (or synthetic soil) and the pH during a 1:1 extraction with MMI A.

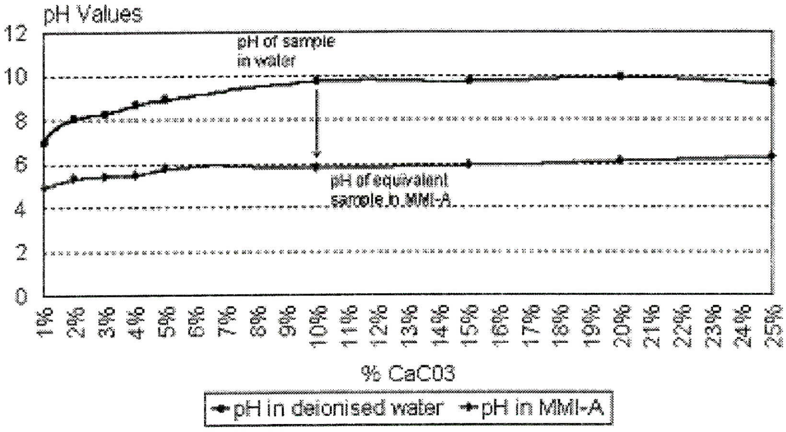

Figure 5. Comparison of pH of synthetic carbonate samples in water and in MMI-A.

As shown above, natural or synthetic soil samples are almost 3 pH units more alkaline than the equivalent sample in an MMI-A solution. Given the shape of the base-metals versus pH solubility curve, it can immediately be stated that base metals will be less soluble (more immobile) in a soil in the natural environment (e.g. after a rainfall event) than during a digestion procedure on the same soil. We do however need to carefully examine the behaviour of any given extractant, to establish its "working range", from both a pH and carbonate perspective, and to assure there is little or no dependence of extracted metal on pH over this working range. Table 3 shows the concentrations of Cu, Pb, Zn, and Cd extracted by MMI-A solution from two samples after various amounts of NaOH are added to provide a (limited) range of pH values.

Table 3. Concentrations of Cu, Pb, Zn and Cd extracted by MMI-A from two samples at different pH values, obtained by various additions of sodium hydroxide.

Sample	pH	Cu	Pb	Zn(ppm)	Cd
SA226	2.47	1250	1770	45.2	106
SA226	2.85	771	1150	44.7	98
SA226	3.58	1000	1080	57.7	98
SA226	4.25	1090	1310	60	92
SR70	2.73	45	15	0.947	28
SR70	3.33	51	12	0.956	25
SR70	4.12	69	16	0.984	23
SR70	4.6	70	16	0.895	23

Over this pH range, there is very little dependence of the amount of metal extracted on pH. Accordingly this weakly buffered extractant is suitable for extraction of base metals in soils with small amounts of carbonate.

The limit to which any extractant (whether it be strong acid, a buffered solution, or weak acid) can tolerate carbonate is governed by the simple neutralisation reaction, which indicates that for every 1g of calcium carbonate in the sample, 20 millimoles of acid is consumed. Experiments with MMI-A demonstrate that solubilities of Cu, Zn and Cd up to 10 ppm can be maintained for pH to 6.5 (soil carbonate up to approximately 25% $CaCO_3$). For Pb, concentrations are comparable with those in water, and above a resulting solution pH = 5.5 (10% $CaCO_3$) Pb solubility is very restricted, presumably due to the formation of lead hydroxy-carbonate.

For samples with higher carbonate content (resulting pH) than this, MMI-A is not recommended. A separate leachant, MMI-C, and a different laboratory protocol are required. In practice, only a relatively small number of soil samples require special treatment (i.e. have high carbonate contents).

METAL AVAILABILITY IN (CARBONATED) AGRICULTURAL SOILS

Partial digests have been used in agriculture for over 25 years in order to obtain a measure of the availability of metals to plants. In many cases a definite linear correlation is observed between the available metal concentration, and the natural pH of the soil sample. Two examples (Lindsay *et. al.,* 1972) are shown in Figure 6.

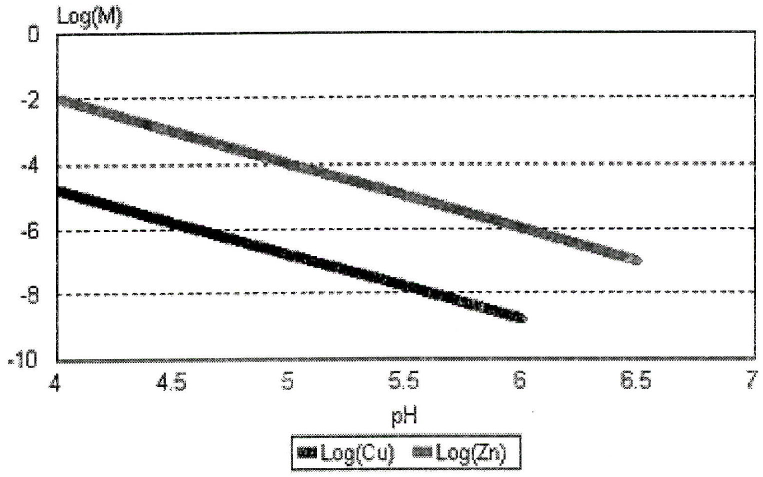

Figure 6. Relationship between Metal Activity and pH (Agricultural Soils, after Lindsay *et. al.,* 1972).

Although Zn is shown to be more available at a given pH than Cu, both show a linear dependence on pH, and therefore implicitly on soil pore water carbonate ion concentration. Similar correlation has been observed in some mineral exploration surveys in carbonate terrain with MMI-A. These have been within a pH range in which the efficacy of the MMI-A extractant is not compromised by the carbonate content nor pH (i.e. below $CaCO_3$ contents of 15%). Given the previously demonstrated relative independence of the extracted concentrations of base metals and pH of the MMI-A extractant, the effect is almost certainly due as in the agricultural examples, to a natural dependence of base metal mobility on soil pH and carbonate content i.e. base metals are in general less mobile in carbonate-containing environments than those without.

In a study of various extractants on English soils (Tills & Alloway, 1983), which included some chalk soils, it was found that EDTA, a weak acid extractant with strong ligand complexes with base metals, produced the best correlation with plant uptake of Cu. In this study, the correlation was between Cu content in digested plant material, and soil extractable Cu during growth. The study included dilute nitric and hydrochloric acids as weak extractants which gave poorer correlation than EDTA. It is also commonly observed in such studies that correlation between total metal content and availability (and uptake) is not good, i.e. that some soils with high base metal concentration, contain metal in a 'bound' form which is unavailable to plants. There are conceptual parallels between the “available metals” of agricultural science, and the “mobile metals” referred to here.

CASE HISTORIES

1. SAN JORGE, ARGENTINA

This study has been supported by: Grupo Minero Aconcagua S.A., a wholly owned subsidiary of Northern Orion Explorations Ltd, MMI Technology, the developers of Mobile Metal Ion technology, and XRAL Laboratories, a laboratory licensed to undertake MMI analyses. W.C. Williams, Project Geologist at San Jorge, and J. Madrid implemented and completed the sampling programme.

The San Jorge Cu-Au project (see Figure 7) is located approximately 100 km northwest of the city of Mendoza along Route 39 some 40 km north of the village of Uspaliata. It is in the Uspallata Valley situated along the eastern flank of the Cordillera Frontal. Elevation is between 2600 and 2685 masl. A desert climate predominates and low-lying vegetation covers the area. No surface water passes through the project area.

Figure 7. Photo overlooking the sampling area at San Jorge in the foreground with mountains in the background.

The San Jorge Cu-Au deposit is at the southern end of a north-south trend of various hydrothermal deposits that outcrop for over 300 km in the Uspallata Valley and its environs. The country rocks are Devonian phyllites, Carboniferous clastics, and Permo-Triassic extrusives that host felsic Permian and Tertiary porphyritic stocks. Unconsolidated gravels, derived from the Cordillera Frontal to the west and Precordillera to the east, filled the valley after Andean uplift in the Tertiary.

San Jorge is a porphyry copper deposit (PCD). It is hosted by the Carboniferous clastics, a felsic porphyry intrusive, dacitic dikes, and a tourmaline breccia. The former is host to higher-grades of hypogene mineralization. The tourmaline breccia and dacite dikes host a volumetrically small portion of the deposit.

The principal structures strike NS to NNE; NW and ENE faults are secondary structures. Even though displacements are not significant, the faults and their related structures were important conduits for meteoric waters that promoted leaching of sulfides, deposition of copper oxides, and the formation of an enriched blanket.

The San Jorge PCD is characterized by potassic, phyllic, and propylitic alteration that is distributed unevenly throughout the deposit. Biotite and tourmaline are the earliest alteration events followed by potassium feldspar alteration as haloes around quartz-sulphide veinlets as well as a replacement of plagioclase; two centres of potassic alteration have been identified. Silicification with subsidiary sericite, i.e., phyllic alteration, affects all rock types. Hairline calcite veinlets, with or without clay or quartz, crosscut all other alteration types and represent the propylitic alteration.

The mineralization trends northeast-southwest. Copper occurs in malachite, chrysocolla, pitch limonite, chalcocite, covellite, digenite, and chalcopyrite; brochantite, azurite, tenorite, native copper, cuprite, and bornite are minor. Mineralization has been divided into five (5) zones: 1) gravels, 2) leached, 3) oxide, 4) enriched, and 5) primary. The oxide body is best developed along the western contact of the granite porphyry with the sedimentary sequence and in the southwest sector of the deposit under gravel cover. Secondary sulphide mineralization occurs as sooty chalcocite in areas of intense faulting and repetitive water recharge, e.g., southwest sector, as well as chalcocite, covellite, and/or digenite rimming chalcopyrite in 'transitional zones'. Three (3) high-grade zones (>0.5%) of primary mineralization are hosted by the sedimentary sequence. Copper grades can exceed 1.0%, and intervals that contain up to 0.5% copper have been encountered to depths as much as 495 m. Native gold occurs in all ore zones averaging approximately 0.2 ppm throughout the deposit. Silver is sympathetic to copper, at a ratio of 1 ppm Ag per 1250 ppm Cu.

Three east-west, and two north-south lines for a total of 95 samples were sampled 10-30 cm below surface. Sample material was typically unconsolidated sands and gravels with cobbles at surface. Samples were extracted and analysed by XRAL Canada. Elements Cu, Pb, Zn, and Cd were analysed following the MMI-A extraction and elements Au, Ag, Ni, Pd, and Co following MMI-B extraction. The MMI results for section 8650E, which traverses the known mineralization, including the southwest sector of the deposit where high-grade copper is encountered in the oxide, enriched, and primary ore zones, are shown in Figures 6 & 7.

Figure 10 is a cross section along line 8650E, showing geology and sub-surface mineralization.

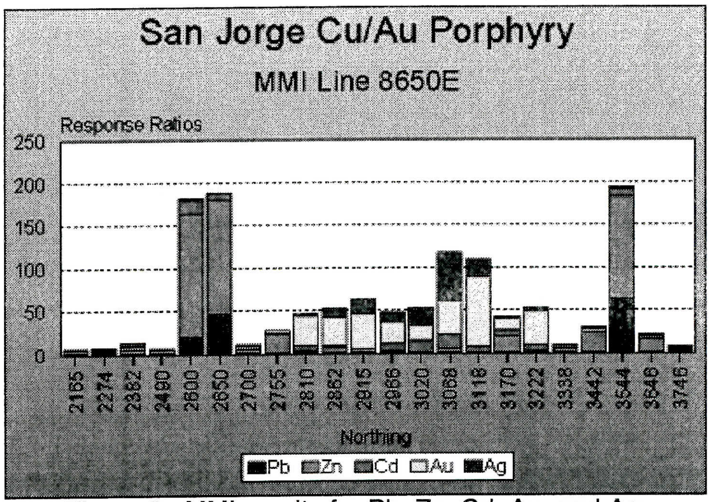

Figure 8. MMI results for Pb, Zn, Cd, Au, and Ag.

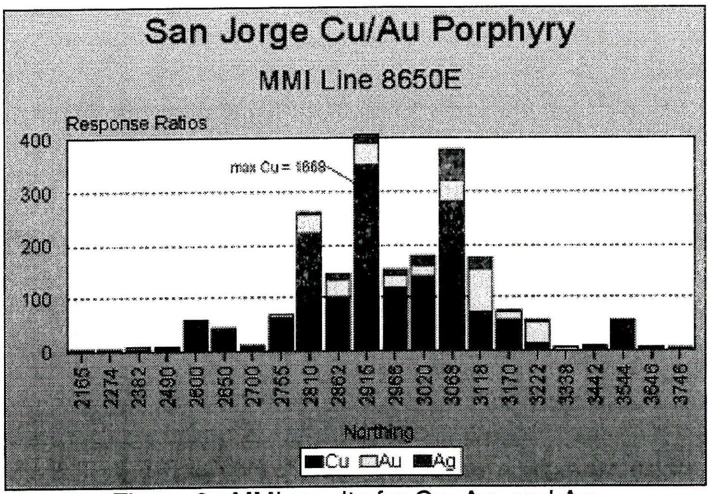

Figure 9. MMI results for Cu, Au, and Ag.

There are a number of interesting features when compared with the MMI results across this line. Firstly, there is a zonation pattern across the deposit, with outlying anomalies of Zn and Cd giving way to anomalous Cu, Au, and Ag over the primary and enriched zones of the deposit. Secondly, whilst Cu is present in considerable concentrations and reports very strongly in the MMI geochemistry, Au and Ag also report with very strong MMI response ratios over the mineralization, considering the tenor of the Au mineralization (average 0.2 ppm). Thirdly, given the varying depth of the gravel cover (and the existence of carbonate hardpan at 1.5-2m), the MMI geochemistry has provided a sharp and accurate surface outline of the sub-surface mineralization, with response ratios for Cu of over 100 times background, and Au and Ag response ratios of over 50 times background.

The study also identified elevated MMI geochemical responses coincident with IP geophysical anomalies as well as offsetting a drillhole with good Cu intercepts. Both areas have approximately 100 metres of gravel cover. Further work is required to assess the relevance of these data.

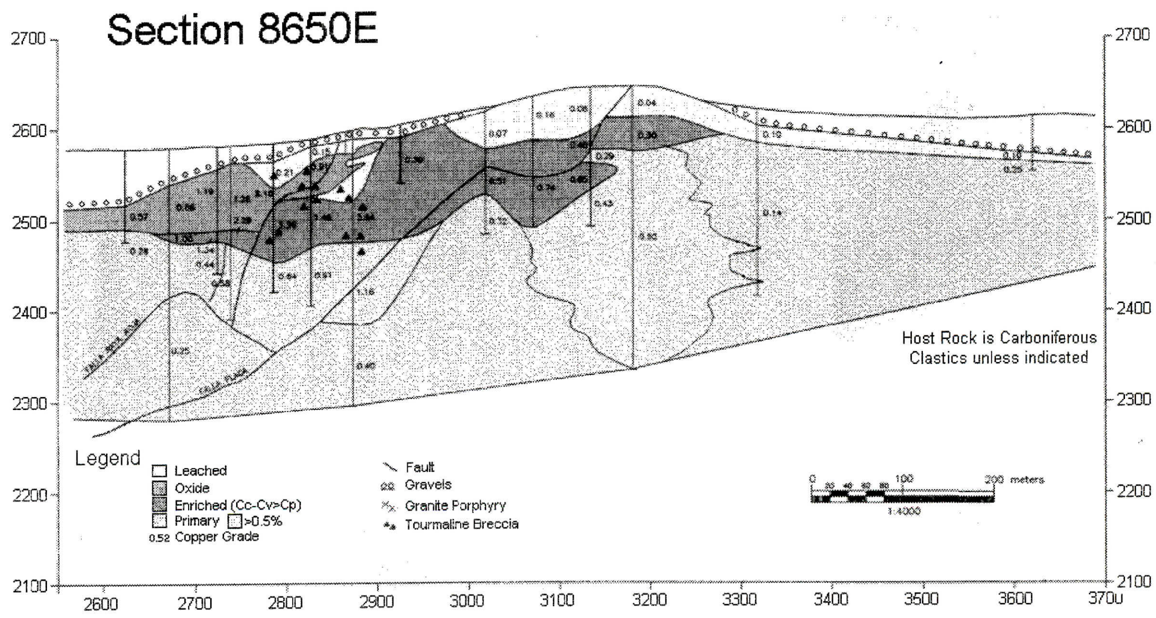

Figure 10. Geology and sub-surface mineralization for section 8650E.

The implications for exploration are:

1) The multi-element suite for MMI provides a useful and elegant surface indication of the zonation within porphyry systems.
2) The MMI technique can provide useful surface geochemistry through veneers of gravel in Andean type environments.
3) The MMI technique can provide surface geochemical indications that are sufficiently sharp and accurate to enable accurate placement of drill-holes in these environments.
4) As other MMI studies have shown, it is important to maintain a consistent sampling depth below surface to avoid variation caused by vertical metal partitioning within soil profiles.

Grupo Minero Aconcagua, S.A., a wholly owned subsidiary of Northern Orion Explorations Ltd provided the San Jorge site for the orientation survey. Dr W.C. Williams, and J. Madrid implemented and completed the sampling programme as well as reviewed the text for accuracy. The hospitality and assistance given by Northern Orion staff were greatly appreciated.

2. SAN NICOLAS

The San Nicolas Project is located 65 kilometres of the city of Zacatecas, Mexico. The Project is a 55/45% joint venture between Teck Corporation and Western Copper Holdings Limited. The partners commenced exploration in mid-1996 within an area typified by gently rolling topography at an altitude of 2100 meters. Initial work focused on previously known copper mineralisation at the El Salvador prospect. Expansion of exploration activities identified the San Nicolas area as prospective based on limited exposures of favourable altered volcanics.

An initial drill target was identified by a follow-up geophysical survey that defined a strong induced polarisation (IP) chargeability anomaly measuring 500x500meters. The first hole into the anomaly was drilled in November 1997 intersected 175 meters of massive sulphide mineralisation starting at a depth of 205meters below the surface.

To date in excess of 50 drill holes have intersected the massive sulphide mineralisation.

The San Nicolas "VMS" deposit contains a zinc rich zone at the top and a copper rich zone at the base. The zinc zone contains 34 million tonnes of 4.28% Zn and 0.76% Cu; while the Cu zone has 38 million tonnes grading 1.89%Cu. A preliminary mineable open pit reserve of 72 million tonnes grading 1.35-%Cu, 2.27%Zn, 0.53g/tAu and 30g/tAg has been defined. (Acknowledgements :Teck Corporation - www.teck.com/ops/adv/adv_san.html andWestern Copper Holdings Ltd - www.westerncopper.com/sannic-4s.html)

A preliminary orientation survey was undertaken at San Nicolas to test the MMI geochemical technique. The site has an arid environment with highly carbonated soils above economic base metal mineralisation, covered by a significant thickness of barren overburden. The typical section above the mineralisation for the MMI orientation line was: Surface gravels – 10 to 20 meters containing a caliche horizon, Tertiary volcanoclastics – 60-80 meters, hanging wall mafic volcanic flows and sediments – 100-160 meters, depth to mineralisation – 180 to 240 meters. Surface samples were collected at 30m intervals along the line.

The dominant MMI element was Pb with subsidiary Zn, Cd and Cu responses. Lead has a peak response of 20 times background as shown in Figure 11. There were no conventional geochemical responses reflecting the known base metal mineralisation.

One anomalous Au zone was defined immediately adjacent to the known mineralisation, an association typically seen in MMI data over VMS deposits. On the opposite side of the deposit, some 200 meters, the last sample (11662) returned a 25 times background Au response.

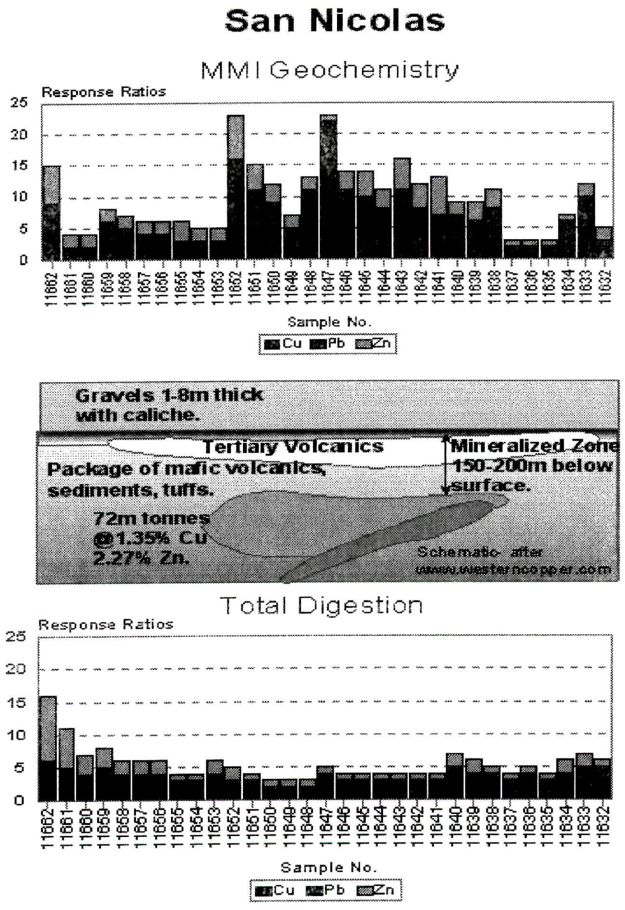

Figure 11. MMI and Conventional Geochemistry, San Nicolas.

3. ARCTIC BOREAL FOREST, EUROPE

The MMI data, and conventional data from an acid digest procedure, from soils taken from glacial till cover in Europe are compared in Figures 12 and 13.

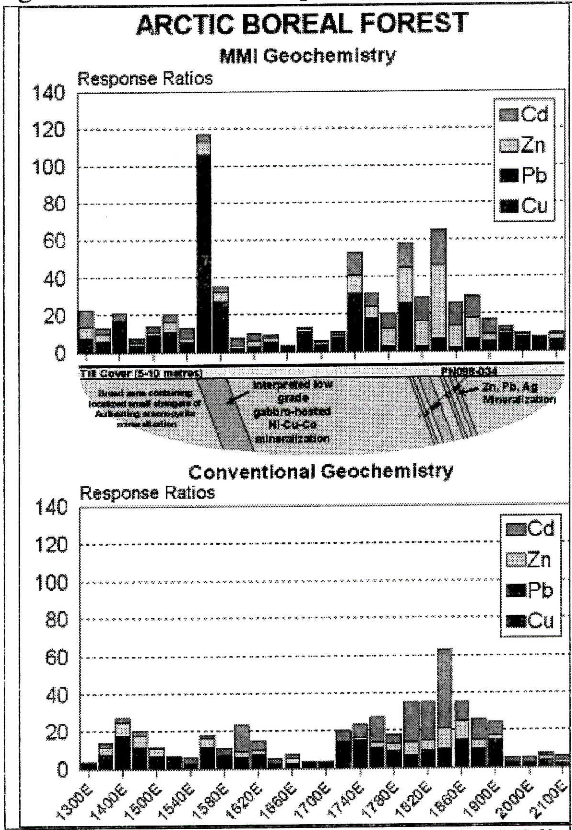

Figure 12. Comparison of MMI geochemistry and conventional geochemistry for Cu, Pb, Zn, and Cd.

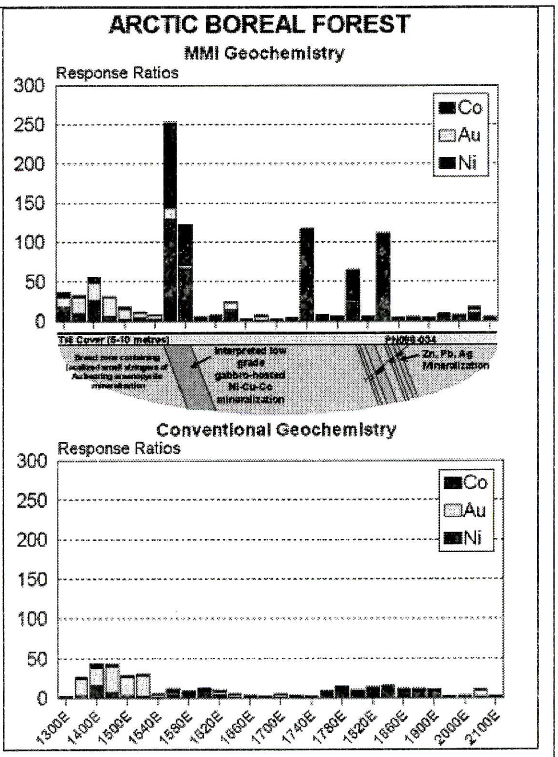

Figure 13. Comparison of MMI geochemistry and conventional geochemistry for Ni, Au, and Co.

Again, the same response ratio scales have been used for the comparison. In this project, the traverse has been placed over three zones of potential interest, (a) stringer-related gold-arsenopyrite mineralisation, (b) gabbro-hosted Ni-Cu-Co mineralisation, and (c) sub-economic base metals mineralisation. For elements such as Au and surprisingly Cd, the MMI and conventional geochemistry signal to noise ratios are similar or slightly superior for conventional geochemistry over the stringer Au and base metals zones. For all other elements, response ratio contrast is higher for MMI geochemistry over zones containing mineralisation. Both samples, in this case were taken from the A horizon. In this type of environment, the B horizon is difficult to locate, and the C horizon is below the 5-10 m of glacial till.

COMPARISON OF MMI AND CONVENTIONAL GEOCHEMISTRY

Comparing the outcomes of partial digestion geochemistry, and conventional (total digestion) geochemistry, achieves two things. As well as providing useful information for the explorationist, it also provides a very good insight into the processes that give rise to the formation of a geochemical anomaly. As noted in the previous chapter, two aspects or attributes of the geochemistry are of particular relevance – the sharpness of the peak over mineralization, and the strength or peak to noise ratio of the anomaly. Together these two features describe the resolution of the particular geochemical technique.

In relation to resolution, comparison of MMI versus conventional or total digestion appears to produce a number of outcomes, dependent on the geological setting, and the elements involved:

1. MMI and conventional geochemistry sometimes show similar anomaly patterns. These involve elements with limited mobility such as Au and Pb. In the case of Au there are additional false anomalies with total digestion (these may constitute a separate category).
2. Commonly MMI exhibits higher resolution than conventional geochemistry, both spatially, and with respect to the amplitude of the anomaly relative to background.
3. Sometimes there is recognizable contrast with MMI, but insignificant contrast by conventional techniques. This case is often observed with the more mobile elements such as Zn, Ni, and Cd.
4. Situations where both types of geochemistry fail to register the presence of underlying mineralization do occur. Such cases are restricted to either deep burial, or zones of very active transport, e.g. aeolian dunes or active alluvial channels.
5. Examples where conventional geochemistry provides greater contrast than does MMI. Appear to occur very infrequently. They are limited to those situations where fresh mineralization is at/or very near the surface.

The approximate percentage distribution of these outcome types is shown in Figure 14.

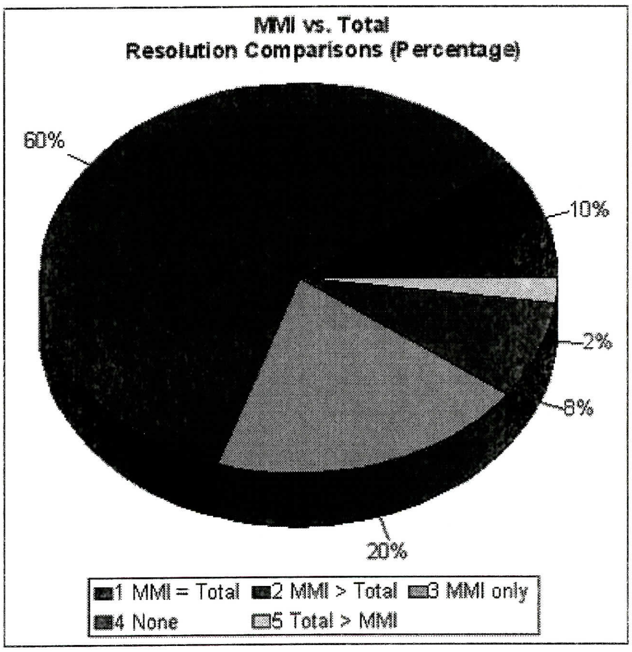

Figure 14. Approximate distribution of resolution comparisons: 1 – MMI = Total, 2 – MMI > Total,3 – MMI only, 4 – None, 5 – Total > MMI.

A SIMPLE GEOCHEMICAL MODEL FOR THE SOLUM

A simple three step geochemical model has been proposed to explain these features. It proposes that a dynamic balance exists in the solum between metals in the unbound and bound forms. The model is shown pictorially in Figures 15(a), (b), and (c).

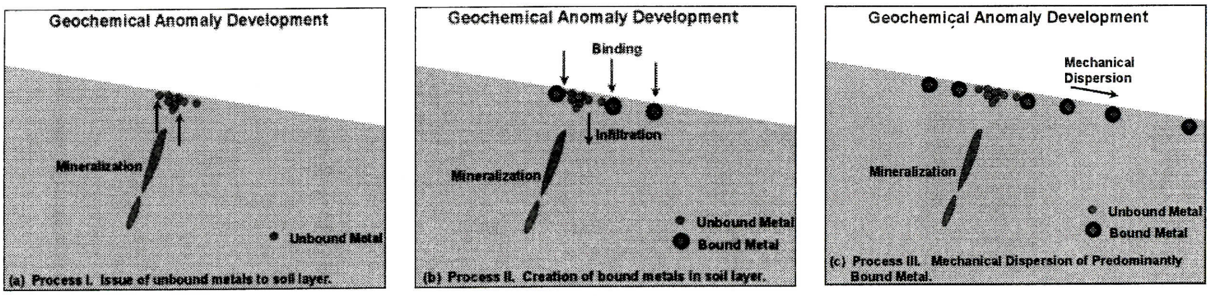

Figure 15(a-c) Geochemical anomaly development stages.

Three processes are considered to be important:

Process 1. Metal input to the A and B horizons as depicted in Figure 15(a) is considered to be ionic in form, and derived from the oxidation of underlying sources and vertical migration. It is essentially a point source input, directly related to the source area (or areas) beneath. These metals constitute the unbound metals of the solum.

Process 2. Through the actions of principally rainfall, these unbound metals are not only subject to downward infiltration, but upward vertical migration (capillary rise and evaporation), and are also subject to being converted to the bound form by pedogenic processes. These pedogenic processes probably take place over a time period that is both long, relative to the rate of normal chemical reaction, but short relative to geological time, i.e. years to thousands of years.

Process 3. Both unbound and bound forms of metal are subject to the agents of lateral migration, such as mechanical creep, sheetwash and aeolian processes. These are essentially planar phenomena, i.e. they occur at all points on the surface.

However, the unbound form is constantly being converted to a bound form at any point on the surface or within the profile. It is only replenished close to the point source. Thus, the proportion of unbound metal decreases (and concomitantly the proportion of bound metal increases) away from the point of issue, i.e the anomaly zone. Background for unbound metals is reduced to very low levels by the conversion to a bound form. The spread of bound metal, and including background values for bound metal is greater than for unbound form. Both the sharpness, and the greater amplitude of the anomaly contrast for a partial digestion method is due to the fact that an intermediate species (i.e. one with a definitive lifetime) is being utilized.

IMPLICATIONS FOR EXPLORATION

There are several important questions that need to be asked by the explorationist. When should a technique such as MMI, be utilised in favour of a conventional (total) digestion technique? Secondly, what can the application of a high-resolution soil geochemistry technique such as MMI do for my exploration programme? Is a technique such as MMI likely to not detect a geochemical anomaly observable by conventional methods?

The first question is best answered by referring back to the comparative case histories. The MMI technique was found to give superior resolution for most metals including Au, when the degree of weathering was great and/or surficial cover was a factor. The discrimination of partial techniques such as MMI against false anomalies from physically transported (nugget) Au has been documented on several continents. For elements such as Zn, Ni, and Cd, which are particularly mobile, the response ratio differences were appreciable. Thus, in tropical weathering terrain, or colluvial environments or those with exotic cover, the additional signal to noise ratio of the partial technique is likely to prove beneficial. For Pb in most terrain this is less likely to be so –due to its immobility. In this respect the San Nicolas case history is interesting, in that the partial digestion for Pb with MMI-A provided significantly better resolution over the deposit than conventional geochemistry.

Where mineralisation is strong, and close to surface, any geochemical method is capable of resolving anomalous zones, and there is less difference in resolution between partial and total techniques. For exploration in residual terrain, with very little weathering, choice of a total digestion technique is justified on cost grounds, providing that, in the case of Au, it is known there is no lateral displacement (false anomalies from bound metal) problems using (say) fire assay. The penalty for incorrect interpretation of the latter can be serious – as serious as non-detection of a viable ore-body or drilling a false anomaly.

In zoned metal systems, resolution of the metal sequence (as shown in the San Jorge example) will allow the geochemical survey to be more intelligently integrated with the geological programme prior to actual discovery. In a similar manner, it is useful to know during Ni exploration which part of the system is being explored, even when it is under surficial cover. Only a precise multi-element technique can do this. From the experimental evidence, case histories so far carried out, and computer modelling it appears unlikely that a technique such as MMI will fail to register a signature for a sub-surface source which has a conventional geochemical anomaly. In short, the worst case scenario for a technique such as MMI is anomaly resolution similar to that from conventional analysis.

In relation to the benefits that might accrue from the application of a high-resolution technique, such as MMI, there are two ways in which the increased resolution can be of value. Firstly, the increased magnitude of the signal to noise ratio can be of benefit in terrain types where conventional geochemistry has resolution problems. Examples include colluvium, and areas with shallow depths of exotic cover, e.g. the Atacama gravels, glacial till, aeolian sands. It also appears likely that A horizon geochemistry, such as MMI, might be appropriate in heavily-leached temperate soils, in which conventional B and C horizon anomalies do not readily accumulate. The ease and cost of sampling the A horizon is also a benefit.

Secondly, the superior spatial resolution can be of potentially great benefit. It is manifest in a number of ways. For example, in a zoned geochemical system, the zoning is only recognisable in surface soil surveys if the geochemical method is spatially precise. The San Jorge example relies very much on the sharpness of the MMI geochemistry for each element in order to display the zoning patterns. Geochemical 'structure', for example the concentration of Au along contacts, and opposing shear systems can only be portrayed if the chemical extraction is 'sharp'. For Ni, delineation of channel-flow facies rock boundaries is only of benefit if it is also spatially precise. Confirming or supporting evidence from an accompanying element (e.g. Cd for Zn and Ag for Au) is only useful if there is good spatial coincidence. Most importantly, the additional spatial resolution can be best utilised in the accurate placement of first-round drilling. In many cases better placement of the drill can obviate reconnaissance drilling, trenching or expensive costeaning exercises.

Finally we need to examine the role of the geochemist, in interpreting "higher resolution" geochemistry. There may be a tendency for some to think that there is less need for expert interpretation due to higher resolution, or to approach the interpretation without due regard to all the possible contributing factors. Integration of landform and soil type into each geochemical survey is an important part of interpretation. Geochemistry, in particular soil geochemistry is the response to any one or a number of possible contributing sources e.g. lithology, regolith, mineralisation, anthropogenic. Defining an anomaly (by definition a relative term) requires the intervention of a geoscientist. Anomalies are not defined *per se* by the geochemical analytical results, although the ease of definition may be assisted or otherwise by the resolution available. Selection of MMI anomalies likely to be related to mineralisation sources requires the same dedication, understanding and skills as the equivalent exercise with conventional geochemistry. The successful mineral exploration geochemist of the future will be one who chooses and uses 'higher resolution geochemistry" with due regard to these facts.

SUGGESTED FURTHER READING

Hall, G.E.M., MacLaurin, A.I. and Vaive, J.E., (1995). Readsorption of gold during the selective extraction of the "soluble organic" phase of humus, soil and sediment samples. *J. Geochem. Explor.,* 54(1):27-38.

Lindsay, W.L., (1972). Inorganic phase equilibria of micronutrients in soils. *In: Micronutrients in Agriculture.,* 41-58. (Soil Sci. Soc. Am.: Madison).

Mann, A.W., Birrell, R.D., Perdrix, J.L., Mann, A.T., Humphreys, D.B. and Gay, L.M. 1995. Project M219: Mechanism of formation of Mobile Metal Ion anomalies. *Meriwa Report No. 153.* Perth, W.A., 407 pp.

Mann, A.W., Mann, A.T., Humphreys, D.B., Dowling, S.E., Staltari, S. and Myers, L., (1997). Soil geochemical Anomalies – their dynamic nature and interpretation. 132 pp. *MERIWA report No. 184,* Perth. **Available in CD form from MERIWA.*

Mann, A.W., Birrell, R.D., Mann, A.T., Humphreys, D.B., and Perdrix, J.L. Application of the mobile metal ion technique to routine geochemical exploration. *Journal of Geochemical Exploration* **61** (1998) 87-102.

Tills, R. and Alloway, B.J., (1983). An appraisal of currently used soil tests for available copper with reference to deficiencies in English soils. *J. Sci. Food Agric.,* 34: 1190-1196.