#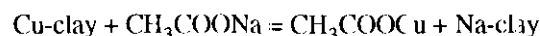 THE SEQUENTIAL EXTRACTION OF COPPER, SILVER, MOLYBDENUM, IRON AND MANGANESE FROM GEOCHEMICAL STANDARDS AND SELECTED SAMPLES

By B.Bhagwanani and R.E.Lett

KEYWORDS: Applied geochemistry, sequential extraction, copper, molybdenum, iron, manganese, silver, lake sediments, glaciolacustrine sediments.

INTRODUCTION

The sequential, selective extraction of elements from geochemical samples using different chemicals is becoming a routine procedure for determining the distribution of metals in mineral phases which commonly constitute weathered materials. Several sequential extraction techniques have been developed to aid in the interpretation geochemical data by measuring the relative mobility of the elements in the near-surface environment (Tessier *et al.*, 1979; Hoffman and Fletcher, 1979; Gatehouse *et al.*,1977). Sequential extraction analysis has been applied to assessing environmental problems by determining the bio-availability of potentially toxic metals such as chromium, lead, mercury and cadmium in contaminated sediments and soils (Campbell *et al.*, 1988). The efficiency of the extraction procedure to selectively remove all of the metal from samples and the quality of the data produced are important for reliably interpreting the results of sequential analysis.

Research has focused on establishing the most suitable sequence of extraction for treating different sample types and for improving the efficiency of the extraction method (Rose, 1975; Chao and Sanzolone, 1992; Papp *et al.*, 1991; Hall *et al.*, 1993). This paper describes the extraction of copper, silver, molybdenum, iron and manganese from geochemical reference materials and selected samples using a sequence of sodium acetate solution, hydroxylamine hydrochloride solution, sodium hypochlorite solution and Lafort aqua regia.

The method used in this study is modified from a procedure developed by Hall *et al.* (1993). Sodium acetate solution (pH 5) removes metal adsorbed on colloidal iron and manganese oxides, metal adsorbed on organic particles, metal held in exchange sites on the surface of clay minerals and metal in the form of carbonates. An example of the exchange of copper from clay with sodium acetate is:

$$Cu\text{-}clay + CH_3COONa = CH_3COOCu + Na\text{-}clay$$

Hydroxylamine hydrochloride ($NH_2OH.HCl$) solution reduces amorphous manganese and iron oxides and releases absorbed trace metals in the process. The reaction between manganese dioxide and hydroxylamine hydrochloride is:

$$2NH_2OH.HCl + MnO_2 = MnCl_2 + N_2O + 3H_2O$$
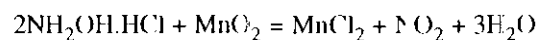
Alkaline sodium hypochlorite (NaOCl) solution oxidizes organic matter to release absorbed and complexed metals. Mineral sulphides are not oxidized by this reagent (Papp *et al.*, 1991). An example of the oxidation reaction for a simple organic compound such as oxalic acid is:

$$2NaOCl + C_2O_4H_2 = 2NaCl + 4H_2O + 2CO_2$$
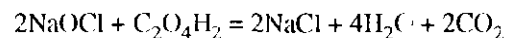
Lefort aqua regia (3 volumes concentrated nitric acid mixed with 1 volume concentrated hydrochloric acid) oxidizes sulphide minerals and dissolves noble metals such as gold and platinum. The initial reaction between nitric acid and hydrochloric acid produces nascent chlorine which dissolves metals and oxidizes sulphides. An example of the reaction for the oxidation of pyrite is:

$$HNO_3 + 3HCl = NOCl + 2H_2O + 2Cl^O$$
$$NOCl = NO + Cl^O$$
$$FeS_2 + Cl^O = Fe^{2+} + Cl^- + 2S$$
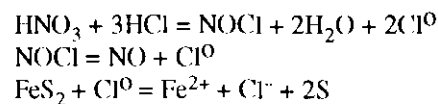
The Lefort digestion was chosen for the final stage of the sequential extraction because this acid mixture is a powerful oxidizing agent, especially for sulphides, and is commonly used in the analysis of regional geochemical samples collected in British Columbia.

In addition to the sequential extraction, the reference materials and samples were also analysed separately for the same elements, using a concentrated hydrofluoric-perchloric-nitric-hydrochloric acid digestion. This

mixture will dissolve most of the silicate, oxide and sulphide minerals found in weathered materials. Certain aluminosilicate and oxide minerals, however, are resistant to the attack by this acid mixture and are only partially dissolved (Chao and Sanzolone, 1992).

ANALYTICAL METHODS

QUALITY CONTROL AND SAMPLES

The CANMET reference materials LKSD 1 and 3, and the United States Geological Survey reference material GXR3 were used to monitor the analytical precision of the extraction data. Each batch of 24 samples contained a replicate sample, LKSD1 and LKSD3 standards and a solution blank. In one batch, GXR1 was substituted for LKSD 1. A description of each reference material, the recommended mean value, the uncertainty range for each element and the loss on ignition are shown in Table 1. The information is taken from compilations by Lynch, 1990 and by Gladney and Roelandts, 1990.

Table 1. Mean values and uncertainty range (± 2 standard deviation) for elements in reference samples

Description	Silver (ppm)	Copper (ppm)	Iron (%)	Manganese (ppm)	Molybdenum (ppm)	LOI (%)
LKSD 1 Lake bottom sediment	0.6+/-0.1	44+/-10	2.8+/-0.2	700+/-60	10+/-4	23.5+/-1.0
LKSD 3 Lake bottom sediment	2.7+/-0.2	35+/-6	4.0+/-0.4	1440+/-160	<0.5	11.8+/-1.2
GXR1 Jasperoid rock sample	31+/-4	1110+/-115	25+/-1.2	880+/-70	18+/-6	5 3+/-.7

Other samples analysed were pulverised lake bottom sediments (Cook, 1993) and the -63 micron fraction of glaciolacustrine sediments (Bobrowsky et al., 1993). All of the samples were collected in central British Columbia.

SEQUENTIAL EXTRACTIONS

Standards and samples were analysed for copper, silver, molybdenum, iron and manganese by the following sequence of extraction reagents.

SODIUM ACETATE SOLUTION

A 2.00-gram sample was weighed into a 25 by 100 millimetre Pyrex test tube (calibrated at 20 mL) and mixed with 20 mL of 1.00 M sodium acetate solution (136.00 g anhydrous sodium acetate dissolved in 800 mL of distilled water and 20 mL glacial acetic acid. The pH

was adjusted to 5.0 ± 0.1 with acid and the solution diluted to 1 L with distilled water). Each tube was stoppered and the contents carefully mixed to avoid loss of material (due to frothing) using a Vortex mixer every 20 minutes for 6 hours. The samples were then centrifuged for 10 minutes at approximately 3000 rpm. Turbid solutions were centrifuged again for another 5 minutes. Clear solutions were decanted into clean 25 by 150 millimetre glass test tubes (calibrated at 30 mL). Residues were mixed thoroughly with 5 millilitres of distilled water, centrifuged for 10 minutes and the washings added to the extracts. The washing was repeated with another 5 millilitres of distilled water and combined washings and extracts diluted to 30 millilitres with distilled water. Samples were stored in the dark to limit loss of silver by precipitation. Residues were digested in hydroxylamine hydrochloride.

HYDROXYLAMINE HYDROCHLORIDE SOLUTION

The residue from the sodium acetate extraction was added to 20 millilitres of 0.25 M hydroxylamine hydrochloride (17.36 g of hydroxylamine hydrochloride dissolved in 500 mL of distilled water, mixed with 21 mL of concentrated hydrochloric acid and diluted to 1 L) in stoppered tubes and mixed thoroughly using a Vortex mixer every 5 to 10 minutes until frothing subsided. The samples were heated at 60°C for 2 hours in a water-bath with shaking and vortexing every 30 minutes. After extraction the residues were washed twice with distilled water using the same procedure as in the sodium acetate extraction. Hydroxylamine hydrochloride extracts and distilled water washings were combined and solutions diluted to 30 millilitres. The residues were digested in sodium hypochlorite solution.

SODIUM HYPOCHLORITE SOLUTION

Twenty millilitres of 5% sodium hypochlorite solution (pH 9.5) was mixed with the hydroxylamine hydrochloride extraction residue. If frothing occurred the samples were carefully mixed every 5 to 10 minutes until the frothing subsided. The samples were heated at 100°C for 1 hour in a water-bath with shaking and vortexing of each sample every 20 minutes. After the extraction stage was completed the residue was washed twice with distilled water using the same procedure as in the sodium acetate extraction. Sodium hypochlorite extracts and distilled water washings were combined and solutions diluted to 30 millilitres. The residues were digested in Lefort aqua regia

LEFORT AQUA REGIA

Five millilitres of concentrated nitric acid (ACS grade) were mixed thoroughly with the sodium

hypochlorite residues and the samples allowed to stand overnight. The sample tubes were then heated at 90°C for 30 minutes in a water-bath, the contents mixed, 1.5 millilitres of concentrated hydrochloric acid added and the mixing repeated. The samples were then heated at 90°C for a further 90 minutes in the water-bath, the contents cooled and then diluted to 20 millilitres with distilled water. The solutions were mixed, centrifuged and the residue discarded.

HYDROFLUORIC-PERCHLORIC-NITRIC-HYDROCHLORIC ACIDS

One gram of sample was mixed with 5 millilitres concentrated hydrochloric acid, 5 millilitres of a nitric-perchloric acid mixture (3:1 v/v) and 5 millilitres hydrofluoric acid in a teflon beaker and reduced to dryness on a hotplate. Residues were heated for 10 to 15 minutes with 4 millilitres concentrated hydrochloric acid and 1.5 millilitres concentrated nitric acid, cooled and the contents of the beaker transferred to calibrated test tubes. The solutions were made up to 15 millilitres with distilled water, mixed thoroughly and centrifuged.

ANALYSIS OF EXTRACTS FOR METALS

The extracted solutions and hydrofluoric-perchloric-nitric-hydrochloric acid digests were analyzed for copper, silver, molybdenum, iron and manganese using a Perkin Elmer 2280 atomic absorption spectrometer. Background correction was applied for silver which was analysed first (preferably on same day as the extraction), to avoid silver loss from solution by precipitation. Approximately 10 milligrams of aluminum chloride was added to a 2-millilitre aliquot of the solutions for the molybdenum analysis. The calibration standards were made with a similar concentration of aluminum chloride.

DISCUSSION OF RESULTS

Copper, silver, molybdenum, iron and manganese precision expressed as relative standard deviations (%RSD) for the reference materials LKSD 1 and LKSD 3 are shown in Tables 2 and 3.

Table 2. Precision for LKSD 1 (mean of 7 analyses)

	Sodium Acetate	Hydroxylamine Hydrochloride	Sodium Hypochlorite	Aqua Regia	Hydrofluoric Acid
Cu-Mean (ppm)	1	8	18	18	44
Cu (%RSD)	28	17	16	15	3
Mo-Mean (ppm)	0.5	0.5	3	2	10
Mo (%RSD)	31	53	48	51	7
Mn-Mean (ppm)	230	86	37	64	686
Mn (%RSD)	7	8	205	18	5
Fe-Mean (%)	0.039	0.043	0.044	1.36	2.79
Fe (%RSD)	48	22	57	22	7

Table 3. Precision for LKSD 3 (mean of 7 analyses)

	Sodium Acetate	Hydroxylamine Hydrochloride	Sodium Hypochlorite	Aqua Regia	Hydrofluoric Acid
Ag-Mean (ppm)	0.5	1.4	1.4	.1	2.8
Ag (%RSD)	0	21	21	.7	3
Cu-Mean (ppm)	3	8	9	1	35
Cu (%RSD)	19	15	34	0	2
Mn-Mean (ppm)	647	435	101	137	1270
Mn (%RSD)	3	6	255	3	8
Fe-Mean (%)	0.029	1.12	0.01	1.83	3.80
Fe (%RSD)	4	20	46	5	.

The mean and RSD values for each element were calculated from seven repeat determination: of the reference materials analysed by the sequent al extractions and by the hydrofluoric-perchloric-nitric-hydrochloric acid digestion. Table 4 shows the copper, molybdenum, iron and manganese precision calculated from sequential extraction data for ten replicate samples inserted in batches during routine analysis. Silver precision for LKSD 1 and for the replicates samples and molybdenum precision for LKSD 3 are not reported because values are below or just above detection limits.

Table 4. Precision calculated from ten replicate samples

	Sodium Acetate	Hydroxylamine Hydrochloride	Sodium Hypochlorite	Aqua Regia
Replicate Mean Cu	100	117	13	90
RSD Cu (%)	9	3	14	3
Replicate Mean Mo	8	3	14	2
RSD Mo (%)	7	17	11	16
Replicate Mean Mn	154	433	11	129
RSD Mn (%)	149	5	5	3
Replicate Mean Fe	0.132	1.04	0.03	1.73
RSD Fe (%)	160	3	21	3

Most precise silver, copper, molybdenum, iron and manganese determinations (< 8% RSD) are for the reference samples analysed with the hydrofluoric-perchloric-nitric-hydrochloric acid digestion. Good precision (< 8% RSD) is also revealed for manganese extracted from the reference samples with sodium acetate and hydroxylamine hydrochloride. The manganese precision for the sodium hypochlorite extraction of the reference samples (Tables 2 and 3) and the sodium acetate extraction of the replicate samples is poor (>140 % RSD) reflecting large differences between repeat determinations (Table 4). However, precision calculated from replicate analyses, improves for the sodium hypochlorite extractable manganese.

Copper precision (RSD) ranges from 34% for the sodium hypochlorite extraction of LKSD 1 (Table 2) to 15% for Lefort aqua regia digestion of LKSD 3 (Table 3). The variation of iron and manganese precision for the different extractions resembles copper in that the largest RSD is for the sodium hypochlorite extraction (Table 3). The relatively poor precision for the sodium hypochlorite

extractable copper, iron and manganese may be due to variations in the amount of organic matter oxidized from the reference sample and precipitation of colloidal hydroxides in the alkaline solution. Replicate sample analysis for iron reveals that RSD values are greater 100% for the sodium acetate extraction. This precision reflects a large difference between the iron values for one of the replicate samples. Molybdenum replicate data reveal improved precision due to the higher concentrations of molybdenum in the replicates compared to the reference samples.

Metal concentrations extracted by each reagent from the reference materials LKSD 1, LKSD 3 and GXR 1 are shown in Table 5. Values are expressed in parts per million and as a percentage of the reported mean concentration for the element in the reference material. Silver distribution in LKSD 1 and molybdenum distribution in LKSD 3 have not been included in Table 5 because many of the element concentrations are below detection limits. Sums of the percentage copper, silver, molybdenum, iron and manganese, extracted at each stage from GXR 1, range from 90 to 110% indicating that the sequential extraction process has removed the bulk of the metals from the reference sample. The sums of percentage silver extracted at each stage from LKSD 3, copper from LKSD 1 and manganese from LKSD 3 are also close to 100%, compared to values obtained using the hydrofluoric-perchloric-nitric-hydrochloric acid digestion. This range shows that the sequential extraction process effectively removes the bulk of these metals in the reference samples. However, the sum of percentage metal extracted for other elements, especially manganese in LKSD 1 and copper in LKSD 3, are much lower or significantly higher than 100%. The analytical error determined in each extract and the depletion of the sample during the extraction process may be contributing factors responsible for excessively large or small sums of percentage extracted metal.

Progressive loss of sample during the extraction process through oxidation or organic matter and transfer of material from stage to stage can also give misleading values because the metal concentration is calculated from the original sample weight rather than the actual weight of the residue from each extraction. The low percentage sums for molybdenum and manganese relate to the more highly organic reference material LKSD 1. Precipitation of metal hydroxides in the alkaline sodium hypochlorite extract, despite the neutralizing effect of the weakly acid distilled water, may be one reason for the low total sums of the extracted iron and manganese. However, this factor does not appear to have influenced the extraction of manganese from LKSD 3 which contains a higher manganese content than LKSD 1.

Table 5. Extraction of metals from GXR 1, LKSD 1 and LKSD 3

	Sodium Acetate	Hydroxylamine Hydrochloride	Sodium Hypochlorite	Aqua Regia	Hydrofluoric Acid	Sum of extracts (%)
Ag in GXR1	0.5	23	3	1	31	
% Ag extracted	2	74	10	3	100	89
Mean Ag in LKSD 3	0.5	1.4	14	0.1	2.8	
% Ag extracted	1	50	50	3		103
Cu in GXR1	184	520	2	360	1160	
% Cu extracted	17	47	0.5	32	100	96
Mean Cu in LKSD 1	3	8	18	18	44	
% Cu extracted	5	18	41	41	100	106
Mean Cu in LKSD 3	3	8	9	21	35	
% Cu extracted	9	23	26	60	100	118
Mo in GXR	0.5	0.5	4	15	19	
% Mo extracted	1	1	22	83	100	105
Mean Mo in LKSD 1	0.5	0.5	3	2	10	
% Mo extracted	10	10	30	20	100	70
Mn in GXR1	143	591	3	88	880	
% Mn extracted	16	67	0.5	10	100	93
Mean Mn in LKSD 1	230	86	37	64	686	
% Cu extracted	33	12	6	10	98	61
Mean Mn in LKSD 3	647	435	101	187	1270	
% Mn extracted	45	30	7	13	88	95
Fe in GXR1	0.99	3.86	0.001	23	Not	
% Fe extracted	0.5	15	0.5	92	determined	107
Mean Fe in LKSD 1	0.039	0.043	0.044	1.36	2.79	
% Fe extracted	2	15	2	50	100	69
Mean Fe in LKSD 3	0.029	1.32	0.01	1.83	3.86	
% Fe extracted	1	33	0.5	46	97	80

Data represents 1 determination of GXR1 and the mean of 7 analyses of LKSD 1 and LKSD 3.

The extraction of metals from two different sample types is shown in Table 6.

Table 6. Mean percent metal extracted from eight lake sediments and twelve glaciolacustrine sediments

	Sodium Acetate % Extracted	Hydroxylamine Hydrochloride % Extracted	Sodium Hyochlorite % Extracted	Aqua Regia % Extracted	Sum of Extracts (%)
Cu-A	4	11	49	48	113
Cu-B	35	40	1	21	97
Mo-A	22	22	42	49	135
Mo-B	9	17	38	13	77
Mn-A	44	30	3	22	98
Mn-B	25	47	0	20	93
Fe-A	1	25	4	58	87
Fe-B	1	30	0.01	43	75

Both groups were analysed as part of the same sample batch. Group A comprises eight pulverised lake-sediment samples (mean LOI of 29%) and group B consists of twelve glaciolacustrine sediment samples (mean LOI of 4%). The stronger association of the copper with organic matter in the lake sediments is clearly revealed by the greater abundance (49%) of sodium hypochlorite extracted copper compared to the much smaller amount (1%) liberated from group B samples. The mean sum of the manganese extracted at each stage from both groups ranges from 90 to 100%. However the mean sum of iron extracted at each stage ranges from 75% in group B to 87% in group A. Precipitation of iron hydroxide in the alkaline sodium hypochlorite may be responsible for the low mean sum of extracted iron.

Extraction of copper and manganese from individual lake sediment and glaciolacustrine sediment samples is shown in Figures 1 and 2.

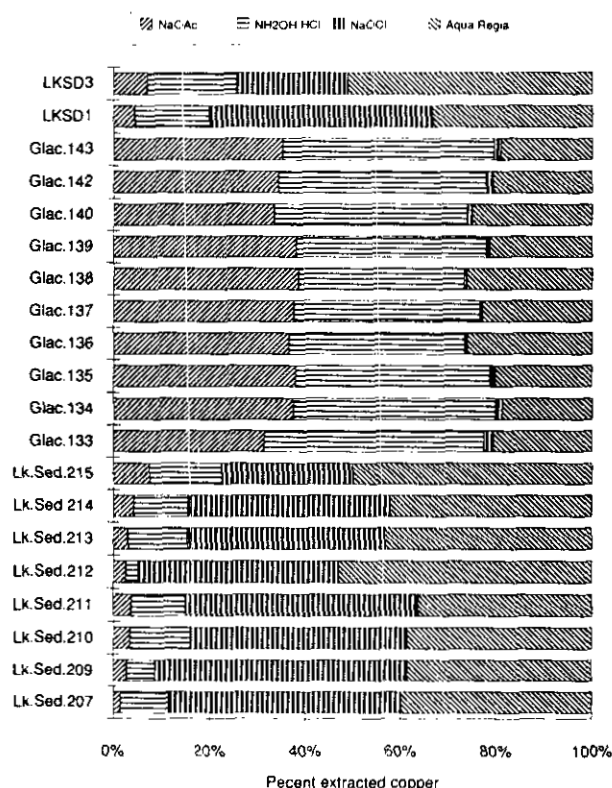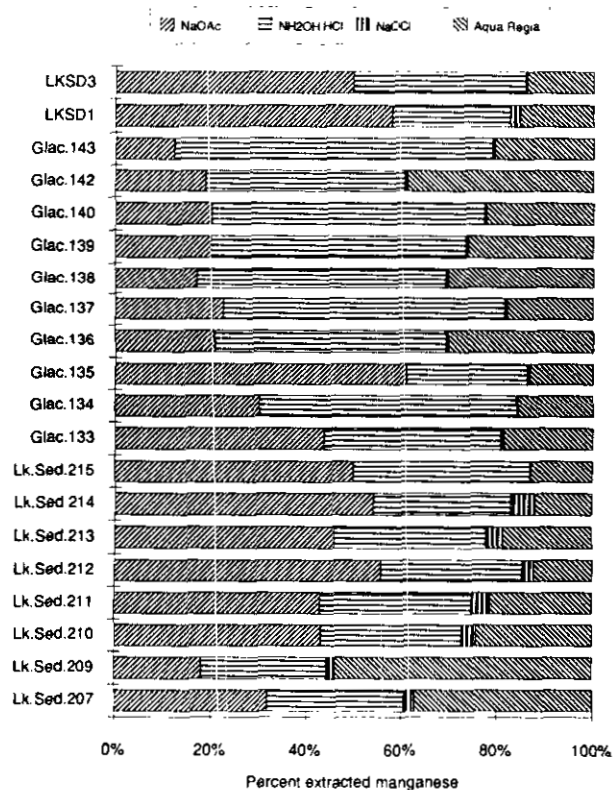**Figure 1. Copper extracted from lake sediments (Lk.Sed.) and glaciolacustrine sediments (Glac.)**

All of the extraction sums have been normalized to 100% for ease of comparison. A greater amount of the copper is extracted by the sodium hypochlorite and aqua regia from the lake-sediment samples and the reference materials LKSD 1 and LKSD 3 than from the glaciolacustrine samples. However, more of the copper is extracted by sodium acetate and hydroxylamine hydrochloride from the glaciolacustrine samples. More manganese is extracted by the hydroxylamine hydrochloride from the glaciolacustrine sediments than from the lake sediments (Figure 2). Unlike copper, manganese distribution in the extractions from the two sample groups is less uniform.

CONCLUSIONS

Results of sequential extraction analysis of geochemical reference samples, lake-sediment samples and glaciolacustrine sediment samples reveals the following features.

- Copper and manganese precision (expressed as relative standard deviation) is less than 20% for the majority of extracts. Sodium hypochlorite extracted copper and manganese determinations are less precise and the larger error may be due incomplete extraction of metals from reference materials. Relatively poor precision for silver and molybdenum extracted from the reference materials LKSD1 and LKSD 3 reflects low element concentrations in the samples. Data for sodium hypochlorite extracted iron for the reference samples reveals a large error and especially for the more organic rich LKSD 1. Precipitation of iron hydroxide during the sodium hypochlorite extraction stage and variation in the amount of organic matter oxidized may the responsible for the poor precision.

- The extraction process removes more than 90% of all metals from the jasperoid reference sample GXR1. The high total of extracted copper for the reference materials LKSD 1 and 3 may reflect loss of sample during the extraction process and analytical error. The low total of extracted iron and manganese for the more organic rich LKSD 1 sample may be due to precipitation of elements as hydroxides during the sodium hypochlorite oxidation.

- Accumulation of copper by organic matter in lake-bottom sediments is clearly revealed by the high concentration of metal in the sodium hypochlorite extract. In glaciolacustrine samples the greater abundance of copper and manganese in the hydroxylamine hydrochloride

Figure 2. Manganese extracted from lake sediments (Lk.Sed.) and glaciolacustrine sediments (Glac.)

and Lefort aqua regia extracts indicate that more of the metals are associated with secondary minerals formed during weathering.

ACKNOWLEDGMENTS

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