PRELIMINARY REPORT ON NINETEEN DIGESTION METHODS TESTED ON VARIOUS GEOCHEMICAL EXPLORATION SAMPLE MEDIAS

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PRELIMINARY REPORT ON NINETEEN DIGESTION METHODS TESTED ON VARIOUS GEOCHEMICAL EXPLORATION SAMPLE MEDIAS

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I. INTRODUCTION

The extractability of metal ions and selectivity of certain sample components by various digestion methods is an important consideration in exploration geochemistry. This subject has been discussed by many authors, some of which are given in the reference section at the back of this report.

For this study, nineteen different digestion methods were tested on seven different types of geochemical samples and analyzed for copper, nickel and zinc. The digestion methods are described in the Appendix. The solutions were analyzed by A. W. Klaysmat (Minerals Division Chemist) on a Perkin-Elmer 303 atomic absorption spectrophotometer. The results of these tests are considered preliminary. The results for each digestion method and sample media are presented in Tables 1, 2 and 3.

II. SOME OBSERVATIONS - MINERAL ACID DIGESTION METHODS

In order to compare the extractability of various mineral acid digestion methods, the concentrations of each metal for each sample type and for each digestion method was divided by the concentrations obtained for the (HF, HNO_3 & HCl) digestion. This digestion is not total, but is nearly total. The results of the "percent of total metal" are presented in Table 4.

The hot methods usually extracted substantially more metal than the cold methods, as would be expected. However, for the Gyttja sample, the difference between hot and cold methods is small.

The aqua regia methods and HCl methods extract less metal from the silicates than the HNO_3 methods as evidenced by the Ni for the Troctolite. HNO_3 will extract a significant portion of metals in silicates (Timperley and Allan, 1974). HCl does not attack silicates to the extent of HNO_3 (Timperley and Allan, 1974). HCl generally attacks only the less resistant silicates (Bradshaw et al., 1974).

Aqua regia and HNO_3 generally extract more metal from the sulfides than HCl as evidenced by Cu for the Troctolite (Mineralized) and Troctolite.

For the organic samples, A-horizon and Gyttja, the various HNO_3 methods extract slightly more metal than the various aqua regia methods. The HCl and HNO_3 methods generally extract about the same amount of metal from the organics. HCl will extract significant amounts of metals from organics (Timperley and Allan, 1974). HNO_3 is known to decompose organic matter (Timperley and Allan, 1974; Rose, 1975). The HF, HNO_3, and HCl digestion, except for some Cu values, extracted more metal than the other methods in the Gyttja sample, which suggests silicates are present in the gyttja.

For the samples containing Fe-Mn hydroxides, B-horizon and Fe-Mn Hydroxide, HCl methods tend to extract slightly more metal than the HNO_3 methods. HCl is generally known to extract more metal from Fe-Mn hydroxides than HNO_3 (Rose, 1975). The C-horizon sample contains lesser amounts of Fe-Mn hydroxides, but can be considered in this comparison. The HCl methods extracted more metal than the aqua regia methods.

III. SOME OBSERVATIONS - WEAK EXTRACTION METHODS

The results of the weak extraction methods expressed as "percent of total metal" is presented in Table 5.

A. 0.5M HCl

The hot method does extract significantly more metal than the cold method.

The 0.5M HCl leach does appear to extract a relatively large amount of Fe-Mn hydroxide and organic held metal as evidenced by the Fe-Mn Hydroxide and Gyttja samples respectively.

It does appear to extract significant amounts of metal held in clay minerals as shown for the C-horizon sample, but a large portion of this metal may be held in Fe-Mn hydroxides. This method, also, did not extract significant amounts of sulfide held Cu from the mineralized Troctolite sample as compared to the other samples.

B. EDTA

The EDTA method did extract a large portion of the metal in the organics: A-horizon and Gyttja samples.

It did not extract any of the sulfide held Cu in the mineralized Troctolite sample.

Only a small portion of the Fe-Mn hydroxide held metal in the B-horizon sample was extracted. However, a large portion of metal was extracted in the Fe-Mn hydroxide sample.

For the C-horizon sample, the EDTA method did extract a large portion of probable clay held metal or loosely bonded metal in the Fe-Mn hydroxides. EDTA will complex exchangeable ions in clay minerals (Rose, 1975).

EDTA, a chelating extractant, does not remove significant metal from silicates. EDTA is mainly specific for organic held metal (Timperley and Allan, 1974).

C. Ammonium Citrate/Hydrogen Peroxide

Ammonium citrate reduces iron hydroxides.

Hydrogen peroxide is known to dissolve Mn Hydroxides (Rose, 1975). Also, hydrogen peroxide is a strong oxidizing agent and, therefore, is known to dissolve organics and sulfides (Rose, 1975).

The observed extraction of metals in the samples containing Fe-Mn hydroxides, B-horizon and Fe-Mn hydroxide samples, probably results from the reduction of iron by the ammonium citrate and dissolution of Mn hydroxides by the hydrogen peroxide. The extracted metal in the C-horizon sample may be the result of hydrogen peroxide acting on the Mn hydroxides and ammonium citrate on the Fe hydroxides.

A significant portion of metal was extracted from the organics in the Gyttja sample. However, a portion of this metal is probably contained in Fe-Mn hydroxides, extractable by the ammonium citrate and hydrogen peroxide and in sulfide form, extractable by the hydrogen peroxide. The A-horizon sample did not indicate that significant organic held metal was extracted by this method.

The Troctolite (mineralized) and Troctolite samples indicate that large portions of sulfide held metal is extracted by the hydrogen peroxide.

D. Hydroxylamine Hydrochloride/Ammonium Citrate

Ammonium citrate reduces iron hydroxides and hydroxylamine hydrochloride Mn hydroxides (Rose, 1975).

This method appears to extract minor amounts of organic and sulfide held metal as evidenced by the A-horizon, Gyttja, Troctolite (mineralized) and Troctolite samples. The higher percents of extracted Ni and Zn for the Gyttja sample probably are from Fe-Mn hydroxides.

The B-horizon, C-horizon and Fe-Mn hydroxide samples, as compared to the other samples, indicate that this method is essentially specific for Fe-Mn hydroxides.

E. Ascorbic Acid/Hydrogen Peroxide

This method is essentially specific for sulfide held metal as compared to hydroxide held metal (Gunton and Nichol, 1974). However, the hydrogen peroxide will attack the organics.

The extraction of organic held metal by the hydrogen peroxide is illustrated by the A-horizon, B-horizon and Gyttja samples. The B-horizon sample generally will contain organic material washed down from the A-horizon.

The almost complete lack of extraction of Fe-Mn hydroxide held metal is evidenced by the C-horizon and Fe-Mn hydroxide samples.

A fair amount of sulfide held metal was extracted from the Troctolite (mineralized) and Troctolite samples, but it is less than expected. A portion of the metal in the Gyttja sample is probably extracted from sulfide in addition to the organic held metal.

F. Evaluation and Comparison of Weak Extraction Methods

Based on the above mentioned results and literature survey, Table 6 has been prepared on the apparent relative extractability of weak extraction methods.

TABLE 1: COPPER (PPM)

	A Horizon	B Horizon (Rainy Lobe)	C Horizon (Indus Till)	Fe-Mn Hydroxide	Gyttja	*Troctolite (Mineralized)	*Troctolite
AN-1(HF, NHO_3 & HCl)	28	71	20	122	28	5265	95
HNO_3 & HCl Cold	8	35	16		27	5180	85
HNO_3 & HCl Hot	20	56	18		28	4880	86
HNO_3 Cold	9	21	12		27	1920	60
HNO_3 Hot	10	50	19		28	5600	92
HCl Cold	10	45	18		25	1260	58
HCl Hot	13	68	22		25	4850	92
4M HNO_3 & 1M HCl Cold	8	21	13	64	17	1820	44
4M HNO_3 & 1M HCl Hot	12	54	20	119	23	4820	86
4M HNO_3 Cold	10	24	12	56	18	250	35
4M HNO_3 Hot	9	61	19	127	26	4780	84
4M HCl Cold	8	23	11	72	15	1800	30
4M HCl Hot	8	55	17	57	16	2500	68
0.5M HCl Cold	2	6	1	34	4	15	8
0.5M HCl Hot(AN-12)	2	18	0	43	4	65	18
EDTA	4	5	4	46	12	17	
AMM. Citrate	1	3	2	22	6	1012	41
H.H. Citrate	0.2	5.4	2.8	6.8	0.4	0.4	0.8
AN-8 Ascorbic Acid/ Hydrogen Peroxide	2	7	0	1	4	320	20

* -100 mesh fraction; all other samples -80 mesh fraction

TABLE 2: NICKEL (PPM)

	A Horizon	B Horizon (Rainy Lobe)	C Horizon (Indus Till)	Fe-Mn Hydroxide	Gyttja	*Troctolite (Mineralized)	*Troctolite
AN-1(HF, NHO_3 & HCl)	0	96	23	29	48	1270	1020
HNO_3 & HCl Cold	0	0	0		9	3140	354
HNO_3 & HCl Hot	0	0	0		0	1990	646
HNO_3 Cold	0	0	0		0	990	200
HNO_3 Hot	0	11	0		33	2970	880
HCl Cold	0	22	11		28	200	334
HCl Hot	0	80	17		45	300	560
4M HNO_3 & 1M HCl Cold	0	0	0	0	0	780	254
4M HNO_3 & 1M HCl Hot	0	24	0	0	5	980	601
4M HNO_3 Cold	0	0	0	0	0	178	498
4M HNO_3 Hot	0	54	0	0	30	200	846
4M HCl Cold	0	0	0	0	0	215	320
4M HCl Hot	0	45	8	4	25	340	512
0.5M HCl Cold	4	2	0	6	11	57	38
0.5M HCl Hot(AN-12)	2	12	4	7	21	96	79
EDTA	0	0	4	6	12	12	
AMM. Citrate	0	0	0	0	0	315	0
H.H. Citrate	1.6	0.2	6.6	2.8	5	27	12
AN-8 Ascorbic Acid/ Hydrogen Peroxide	0	0	0	0	0	9	42

* -100 mesh fraction; all other samples -80 mesh fraction

TABLE 3: ZINC (PPM)

	A Horizon	B Horizon (Rainy Lobe)	C Horizon (Indus Till)	Fe-Mn Hydroxide	Gyttja	*Troctolite (Mineralized)	*Troctolite
AN-1(HF, NHO_3 & HCl)	66	76	48	88	101	210	96
HNO_3 & HCl Cold	10	16	19		83	57	41
HNO_3 & HCl Hot	14	36	26		94	70	62
HNO_3 Cold	30	1	4		68	41	10
HNO_3 Hot	59	25	22		99	98	60
HCl Cold	6	25	22		83	68	45
HCl Hot	71	47	35		98	110	75
4M HNO_3 & 1M HCl Cold	6	8	15	42	68	67	30
4M HNO_3 & 1M HCl Hot	16	34	27	58	89	104	70
4M HNO_3 Cold	8	10	20	40	64	61	38
4M HNO_3 Hot	19	41	33	57	98	105	66
4M HCl Cold	10	13	15	42	81	74	46
4M HCl Hot	19	41	35	57	89	104	73
0.5M HCl Cold	7	1	0	20	52	8	5
0.5M HCl Hot(AN-12)	4	6	0	26	65	17	13
EDTA	23	0	3	112	176	40	
AMM. Citrate	2	4	1	14	44	350	2
H.H. Citrate	0.6	0	0	3.0	11	0	0
AN-8 Ascorbic Acid/ Hydrogen Peroxide	6	5	0	1	48	480	2

* -100 mesh fraction; all other samples -80 mesh fraction

TABLE 4: PERCENT OF TOTAL METAL FOR EACH MINERAL ACID DIGESTION METHOD
(TOTAL METAL = HF, HNO_3 & HCl DIGESTION)

	A Horizon			B Horizon (Rainy Lobe)			C Horizon (Indus Till)			Fe-Mn Hydroxide			Gyttja			Troctolite (Mineralized)			Troctolite		
	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn
HNO_3 & HCl Hot	71	*	21	79	0	47	90	0	54	--	--	--	100	0	93	93	157	33	91	63	65
HNO_3 Hot	36	*	89	70	11	33	95	0	46	--	--	--	100	69	98	106	234	47	97	86	63
HCl Hot	46	*	108	96	83	62	110	74	73	--	--	--	89	94	97	92	24	52	97	55	78
4M HNO_3 & 1M HCl Hot	43	*	24	76	25	45	100	0	56	98	0	66	82	10	88	92	77	50	91	59	73
4M HNO_3 Hot	32	*	29	86	56	54	95	0	69	104	0	65	93	63	97	91	16	50	88	83	69
4M HCl Hot	29	*	29	77	47	54	85	35	73	47	14	65	57	52	88	47	27	50	72	50	76
0.5M HCl Hot(AN-12)	7	*	6	25	13	8	0	17	0	35	24	30	14	44	64	1.2	8	8	19	8	14
HNO_3 & HCl Cold	29	*	15	49	0	21	80	0	40	--	--	--	96	19	82	98	247	27	89	35	43
HNO_3 Cold	32	*	45	30	0	1	60	0	8	--	--	--	96	0	67	36	78	20	63	20	10
HCl Cold	36	*	9	63	23	33	90	48	46	--	--	--	89	58	82	24	16	32	61	33	47
4M HNO_3 & 1M HCl Cold	29	*	9	30	0	11	65	0	31	52	0	48	61	0	67	35	61	32	46	25	31
4M HNO_3 Cold	36	*	12	34	0	13	60	0	42	46	0	45	64	0	40	5	14	29	37	49	40
4M HCl Cold	29	*	15	32	0	17	55	0	31	59	0	48	54	0	80	34	17	35	32	31	48
0.5M HCl Cold	7	*	11	8	2	1	5	0	0	28	21	23	14	23	51	.3	4	4	8	4	5

* Ni for A-Horizon sample was zero except for 0.5M HCl extractions

TABLE 5: PERCENT OF TOTAL METAL FOR EACH WEAK EXTRACTION METHOD (TOTAL METAL = HF, HNO_3 & HCl EXTRACTION)

	A Horizon			B Horizon (Rainy Lobe)			C Horizon (Indus Till)			Fe-Mn Hydroxide			Gyttja			Troctolite (Mineralized)			Troctolite		
	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn
0.5M HCl Cold	7	*	11	8	2	1	5	0	0	28	21	23	14	23	51	.3	4	4	8	4	5
0.5M HCl Hot(AN-12)	7	*	6	25	13	8	0	17	0	35	24	30	14	44	64	1.2	8	8	19	8	14
EDTA	14	*	35	7	0	0	20	17	6	38	21	127	43	25	174	0	1	19	--	--	--
Amm. Citrate	4	*	3	4	0	5	10	0	2	18	0	16	21	0	44	19	25	167	43	0	2
H.H. Citrate	1	*	1	8	0	0	14	29	0	6	10	3	1	10	11	0	2	0	1	1	0
AN-8 Ascorbic Acid/ Hydrogen Peroxide	7	*	9	10	0	7	0	0	0	1	0	1	14	0	48	6	1	229	21	4	2

*Zero concentration for total metal

TABLE 6: RELATIVE EXTRACTIBILITY OF WEAK EXTRACTION METHODS FOR VARIOUS SAMPLE TYPES

	Organics	Fe-Mn Hydroxides	Clay Minerals	Sulfides	Silicates
0.5M HCl	V	V	G	L	L
EDTA	V	G	G	L	L
Amm. Citrate/ HP	V	V	G	V	F
Amm. Citrate/ HH	L	V	F	L	L
Ascorbic Acid/ HP	V	L	G	V	F

Extractibility: V - very good
G - good
F - fair
L - low

APPENDIX: DIGESTION PROCEDURES

1. HF, HNO_3 and HCl (concentrated) - Hot (90^oC)

2. HNO_3 and HCl - Cold

   1.0000gm sample digested with 10mls of concentrated HNO_3 and 10mls of concentrated HCl. Final volume in the analysis was 100mls. The sample was kept at room temperature for two hours and then filtered through 40 Whatman filter paper.

3. HNO_3 and HCl - Hot

   1.0000gm sample digested with 10mls of concentrated HNO_3 and 10mls of concentrated HCl. Final volume in the analysis was 100mls. The sample was digested at 90^oC for two hours and then filtered through 40 Whatman filter paper.

4. HNO_3 - Cold

   1.0000gm sample was digested with 20mls of concentrated HNO_3. The final volume in the analysis was 100mls. The sample was digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

5. HNO_3 - Hot

   1.0000gm sample was digested with 20mls of concentrated HNO_3. The final volume in the analysis was 100mls. The sample was digested at 90^oC for two hours and then filtered through 40 Whatman filter paper.

6. HCl - Cold

   1.0000gm sample digested with 20mls of concentrated HCl. The final volume in the analysis was 100mls. The sample was digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

7. HCl - Hot

   1.0000gm sample digested with 20mls of concentrated HCl. The final volume in the analysis was 100mls. The sample was digested at 90°C for two hours and then filtered through 40 Whatman filter paper.

8. 4M HNO_3 and 1M HCl - Cold

   1.0000gm sample digested with 10mls of 4M HNO_3 and 10mls of 1M HCl. The final volume in the analysis was 100mls. The sample was digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

9. 4M HNO_3 and 1M HCl - Hot

   1.0000gm sample digested with 10mls of 4M HNO_3 and 10mls of 1M HCl. The final volume in the analysis was 100mls. The sample was digested at 90°C for two hours and then filtered through 40 Whatman filter paper.

10. 4M HNO_3 - Cold

    1.0000gm sample digested with 20mls of 4M HNO_3. The final volume in the analysis was 100mls. The samples were digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

11. 4M HNO_3 - Hot

    1.0000gm sample digested with 20mls of 4M HNO_3. The final volume in the analysis was 100mls. The sample was digested at 90°C for two hours and then filtered through 40 Whatman filter paper.

12. 4M HCl - Cold

    1.0000gm sample digested with 20mls of 4M HCl. The final volume in the analysis was 100mls. The samples were digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

13. 4M HCl - Hot

1.0000gm sample digested with 20mls of 4M HCl. The final volume in the analysis was 100mls. The sample was digested at 90°C for two hours and then filtered through 40 Whatman filter paper.

14. 0.5M HCl - Cold

3.000gms sample digested with 20mls of 0.5M HCl. The final volume in the analysis was 100mls. The samples were digested at room temperature for two hours and then filtered through 40 Whatman filter paper.

15. 0.5M HCl - Hot

3.0000gms sample

16. EDTA

Dissolved 37.22gms EDTA disodium salt in 500mls of distilled water using a 1000ml beaker. The pH was 4.3 and it was adjusted to 4.8 using ammonium hydroxide. Dilute this solution to one liter using 1000ml volumetric flask.

Digestion procedure: 1.0000gm sample was digested for 18 hours stirring every half hour. 15ml of EDTA solution was added to the 1gm sample. After 18 hours, the sample was diluted to 100mls with deionized water and filtered through 40 Whatman filter paper.

17. Citrate

Dissolve 50.0gm ammonium citrate and 50.0gms hydroxylamine hydrochloride in 300mls distilled water using a 1000ml beaker. The pH was 3.7 adjusted to 4.3 using ammonium hydroxide. Dilute this solution to 500mls in a volumetric flask.

Digestion procedure: 5.0000gm sample was digested for 18 hours stirring every half hour. 50.0mls of ammonium citrate solution was added to the 5.0gm sample. After 18 hours, the sample was diluted to 100mls with deionized water and filtered through 40 Whatman filter paper.

18. Ascorbic Acid/Hydrogen Peroxide

Used 5.000gm sample.

19. Ammonium Citrate Digestion

Weigh .5000gm sample. Add to 40mls of a 10% w/w ammonium citrate and 20mls hydrogen peroxide 30% (conc.). Shake or stir every half hour for 18 hours. Filter through 40 Whatman filter paper into a flask. Wash carefully with distilled water. Add 5mls of concentrated HCl - 12M. Boil for one-half hour or until hydrogen peroxide is gone (slight light color change). Do not take to dryness. Bring to 100ml volume with deionized water in volumetric flask.

Comments:

All standards were made up with the same concentration of acids that were used in the digestion procedure. It was very difficult to wet some of the organic samples in the cold digestions. Hence some of the fine organic particles floated on the surface tension of the solutions. When it states in the procedure that the samples were stirred every half hour, no stirring took place during non-working hours in the lab. Some of the samples filtered very slowly (4 hours or more); consequently, sometimes the samples were in contact with the digesting solutions longer than the two hour limit. The mineralized troctolite sample was usually off scale when a 1.0000gm sample was diluted to 100mls; therefore, the concentration had to be diluted before the analysis could be completed. (The original 100ml sample was diluted 5 to 20 times depending on the concentration of the elements of interest). The original standards were still used when this happened; consequently, the standards had a higher concentration of acids than some of the diluted samples. All samples were brought to final volume with deionized water.

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