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Availability of metals in the earth's crust – Leaching tests on silicate minerals

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Abstract

The possibility was investigated to produce metal concentrates from bedrock and other types of minerals than those that today are regarded as ores. Reference samples, which are well analysed, were used. The samples were ground down to particle sizes less than app. 200-mesh (~0.075 mm). The samples were leached and the concentrations in the solutions were determined by means of ICP. The efficiency in yield of metals (as percent) of a number of leaching methods was investigated. Leaching by means of hydrochloric acid was found to be preferable. The consumption of hydrochloric acid per mass of treated mineral/ bedrock type was measured. Aluminium is to a very low extent leached by acids, and other methods need to be used. The concentration of the platinum group metals is in most minerals extremely low. For the Pt metals it is recommended to process certain basic/ultra basic minerals, even if this means that this methods perhaps is somewhat less sustainable. The results form a basis for the development of life cycle analysis methodology (Steen & Borg, 2002).

Introduction

The increasing consumption of a number of metals last centuries has given rise to concern about their long-term sustainable production and use. There is a risk that some metals will become less available in the near future, with strong negative influence on economy and technology of the human society.

Only a very small part of all scarce metals exists as ores, perhaps less than 0.01 % (Skinner, 1986). The definition of an ore is that it is an economical gain to process the site containing the ore. Sustainable access to different metals makes it necessary to process other minerals/ bedrock types than are mined today, in order to use some of the other 99.99 %. New technology therefore has to be studied and suggested.

The present study is a part of a project where we try to find an ecological value of an ore by estimating what it would cost producing similar metal concentrates starting from a sustainable resource, such as common bedrock, see Steen & Borg (2002).

The processing of bedrock/minerals in the scope of he present project includes crushing of boulder to a powder. The energy cost is very dependent on the grain size needed. If the metal atoms are located evenly distributed inside the silica crystals, that would mean that the grain sizes must be finer, and the energy consumption will he higher, than if the metal atoms are located on the crystal surface. An attempt was made to study their location by means of laser ablation MS.

Aim of this study

The aim of this study is to find a long-term sustainable process to manufacture some scarce metals. The results are thought to be able to form back-ground to further studies to estimate the cost of sustainable production of metal concentrates from earth's crust. See Steen & Borg (2002).

Standard reference material used in the present project

Standard reference material was used in evaluation of the effectiveness of different extraction methods. The standards used are very accurately investigated chemically and they represent very abundant rocks and minerals, which are easily accessible. It is important that very common minerals / rock types are investigated, in order to achieve a good estimate of the average conditions.

Wedepohl (1995) compiles data from a number of investigations to calculate the composition of the continental crust. The proportions of major rock units derived from mapping were calculated to be: 14% sedimentary rocks, 25% granites, 20% granodiorites, 5% tonalites, 6% gabbros, and 30% gneisses and mica schists (*Ibid*).

Table 1, which is revised after Troedsson & Nykvist (1973), shows the ten most common minerals in Sweden. The number of known minerals is very high, but it is a limited number that is dominating. As can be seen in Table 1 all the ten most common minerals in the Swedish bedrock contain oxygen, and eight minerals are different types of silicates, the exceptions are calcite and magnetite. The main part of the earth crust comprises different silicate minerals; dominating are quartz and different feldspars (plagioclase, microcline, orthoclase etc.).

Table 1 The ten most common minerals of the Swedish bedrock (reworked after Troedsson & Nykvist, 1973)

Mineral		Hardness according to Mohs [1/]	Elements	Weathering group [2/]
1	Quartz	7	Si, O	5
2	Plagioclase	6	Ca, Na, Al, Si, O	3-4
3	Microcline/orthoclase	6	K, Al, Si, O	4
4	Biotite (dark mica)	2	K, Fe, Mg, Al, Si, O, H	3
5	Hornblende	5	Ca, Mg, Fe, (K, Na), Al, Si, O, H	3
6	Muscovite (light mica)	2	K, Al, Si, O, H	4
7	Calcite	3	Ca, C, O	1
8	Chlorite	2	Mg, Fe, Al, Si, O	3
9	Pyroxene	5	Ca, Mg, Fe (Al), Si, O	3
10	Magnetite	5	Fe, O	-

[1/] The higher value, the harder mineral, on a scale 1 – 10.
[2/] Weathering group 1 denotes fast weathering minerals, 5 very slow weathering minerals.

The standard samples were purchased from National Bureau of Standards, U. S. Department of Commerce, USA (Refined silicon & potassiumfeldspar), respectively US Geological Survey, USA (basalt, granite & granodiorite). The standard reference material samples are ground and accompanied by certificates showing the results of performed chemical analyses. The following textbooks: Lundegårdh & Laufeld (1984); Fredén (1994) and Bland & Rolls (1998), yield information about the different minerals and rock types used in the present project, in addition to the information of the certificates from the suppliers of the standard materials.

The standard reference materials investigated in the present project are:

- **Refined silicon 57.** The different types of silicates are important minerals in a number of frequent occurring crystalline rock types. (Quartz SiO_2).

  Information on Refined silicon 57 is found on the following internet site: http://srmcatalog.nist.gov/srmcatalog/certificates/srm-57a.htm. (As visited 2001-09-11).

- **Potassium feldspar 70A**. The weathering processes of potassium feldspar ($KAlSi_3O_8$) release plant nutrients, and therefore is this mineral examined in a number of investigations, because of its significance for the fertility of land. The mineral is common in a number of frequent crystalline rocks.

  Information on potassium feldspar 70A is found on the following internet site: http://srmcatalog.nist.gov/srmcatalog/tables/111-5.htm (As visited 2001-09-11).

- **Analyzed Basalt. BCR-1** Split 13, position 10. Basalt is a magmatic volcanic rock, very common international, also somewhat occurring in Sweden. The main minerals of basalt comprise (most important first): plagioclase (mixture of $NaAlSi_3O_8$ & $CaAl_2(SiO_4)_2$), olivine (80-85% Mg_2SiO_4 + 15-20% Fe_2SiO_4) and pyroxene minerals (several minerals; $CaMgSi_2O_6$; $Mg_2Si_2O_6$; $NaAlSi_2O_6$; $LiAlSi_2O_6$). The content of silica should by definition be less than 52 %.

  Basalt, Columbia River Group (Yakima type), collected by Aaron C Waters, U.S. Geological Survey, from the Bridal Veil Flow Quarry, NW/4 of SW/4, sec. 14, T.1 N, R5 E, Bridal Veil Quadrangle (Washington – Oregon). (Flanagan, 1967)

  See: http://www.geostandards.lanl.gov/MaterialsByNumber.htm , and then choose BCR-1. (As visited 2001-09-11).

- **Analyzed Granite G-2** Split 108, position 16. Granite is a magmatic plutonic rock, very common both international and in Sweden. The main minerals of granite comprise (most important first): Potassiumfeldspar ($KAlSi_3O_8$), quartz (SiO_2), plagioclase (mixture of $NaAlSi_3O_8$ & $CaAl_2(SiO_4)_2$), and mica (either biotite $(OH)_2K(Mg,Fe)_3Si_3AlO_{10}$ or muskovite $(OH,F)_2KAl_2Si_3AlO_{10}$).

  Westerly Granite, from Sullivan quarry, Bradford, Rhode Island, collected by Felix Chayes, Geophysical Laboratory, Carnegie Institution of Washington. Sample collected in the SW/4 of SW/4 of Carolina (R. I.) 7.5 min quadrangle. (Flanagan, 1967)

  See: http://www.geostandards.lanl.gov/MaterialsByNumber.htm , and then choose G-2. (As visited 2001-09-11).

- **Analyzed Granodiorite GSP-1** Split 61, position 7. Granodiorite is a magmatic plutonic rock, rather close related to granite, but with somewhat less content of potassiumfeldspar, and higher content of plagioclase, very common both international and in Sweden. The main minerals of granodiorite comprise (most important first): plagioclase (mixture of $NaAlSi_3O_8$ & $CaAl_2(SiO_4)_2$), quartz (SiO_2), biotite ($(OH)_2K(Mg,Fe)_3Si_3AlO_{10}$), and often hornblende ($(OH)_2NaCa_2(Mg,Fe)_4Al_3Si_6O_{22}$).

  Granodiorite, collected by Leonard B. Riley, U. S. Geological Survey, from the Silver Plume Quarry on Highway U.S. 6, about 1500 feet west of Silver Plume, Colorado. (Flanagan, 1967)

  See: http://www.geostandards.lanl.gov/MaterialsByNumber.htm , and then choose GSP-1. (As visited 2001-09-11).

Table 2. The elemental concentrations of the reference samples according to the supplier. If not otherwise is stated in the table, the concentrations are given in PPM. In case the oxide is analysed instead of the individual element, this has been indicated. For information about more elements and analyse methods used se the above-mentioned Internet addresses, the certificates and Flanagan 1973.

Element	**Refined silicon 57 %**	**Potassium feldspar 70A %**	**Basalt BCR-1 PPM**	**Granite G PPM -2**	**Granodiorite GSP-1 PPM**
Ag			0,036	0,049	0,10
Al	0,67 %	Al2O3 17,9 %	Al2O3 13,61 %	Al2O3 15,40 %	Al2O3 15,25 %
As			0,70	0,25	0,09
Au			0,95 PPB	1,0 PPB	1.6 PPB
B			5	2,0	<3
Ba		BaO 0,02 %	675	1870	1300
Be			1,7	2,6	1,5
Bi			0,050	0,043	0,037
Br			0,15	0,3	
C			330		
Ca	0,73 %	CaO 0,11 %	CaO 6,92 %	CaO 1,94 %	CaO 2,02 %
Cd			0,12	0,039	0,06
Ce			53,9	150	394
Cl			50	50	300
CO2			0,03 %	0,08 %	0,15 %
Co			38	5,5	6,4
Cr	0,025 %		17,6	7	12,5
Cs			0,95	1,4	1,0
Cu	0,02 %		18,4	11,7	33,3
Dy			6,3	2,6	5,4
Er			3,59	1,3	3,0
Eu			1,94	1,5	2,4
F			470	1290	3200
Fe	0,65 %	Fe2O3 0,075 %	Fe2O3 3,68 % FeO 8,80 %	Fe2O3 1,08 % FeO 1,45 %	Fe2O3 1,77 % FeO 2,31%
Ga			20	22,9	22
Gd			6,6	5	15
Ge			1,54	1,15	1,3
Hf			4,7	7,35	15,9
Hg			10,7 PPB	39 PPB	15,5 PPB

Ho			1,2	0,4	<5
I			<1		0,05
In			0,095	0,034	
Ir			0,004 PPB	0,002 PPB	0,012
K		K2O 11,8 %	K2O 1,70 %	K2O 4,51%	K2O 5,53 %
La			26	96	191
Li			12,8	34,8	32,1
Lu			0,55	0,11	0,23
LOI		0,40 %			
Mg	0,01 %		MgO 3,46 %	MgO 0,76 %	MgO 0,96 %
Mn	0,034 %		1406 MnO 0,18	260 MnO 0,034 %	331 MnO 0,042 %
Mo			1,1	0,36	0,9
N			30	56	48
Na		Na2O 2,55 %	Na2O 3,27 %	Na2O 4,07 %	Na2O 2,80 %
Nb			13,5	13,5	29
Nd			29	60	188
Ni	0,002 %		15,8	5,1	12,5
O			45,48 %	48,34 %	47,78 %
Os			0,1 PPB		<32 PPB
P	0,008 %		P2O5 0,36 %	P2O5 0,14%	P2O5 0,28 %
Pb			17,6	31,2	51,3
Pd			12 PPB	<0,5 PPB	<0,5 PPB
Pr			7	19	50
Pt			2 PPB	<0,5 PPB	<0,5PPB
Ra			0,56 PPB	0,71 PPB	0,66 PPB
Rb		Rb2O 0,06 %	46,6	168	254
Re			0,8 PPB	<7 PPB	<2 PPB
Rh			0,2 PPB		
Ru			1 PPB		
S	0,005 %		392	24	162
Sb			0,69	0.1	3,1
Sc			33	3,7	7,1
Se			0,10	<0,7	<0,04
Si	Silicon 96,80 %	SiO2 67,1 %	SiO2 54,50 %	SiO2 69,11 %	SiO2 67,38 %
Sm			6,6	7,3	27,1
Sn			2,6	1,5	6,3
Sr			330	479	233
Ta			0,91	0,91	1,0
Tb			1,0	0,54	1,3
Te			<1	<1	<1
Th			6,0	24,2	104
Ti	0,10 %	TiO2 0,01 %	12750 TiO2 2,20 %	2780 TiO2 0,50 %	3990 TiO2 0,66 %
Tl			0,30	1,0	1,3
Tm			0,6	0,3	
U			1,74	2,0	1,96
V	0,0 %		399	35,4	52,9
W			0,40	0,1	0,1
Y			37,1	12	30,4
Yb			3,36	0,88	1,8
Zn			120	85	98
Zr	0,025 %		190	300	500

Laboratory methods

In Table 3 an overview of the different extractions performed is presented.

The chemical analyses were performed by means of inductively coupled plasma – mass spectrometry (ICP-MS). Perkin Elmer manufactures the equipment (ELAN 6000) used in the present investigation. Prior to the analyses by means of ICP the samples were diluted and pre-treated according to the manual of the instrument.

Due to practical reasons, the measurements by means of the ICP equipment were performed in three parts. The reason is that not all combinations of elements are suitable to mix in the same standard solution, because of different chemical interactions between the individual elements. Three groups of elements were defined: Heavy metals, precious metals and platinum metals. See Table 3. In that table the different isotopes measured by the ICP-equipment in this project are listed.

Often the extractions were performed as duplicates to increase the reliability of the laboratory and analytical work. For the same reason some comparisons between measurements with and without internal standard of the ICP-equipment was made.

The measurements of the ICP-equipment give most optimal results in a certain range of concentrations, individual for each isotope measured. Therefore several different combinations of dilutions of the extracted solutions prior to measurements were prepared. Some semi-quantitative measurements were also performed to give an overall view of the size of magnitude of the different isotopes.

The samples to be analysed for the platinum group metals were frozen to hinder secondary reactions of the dissolved platinum, which can lower the measured values (Dr. Sebastien Rauch, WET, Chalmers pers. comm.).

Earlier investigations – extraction methods

According to literature (See e.g. Hesse, 1971), strong bases can be used to dissolve silica crystals by means of fusing. In the present project milder base methods were used, see the chapter “The different extraction methods used”.

Ronge & Claesson, (1982 Fig. 7) publish a diagram showing relative solubility at different pH for some species. They refer to Pickering (1962). According to that diagram, the solubility of SiO_2 in water increases rapidly when pH reaches 8.5 or higher. Ronge and Claesson (1982 Fig 9), referring to Truesdell & Jones (1974) also presents the relationship between dissolution in water of a number of different silicate minerals and rock types. Except for biotite, the dissolution of the investigated minerals increases with higher temperatures, individual minerals different much. The rate of dissolution of albite (a feldspar mineral containing $Na[AlSi_3O8]$) is lowest at approximately neutral pH (5.5 – 7.5), and higher at either low or high pH, Nyström- Claesson (1995 Figure 2.3) citing Chou & Wollast (1984 & 1985).

Andersson (1975) compared the efficiency of nine different extraction methods. He studied the yield of a number of metals extracted from a cultivated illitic clay soil with 39% clay, 1.8% humus and pH 6.8. The two most efficient methods were reported (*Ibid* Fig. 2) to be 2M HNO_3 (Wiklander, 1970) and 2M HCl (Egnér et. al 1960), in both cases heated to 100 °C in a water bath and swirled every 30 minutes. The exception was that the efficiency of HCl in extraction of Cd was found to be lower than for some of the other methods.

The results of Anderson (1975) agree with the findings of a methodological study performed of the effectiveness of different extraction methods of minerals and soil samples between a number of laboratories. The results, as related by Drs Inger Påhlsson & Ulf Qvarfort Department of Earth Sciences Uppsala University (personal communication), show that extracting of silica minerals by means of hydrofluoric acid is the outstanding most effective (acid) method. In addition, a number of (acid) methods were considered to be approx. equal effective, but less effective than the hydrofluoric acid method. The methods in question were extraction by means of *aqua regia* (a mixture of hydrochloric and nitric acids), sulphuric acid, hydrochloric acid and nitric acid.

The different extraction methods used (See table 3)

Extraction by means of sodium hydroxide (NaOH). Two series of grounded dried standard mineral (approx. 0.2 g, accuracy 5 decimals) were mixed with 2.5 ml 10 M NaOH. One of the series was heated to 50°C on a shaking water bath during 1 hour, then he heat and shaking was turned off, and the sample was extracting until next day. After that the solution was diluted 10 times and filtered. The other one series was treated the same, except of heating. The aim was to study the influence of the temperature of the extraction solution. Prior to the analysis by means of ICP the pH of the filtered solution was lowered to 2 by means of HNO_3 , according to the instructions of the equipment to be used.

Extraction by means of nitric acid (HNO_3). Two series of grounded dried standard mineral (approx. 0.2 g, accuracy 4 decimals) were mixed with 5 ml concentrated (~14 M) nitric acid. One of the series was heated to 85°C on a shaking water bath during 1 hour, then he heat and shaking was turned off, and the sample was extracting until next day. After that the solution was diluted 10 times and filtered. The other one series was treated the same, except of heating. The aim was to study the influence of the temperature of the extraction solution.

Mixed extraction (Sodium hydroxide /NaOH followed by nitric acid /HNO_3).
Bedrock/mineral samples of 0.2 g, (accuracy 5 decimals) were mixed with 2.5 ml 10 M NaOH. The series was heated to 50 ºC during one hour on a water bath and agitated. Then the heat was turned off and the samples were diluted ten times the next day. Ten ml solution was taken away by pipette and the pH was lowered to 2 in this sample prior to the ICP analysis.

The original samples were then decanted and the extraction continued by means of HNO_3 (~14 M). The series was heated, agitated and cooled the same way as the NaOH extraction. The series was diluted and filtered the next day prior to the ICP analyses.

Mixed extraction (Sodium hydroxide /NaOH followed by hydrochloric acid /HCl). Duplicate bedrock / mineral samples of 0.5 g (accuracy 5 decimals) were extracted by means of 5 ml NaOH. The first hour the samples were warmed to 50 ºC and agitated. Then the heat was turned off and the samples were diluted ten times the next day. Ten ml solution was taken away by pipette and the pH was lowered to 2 prior to the ICP analysis.

The original samples were then decanted and the next extraction continued by means of HCl. The series was heated, agitated and cooled the same way as the NaOH extraction. The series was diluted and filtered the next day prior to the ICP analysis.

One series was prior to the ICP measurements prepared by means of internal standard (IS) in accordance to the manual of the ICP equipment. This was performed in order to enhance the accuracy of the measurements and to compare with the series measured without IS.

Extraction by means of hydrochloric acid (HCl). Duplicate mineral samples of 0.5 g (accuracy 5 decimals) were extracted by means of 5 ml HCl (supra). The series was heated to 50 ºC and agitated during one hour. The water got colder and the samples were diluted, filtered and frozen the next day.

In the same way as for the previous described extraction method some of the measurements were performed with IS.

Extraction by means of *AQUA REGIA* (75 % HCl + 25 % HNO_3). Mineral samples of 0,2 g (accuracy 5 decimals) were extracted by means of 5 ml aqua regia (HNO_3 25% + HCl 75%) on a heated (50 °C) water bath in duplicates except granite (single sample due to less reference material left). The solution was stirred every ten minutes during the first hour. Then the heat was turned off, and the extraction procedure ended next day. The solution was diluted and filtered prior to the measurements by means of ICP.

In the same way as for the previous described extraction method some of the measurements were performed with IS.

TABLE 3 The different extractions performed.

	Granite1	Granite 2	Granodiorite 1	Granodiorite 2	Basalt 1	Basalt 2	K-Feldspar 1	K-Feldspar 2	Refined silicon 1
NaOH 20 ºC	$A^{1/}$		A		A		A		A
NaOH 50 ºC	A		A		A		A		A
HNO3 20 ºC	A		A		A		A		A
HNO3 85 ºC	A		A		A		A		A
NaOH M 50 ºC	A		A		A		A		A
HNO3 M 50 ºC	A		A		A		A		A
NaOH+HNO3 50 ºC	*A*		*A*		*A*		*A*		*A*
NaOH M 50 ºC	A C	A C	A C	A C	A C	A C	A C	A C	
HCl M 50 ºC	A C	A C	A C	A C	A C	A C	A C	A C	
NaOH+HCl 50 ºC	*A C*	*A C*	*A C*	*A C*	*A C*	*A C*	*A C*	*A C*	
NaOH M 2*sp 50 ºC	A	A	A	A	A	A	A	A	
HCl M 2*sp 50 ºC	A	A	A	A	A	A	A	A	
*NaOH+HCl 2*sp* 50 ºC	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	
NaOH 50 ºC	B	B	B	B	B	B			
NaOH + HCl 50 ºC	B	B	B	B	B	B			
NaOH+HCl tot 50 ºC	B	B	B	B	B	B			
NaOH IS 50 ºC	B	B	B	B	B	B			
NaOH HCl IS 50 ºC	B	B	B	B	B	B			
NaOH + HCl IS tot 50 ºC	B	B	B	B	B	B			
HCl 50 ºC	A C	A C	A C	A C	A C	A C	A C	A C	
HCl 2*sp 50 ºC	A	A	A	A	A	A	A	A	
HCl 50 ºC	B	B	B	B	B	B			
HCl IS 50 ºC	B	B	B	B	B	B			
Aqua Regia 50 ºC	A C	A C	A C	A C	A C	A C			
Aqua regia IS 50 ºC	A C	A C	A C	A C	A C	A C			
Aqua regia 100 sp 50 ºC	A		A	A	A	A			
Aqua regia IS 100 sp 50 ºC	A		A	A	A	A			
Aqua regia 1000 sp 50 ºC	A		A	A	A	A			
Aqua regia IS 1000 sp 50 ºC	A		A	A	A	A			

italic = calculated tot

$A^{1/}$ = Heavy metals (Al 27, Cr 52, Fe 54, Mn 55, Ni 58, Co 59, Ni 60, Ni 61, Ni 62, Cu 65, Zn 66, Sr 88, Cd 114, Ba 138, Pb 208)
B = Precious metals (Sn 116, Sn 117, Sn 119, Sn 120, W 182, W 183, W184, W 186, Au 197)
C= Platinum metals (Rh 103, Pd 105, Pt 195)

Extraction yields

In a number of internal reports (See Appendix!) the measured values of the yield of the individual metals in relation to the different bedrock types and the extraction methods used are presented in various ways, i.e. the raw data in form of excel files. For information about a single metal, these internal reports are recommended.

The aim of the present project is to calculate the cost of sustainable production of metal concentrates from earth's crust (Steen & Borg, 2002), therefore the cumulative yield of a number of metals normally is more interesting than the yield of a single individual metal.

The investigated metals are placed in three different groups ("heavy metals"; "precious metals"; and "platinum metals"). The reason is that they might exhibit differences in yield in relation to leaching procedure to be used. Another reason is the great variation in the investigated metals abundance in the earth's crust. Especially the concentration of the platinum group metals is low in the investigated bedrock types. Because the measured values of the platinum group metals in the extraction solutions typically are close to the detection limit, other methods (or minerals to be used) might be preferred. This is the reason why the results of the extraction yields in this presentation of results are given as averages and median yields respectively for different groups of metals investigated.

When the results are presented below, mean yields are discussed.

Table 4. The efficiency of the different extraction methods used for the group "heavy metals". See table 3.

	Average yield (%)	Median yield (%)
Aqua Regia every two samples internal standard 50 ˚C	48.0	46.2
HCl diluted two times 50 ˚C	48.2	44.9
HCl 50 ˚C	46.1	42.5
NaOH + HNO_3 = total 50 ˚C	40.7	40.4
Total NaOH + HCL diluted 2 times 50 ˚C	39.7	39.6
HNO_3 after NaOH 50 ˚C	38.3	30.5
NaOH + HCL = total 50 ˚C	32.7	28.6
HNO_3 85 ˚C	30.2	25.3
HCl after NaOH diluted 2 times 50 ˚	26.0	17.8
HCl after NaOH 50 ˚C	24.8	16.4
HNO_3 20 ˚C	22.4	17.7
Aqua Regia Diluted 100 times, every two samples internal standard 50 ˚C	26.1	9.8
NaOH Diluted 2 times. 50 ˚C	14.4	9.0
NaOH 20 ˚C	5.8	4.2
NaOH 50 ˚C	5.9	3.1
Aqua Regia Diluted 1000 times, every two samples internal standard 50 ˚C	8.9	0.0

The results show (See Tables.4 to 6) that the yield was highest in the warm series. The influence on the individual species was varying, however. As an example, if the temperature was raised from 20 to 85 centigrade the mean yield for the group heavy metals was raised from 22.4 to 30.2 %.

As i shown in table 4 the average efficiency, calculated as percentage yield of heavy metals of the standard minerals is in the same order comparing *Aqua Regia* and hydrochloric acid at the same temperature (50 centigrade). The average yield is in the ranges 46 – 48 %, the median yield is a few percent less.

The yield at sodium hydroxide extraction was found to be dependent on temperature, but lower than 15%, See Tables 4 and 5!

As can be seen in table 4 (heavy metals) the *Aqua Regia* and Hydrochloric Acid methods are more efficient (46 – 48 %) than the methods, which started with a sodium hydroxide extraction, followed by acid leaching by hydrochloric and nitric acids respectively. The efficiency of the latter methods is in the ranges of approximately 30 to 40%. The efficiency of nitric acid is higher at higher temperature, but even at a temperature at 85 centigrade the yield is around 30 %. The reason why the yield of diluted nitric acid is much lower than of concentrated nitric acid is interpreted to be due to that the concentrations became very low, near detection limit.

For the group called "precious metals" (Table 5) the extraction by means of hydrochloric acid is the most efficient of the methods tested. The average yield is approximately 60 %.

Table 5. The efficiency of the different extraction methods used for the group "precious metals". See table 3

	Average yield (%)	Median yield (%)
HCl Every two samples internal standard. 50 ˚C.	60.7	66.0
NaOH+HCl=total Every two samples internal standard 50 ˚C.	46.3	48.8
HCl after NaOH Every two samples internal standard 50 ˚C.	42.9	46.2
NaOH Every two samples internal standard 50 ˚C.	4.3	3.1

As can be seen in Table 6, the average and median yield of the platinum group metals is very diverting compared to the other groups of metals. The Platinum group is presented in a chapter of it's own, see later.

When the efficiencies of the different extraction methods are compared it is obvious that extraction by means of hydrochloric acid can be recommended. From the point of view of sustainability the manufacturing of hydrochloric acid is attractive in that is fairly simple and straightforward (electrolysing of sea salt solutions).

The higher the temperature of the extraction process, the higher yield (see table 4). Because higher temperature requires more energy supply, 50 centigrades during the first hour was supposed to be a reasonable compromise.

In the present project it is recommended to use hydrochloric acid with heating to a temperature of 50 centigrades during the first hour.

The suggestion above agrees with the findings of the earlier presented methodological studies performed (Andersson, 1975 and Påhlsson & Qvarfort, pers. comm.).

The use of the hydrofluoric acid method is not regarded as a competitive method in the frames of the present project because the production methods of hydrofluoric acid, and also because of the precaution needed when handling hydrofluoric acid.

Platinum group metals

The great deviation between the average and the median yield of the platinum group metals (see Table 6) indicates that either the method used is not the optimal one for measurements of Pt-group metals, or that other bedrock types are to be considered as source material. Some comments may be made.

- The content of the investigated platinum group metals is low in the samples investigated. See Table 7. The extraction method used involves leaching of a finely ground mineral sample by a certain amount of acid. The solution is then somewhat diluted as a preparation for the ICP measurement to be performed. The accumulative effect is that the concentration of the platinum group metals in the solution to be analysed by ICP is very low, possible close to, or below, the detection-limit. This might make the measurements unreliable.
- The extracted samples (solutions) were frozen to hinder secondary reactions of the dissolved platinum, which could influence the measurements. Possibly, the strategy for treatment of the solutions prior to measurements has to be improved.
- One of the aims for the present project is to find a method suitable for extracting a number of metals simultaneously from the most common bedrock, as a way of sustainable production of metals. This strategy has to be modified in the case of the Pt-group metals. The content of the mentioned metals is very low in the samples analysed, and other bedrock types contain significantly more of the metals. See table 7!

Table 6. The efficiency of the different extraction methods used for the group “platinum metals”. See table 3.

	Average yield (%)	Median yield (%)
HCl 50 ˚C	30.4	0.5
NaOH + HCl = total 50 ˚C	23.0	0.0
HCl after NaOH 50 ˚C	22.2	0.0
Aqua Regia Every two samples internal standard 50 ˚C	1.5	0.0
NaOH 50 ˚C	0.8	0.0

According to Hägg (1969) the platinum group metals can be found as sulphides, arsenic minerals and pure metals in bedrock types containing a high degree of the mineral olivine $(Mg, Fe)_2SiO_4$, see e. g. Loberg (1993). Olivine can be found in varying degree in several basic or preferable ultra-basic bedrock types. Basic bedrock types are *e.g.*: basalt, diabase/dolerite and gabbro. Ultra-basic bedrock types are e.g. peridotite or dunite. *Cf e.g.* Loberg (1993) and table 7 below.

A survey was performed to see which kinds of minerals/bedrocks that contain platinum group metals. The result is shown in Table 7. The standard samples containing most platinum are USGS DNC-1 Dolerite and USGS W-1 Diabase. The highest concentrations of rhodium are found in sample USGS DTS-1 Dunite and USGS PCC-1 Periodotite, and of palladium in samples USGS DNC-1 Dolerite and USGS W-1 Diabase. Normally (in the scope of this project), dolerite and diabase are considered to be the same bedrock type.

Table 7. The content of the platinum group metals in a number of standard samples (See the above mentioned www addresses!). The samples investigated in the present project are marked with bold letters.

	Pt µg/g	Rh µg/g	Pd µg/g
CRPG BE-N Basalt	0,0008		0,0005
CRPG CHR-Pt Chromite	58 ± 2,6	4,7 ± 0,4	80,8 ± 5
CRPG MA-N Granite			0,0004
USGS AGV-1 Andesite	0,0011	< 0,0001	0,0022 ± 3
USGS BCR-1 Columbia River Basalt	**0,002**	**0,00023**	**< 0,01**
USGS BHVO-1 Hawaiian Basalt	0,0022	0,0002	3 ± 0,4
USGS BIR-1 Icelandic Basalt	0,0028	0,00035	0,0056
USGS DNC-1 Dolerite	***0,036***	0,00035	0,016
USGS DTS-1 Dunite	0,0031	0,00083	0,003
USGS G-1 Granite	0,0082	< 0,005	0,0019
USGS G-2 Granite	**0,0059**	**< 0,0001**	**0,00025**
USGS GSP-1 Granodiorite	**< 0,0005**	**< 0,0001**	**0,0012**
USGS MAG-1 Marine Mud	0,001	< 0,0001	0,0017
USGS PCC-1 Periodotite	0,008	0,0014	0,0054
USGS QLO-1 Quartz Latite (Dellenite)	< 0,001	< 0,0001	0,0001
USGS RGM-1 Rhyolite	< 0,001	< 0,0001	0,0002
USGS SCO-1 Cody Shale	< 0,001	< 0,0001	0,001
USGS SDC-1 Mica Shist	0,0011	< 0,0001	0,0011
USGS SGR-1 Green River Shale	0,003	< 0,0001	0,0052
USGS STM-1 Nepheline Syenite	< 0,001	< 0,0001	0,0004
USGS W-1 Diabase	***0,013***	< 0,003	0,014
USGS W-2 Diabase			0,011

The methods, which are recommended in this project, are designed to be used as reasonable “average” method suitable for a number of metals (Steen & Borg, 2002). But, for the platinum group metals another strategy is to be recommended.

- Instead of treatment of the most common bedrock types, basic or ultra basic bedrock types have to be chosen. Chromite is omitted, because it is too rare.
- It is reasonable to suggest acid leaching of these basic bedrock types, but parts of the treatment procedure might have to be somewhat changed.

Determination of the amount of hydrochloric acid consumed in the extraction procedure

To get the different extraction procedures to work well, an excess of acid in relation to crushed bedrock is needed. A tentative estimate of how much acid that was consumed during the different acid extraction procedures was performed by means of a titration procedure. The method used was titration by means of sodium hydroxide, to determine the amount of acid in the extraction solution before and after the extraction of rock samples. The method is rather crude, but it showed that the used up acid is in the order of two to five percent. The excess of acid is judged to be enough to leach the mineral samples, but a more accurate method to determine the used up acid in relation to the yield of different elements was needed.

The following method was finally chosen.

The filtered frozen solutions (no ground rock residues) from the hydrochloric extraction used for the measurements by means of ICP were used. Samples from duplicate extractions were used, like two zero samples to yield background values. These "zero" solutions were treated in the extraction procedure as the rest of the samples, but without ground rock samples.

Of the solution 5 ml (accuracy five digits, controlled pipette) were taken to erlenmeyer flasks and mildly evaporated. The samples was let to cool in a desiccator. The solid residue when the hydrochloric acid was evaporated was a mixture of metal-chlorides. The solid residues were dissolved in 2 ml 1M nitric acid and the beakers were treated five minutes in an ultrasound bath. The samples were then diluted to 50 ml by means of nanopuric water (18Mohm*cm^{-1}).

The method used for the determination of chloride was potentiometric autotitration (accuracy four digits) by means of 0.01 M silver nitrate ($AgNO_3$) prepared from ampoule. Five zero samples were used.

Table 8 The results of the determination of used up acid

Rock sample	Δm (g)	V1 (ml)	M1 (g)	Used up acid (%)	V10 (l/tonne)
P-feldspar 1	0.00052	0.388	0.000101	0.12024	11.88
P-feldspar 2	0.00046	0.371	9.48E-05	0.113052	11.27
Basalt 1	0.00581	6.230	0.002172	2.590144	252.4
Basalt 2	0.00569	6.258	0.002182	2.601982	257.7
Granodiorite 1	0.00367	3.663	0.001262	1.504857	147.6
Granodiorite 2	0.00436	4.402	0.001524	1.817295	179.8
Granite 1	0.00334	3.502	0.001205	1.436789	141.5
Granite 2	0.00341	3.195	0.001096	1.306994	129.3
Zero sample 1	0.00011	0.038	-2.3E-05	-0.02773	
Zero sample 2	-2E-05	0.041	-2.2E-05	-0.02647	

Δm (g) Weight of evaporated residue in beaker
V1 Volume used up 0.01M AgNO3 to the endpoint
M1 = Amount chloride in the sample (ml)
V10 = used up amount of hydrochloric acid (30%) per tonne rock sample

Grain sizes of the investigated standard materials

Introduction

The amount of energy needed to crush bedrock to fine particles is dependent on the final grain size and the individual minerals (see Steen & Borg 2002). Therefore, it is important for the purpose of the present project to know the grain size of the extracted mineral particles.

Grain sizes according to certificates

Flanagan (1967) describes the treatment of the silicate rock standards of U. S. Geological survey. Of these, the standards of basalt (BCR-1), granite (G-2), and granodiorite (GSP-1) are used in the present project. The rock samples were crushed and milled. The aim of Flanagan (*Ibid.*) was to prepare the samples fine enough so that at least 80 % (by weight) of each would pass a 200-mesh (~ 0.075 mm) screen. According to Flanagan (*Ibid.* Table 1) 98.5 % of G-2 (granite), 96.1 % of GSP-1 (granodiorite), and 99.3 % of BCR-1 (basalt) passed this screen. As can be seen from the same table almost the rest of the samples, which was coarser than 200 mesh (~0.075 mm) was finer than 170 mesh (~0.09 mm). For the granite sample 0.6 % of the material is coarser than ~0.09 mm, the figure for granodiorite is 1.4 %, and for basalt 0.1 %. The sieving method is based on the assumption that the grains are spherical.

Microscopy test of grain sizes

Sieving is only effective on material coarser than ~ 0.075 mm, the grain size of finer material is normally obtained by different sedimentation methods. These methods need more material than was available in the present project.

To study the grain sizes of the different standard materials a microscope with a camera was used. The diameter of several hundreds of particles in the photograph was measured in the computer.

Three to five different classes were defined, individually for each standard sample. The difference in the number of classes is due to that the spreading of grain sizes is different for the individual samples.

The density for a given mineral is expected to be uniform. Therefore it was possible to calculate the cumulative grain size curve (based on weight) from the diameter of the individual grains for each individual reference sample. In Table 9 the different median diameters are shown of the different standard minerals studied.

Table 9. Calculated median diameters of the different samples.

	Median diameter (mm)
Granite	0.14
Basalt	0.028
Granodiorite	0.070
Potassiumfeldspar	0.036
Silica	0.064

Laser ablation

One of the aims of the present project was to investigate whether the different metals are located near the surface of the silica crystals ore if they are randomly distributed inside the crystals. It is possible that different metals are located differently due to charge, atomic size etc.

The measurements on solid stones were performed by means of laser ablation MS. The laser beam was penetrating deeper and deeper in the solid crystal while gasifying the material. The intensity of the light emitted from the plasma was measured at various wavelengths on 20-22 different levels downwards into the crystal. Glass reference samples were used as background to recalculate the measured intensities to absolute concentrations.

Two measurement campaigns were performed.

In the first measurement campaign twelve different stones (different granites, gneiss, granodiorite, syenit, diabase, quarts, potassiumfeldspar, biotite, muscovite and basalt) were analysed. Because several bedrock types comprise several different minerals, totally 27 measurements by means of laser ablation MS were performed. In each measurement 20 levels into the crystal were measured. The concentrations of the following elements were calculated: Cr, Fe, Mn, Co, Ni, Cu, Zn, Sr, Rh, Pd, Ag, Cd, Sn, Ba, W, Pt, Au and Pb.

The result was difficult to interpret, the trends were not clear. One possible reason for this is that it was sometimes unclear if the beam (diameter 350 µm) was too coarse and if it was crossing over two different mineral grains located side by side. So the problem was to interpret if the recorded changes were due to different concentrations in relation to the depth in the silicate crystal or if it was a mixture of different mineral grains.

Another measurement campaign of 11 measurements of 7 stones was later performed. This time the diameter of the beam was reduced to 50 µm because of the problems mentioned earlier and 22 levels were measured. The intensities of the following elements were measured: Al, Cr, Fe, Mn, Ni, Co, Cu, Zn, Sr, Rh, Pd, Cd, Sn, Ba, Pt, Au, Pb

The second measurement campaign was performed with close optical controls, so the beam really was working inside the individual mineral grains. The crater in the mineral made by the laser beam was very thin this time (diameter 50 µm), to be compared with 350 µm in the first measurement campaign. If the depth of the crater is too deep in relation to the diameter, the measured intensity of the light emitted from the plasma is less reliable (Dr. Sébastien Rauch, WET Chalmers personal comm.). In this second measurement campaign with a small crater diameter (50 µm) the quotient between diameter and depth in the mineral might have become too low for reliable measurements in the later parts of the individual analyse.

Some material might then get stuck on the walls making the registration too low, and then suddenly it might be pushed upwards and increase the measured value. This could cause a false impression of a varying concentration with depth, and thus a false support to our hypothesis that many elements were concentrated to the crystal surfaces.

Therefore, the conclusion was that it was difficult to interpret the results of this part of the investigation and it is a rather weak support of our hypothesis.

Diagrams, photos and tables can be obtained electronically from Gunnar Ch Borg (see the heading for address!)

Overview of leaching efficiencies

To be able to get a cost efficient method to extract metals from common silicate bedrock types, a number of elements ought to be extracted simultaneously, not only one or two. Steen & Borg (2002) assumed that concentrations of 10 different metals were produced at the same time. This means, it is more important to find a method, which gives a high amount of a number of elements than to develop a method, which is designed for a certain metal.

It is possible to arrange the measured results in a number of different ways. You can choose between to interpret the yield as percentage of the content in the investigated minerals / bedrock types, or as gram per tonne material. See Tables 10 & 11 + the appendix. To make future investigations more convenient the primary data material is collected in several appendixes in a number of internal reports. These are listed in appendix 1.

The results of the present investigation are condensed in Tables 10 & 11. These tables are used as a part of the basis for the estimation of the cost of sustainable production of metal concentrates from earth's crust (Steen & Borg, 2002). Here the three bedrock types, granite, granodiorite and basalt are chosen, because they are internationally very abundantly (see e.g Wedepohl, 1995).

The two dominating extracted metals are aluminium and iron. These two metals are reasonable abundant on the earth, so most probably bedrock types are chosen which can yield much of the other metals. As presented by Table 11, the difference in yield as all elements measured except aluminium and iron, as yield in gram per tonne bedrock is not very great for the three bedrock types thoroughly investigated. The ranges are between 550 to app. 630.

Table 10. The yield of some elements both as % and as g/tonne bedrock extracted by means of hydrochloric acid

	GRANITE			**GRANODIORITE**			**BASALT**		
	Content g/tonne	Mean yield Granite (%)	Yield g/tonne granite	Content g/tonne granod.	Mean yield Grano (%)	Yield g/tonne granod.	Content g/tonne basalt	Mean yield Basalt (%)	Yield g/tonne basalt
Al 27	81496.8	9.9	8076.0	80703.0	14.5	**11728.1**	72182.3	5.6	*4066.4*
Cr 52	7.0	100.8	7.1	12.5	62.0	**7.7**	17.6	10.2	*1.8*
Fe 54	18824.5	86.1	*16201.8*	30335.0	80.1	24295.4	94139.0	44.6	**42006.5**
Mn 55	260.0	90.9	*236.3*	331.0	81.8	270.8	1406.0	27.8	**390.7**
Co 59	5.5	73.3	*4.0*	6.4	76.9	4.9	38.0	35.5	**13.5**
Ni 60	5.1	44.9	*2.3*	12.5	51.0	**6.4**	15.8	24.2	3.8
Cu 65	11.7	79.9	*9.3*	33.3	80.2	**26.7**	18.4	(126.6)	23.3
Zn 66	85.0	90.5	76.9	98.0	85.1	**83.4**	120.0	62.9	*75.5*
Sr 88	479.0	5.5	**26.2**	233.0	8.5	19.8	330.0	5.5	*18.2*
Cd 114	0.0	22.5	*0.009*	0.1	50.0	0.030	0.1	33.7	**0.040**
Ba 138	1870.0	14.0	**261.7**	1300.0	11.3	147.3	675.0	2.7	*17.9*
Pb 208	31.2	22.1	6.9	51.3	65.3	**33.5**	17.6	38.4	*6.8*
Sn 117	1.5	76.2	*1.1*	6.3	72.9	**4.6**	2.6	58.3	1.5
W 186	0.2	27.6	*0.06*	0.3	22.3	0.07	0.4	63.4	**0.3**

Bold = highest values Normal = intermediate values *In italics = lowest values*

Table 11. The total yield / tonne of some metals and the consumption of hydrochloric acid

	GRANITE		**GRANO-DIORITE**		**BASALT**	
	Yield g/tonne	Granite	Yield g/tonne	Grano-diorite	Yield g/tonne	Basalt
Consumption (litres 30% HCl / tonne treated bedrock)		*135.0*		164.0		**255.0**
Yield (all elements) (g/tonne)	*24909.7*		36628.7		**46626.2**	
Yield g (all elements) / litre consumed 30% HCl		184.5		**223.3**		*182.8*
Yield g (all elements except Al) (g/tonne)	*16833.8*		24900.6		**42559.6**	
Yield g (all elements except Al) / litre consumed 30% HCl		*124.7*		151.8		**166.9**
Yield g (all elements except Fe) (g/tonne)	8707.9		**12333.3**		*4619.7*	
Yield g (all elements except Fe / litre consumed 30% HCl		64.5		**75.2**		*18.1*
Yield g (all elements except Fe and Al) (g/tonne)	**632.0**		605.2		*553.3*	
Yield g (all elements except Fe and Al) / litre consumed 30% HCl		**4.7**		3.7		*2.2*

Bold = highest values Normal = intermediate values *In italics = lowest values*

Discussion

During the crystallisation of e.g. a silicate it is reasonable that elements, which can substitute for the central atoms, might be rather evenly distributed in the formed crystal. This could make the yield (in percent) low when leached by the methods used in this project. In the opposite, elements not fitting in the crystal structure are likely to be transported outwards nearer the surface during the crystallisation process. These elements could be expected to give high yields (in percent) when leached by the actual methods. The same is valid if the elements are evenly distributed within the crystal structure or concentrated more or less at the crystal structure of other reason than discussed above. The aim of the measurements by means of laser ablation MS was to confirm this, but as explained earlier, the results were difficult to interpret.

As seen in Table 10, the yield (in percent) of most of the elements investigated is rather high, with three very obvious exceptions, aluminium, strontium and barium.

The yield in percent of aluminium is relatively low (5 to 15 %) in relation to most of the other metals when the acid methods were used. According to Sharpe (1984 p. 148) the ionic radius of Al^{3+} is 0.53 Å (for sixfold co-ordination) and (theoretically calculated) Si^{4+} is 0.50 Å. Brady and Weil (1999 p. 314-15) describe the isomorphous substitution of Al^{3+} for Si^{4+} in silicate clays. It is reasonable to assume that the isomorhous substitution of Al^{3+} for Si^{4+} makes the Al^{3+} ions to be evenly distributed in the whole of the silica crystals, and this would explain the low yield (in percent) because of the extraction methods used. Aluminium is the third most abundant metal in the earth's crust (Mason & Moore, 1982) after oxygen and silica, therefore the development of methods to process aluminium in this context is less prioritised.

The other two elements showing low yield (in percent) are the two alkali-earth metals strontium and barium. All bedrock types investigated in the present project comprise the alkali-earth metals calcium and magnesium in different minerals;b see the description of the standard reference minerals used. A possible explanation for the low yield (in percent) of these two elements could be isomorphous substitution of Sr^{2+} and Ba^{2+} for Mg^{2+} and Ca^{2+}, even if the ionic radii are differently, they belong to the same group in the periodic table and the structures are similar. The ionic radii for sixfold co-ordination of a number of elements is presented in Sharpe (1984 Table 6.2), and a figure of ion radii in relation to different groups in the periodic table are presented in Hägg (1963 Fig. 5.5).

According to the certificates of the reference samples about 95% or more of the grain size of the particles are less than 200 mesh (~75 µm). By means of the laser-ablation MS equipment some photos of the solid minerals were taken, which are electronically available from Dr. Gunnar Ch Borg. On these pictures of the solid minerals (same types as in the ground reference samples) the fissures and internal structures of the silicate crystals can be seen. It is reasonable to think that the crystals most easily will be broken down at the internal fissures and structures, when grounded to still smaller particles this will be more energy consuming. As can be seen on the photos the grinding procedure used to manufacture the “powder” of the reference samples creates grains of the same magnitude as the optimal procedure because of crystal internal fissures and structures was expected to do.

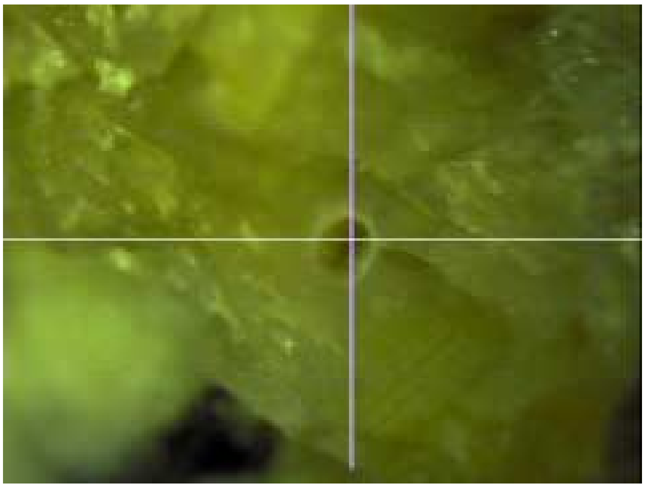

Figure 1. Photo taken during measurement campaign by means of laser ablation MS. The mineral is potassium feldspar, and the diameter of the crater created by means of the laser beam is 0.35 mm.

Conclusions

It was not possible to verify the hypothesis that the atoms of a metals that were efficiently extracted are concentrated at the surfaces of the crystals of the minerals of the investigated bedrock, but on the other hand there was no contradiction.

Because the results of the measurements on solid samples by means of laser ablation MS were difficult to interpret, the conclusions were drawn from the results of the leaching experiments.

- The comparison of the yield of metals in relation to different leaching methods indicates that the chosen method (leaching by means of hydrochloric acid) is reasonable from the efficiency point of view (high yield) as well as in relation to sustainability (electrolysing of sea salt solutions). The consumption of hydrochloric acid per tonne treated bedrock is calculated (see Table 11), and not higher than the use might be considered as “reasonable” sustainable.

- The amount of energy needed to crush bedrock to fine particles is dependent on the final grain size and the individual minerals (see Steen & Borg 2002). The grain sizes used in the present project (see Table 9) seem to be realistic when compared to the yield. It is not believed that further use of energy is needed to grind the particles to achieve even finer grain sizes in order to increase he yield of metals.

- The results also might indicate that the majority of the atoms of the different metals investigated are more or less concentrated at the surface of the crystals, because of the high yield (in percent) of many of the metals without dissolving the mineral particles.

- Some exceptions from the normal trend were found. Acid leaching leaches aluminium to a rather low degree (in percent). Other (basic) methods are far more efficient, but because aluminium is an abundant metal in the earth's crust, methods for successful leaching of the other metals concerned are preferred.

- The yield (in percent) of some alkali-earth metals was low.

- The platinum group metals exist in very low concentrations in "average" bedrock. In this case it is recommended to use "semi ores", i.e. to search for certain basic or ultra basic bedrock types containing the mineral olivine.

- An important result is that the high yield (in percent) of the majority of the metals investigated indicates that the proposed method for the first step to manufacture metal concentrates is reasonable (see Steen & Borg, 2002). This method comprises grinding of solid minerals and thereafter the use of the suggested acid leaching method. The suggested leaching method consumes hydrochloric acid, from 135 (granite) to app. 250 l 30% HCl per tonne treated bedrock. (basalt). As motivated in Steen & Borg (2002) the use of hydrochloric acid can be assumed to be (rather) sustainable.

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Literature review

A brief preliminary literature survey was performed. The following list is to great extent taken from the reference list of Bland & Rolls (1998) with some other additions as well. The aim to publish the list here is to help the readers who want to be introduced in this field. The book of Bland & Rolls (1998) is recommended reading.

Andersson, A. 1975. Relative Efficiency of Nine Different Soil Extractants. Swedish J Agric. Res. 5:125 – 135.

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Berner, R.A. 1978. Rate control of mineral dissolution under earth surface conditions. American Journal of Science. 278:1235-1252.

Bland & Rolls: 1998. Weathering An introduction to the scientific principles. 271 p.

Brewer, R. 1964. Mineral stability and weathering. In Fabric and mineral analysis of soils. Chapter 5. This classic reference is still helpful as a survey of some of the earlier ideas about mineral stability and the measurement of weathering intensity.

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Bustin, R.M. & Mathews, W.H. 1979. Selective weathering of granitic clasts. Canadian Journal of Earth Sciences 16, 215-223.

Colman, S.M. and Dethier, D.P. 1986. An overview of rates of chemical weathering. In Colman, SM and Dethier (Eds.) Rates of chemical weathering of rocks and minerals. 1-18. The influence of weathering fluids and the nature of reactions on weathering rates, and the measurement of rates by mineral, rock and water-chemistry studies.

Deer, W.A., Howie, R.A. and Zussman, J. 192. An introduction to the rock forming minerals. 2nd edn.

Drever, J.L. 1994. The effect of land plants on weathering rates of silicate minerals. Geochimica et Cosmochimica Acta, 58. 2325-2332.

Eckhardt, F.E.W. 1985. Solubilization, transport, and deposition of mineral cations by micro-organisms – efficient rock weathering agents. In Drever (ed.) The chemistry of weathering. P. 161-173. Reviews the contributipn of bacteria, algae, fungi and lichens to weathering processes

Faure, G 1991. Principles and applications of inorganic geochemistry. This is a good examp,e of a geochemical text in which various aspects are covered, often at an advanced level.

Fung, P.C., Bird, N.S., McIntyre, G.W., and Sanipelli, G.G. 1980. Aspects of feldspar weathering. Nuclear technlogy, 51:188-196.

Garrels, R.M. and Howard, P. 1957. Reaction of feldspar and mica with water at low temperatures and pressures. In 6th National Conference on Clay and Clay Minerals, pages 68-88. Pergamon Press, Oxford.

Greenwood. N.N. and Earnshaw, A. 1997. Chemistry of the elements, 2nd edn. (This textbook contains a clear and comprehensive description of the structure of the silicate minerals.)

Hall, K and Otte W 1990. A note on biological weathering of nunataks of the Juneau Icefield, Alaska. Permafrost and Periglacial Processes 1, 189-96. A discussion of the ways in which algae may break down granitic rocks.

Hall, R.D. and Martin, R.E. 1986. The etching of hornblende in the matrix of alpine tills and periglacial deposits. In S. Coleman and D. Dethier (Eds.) Rates of chemical weathering of rocks and minerals, pages 101-127. Academy Press

Holdren, G.R. and Speyer, P.M. 1986. Stochiometry of alkali feldspar dissolution at room temperature and various pH values. In S. Coleman and D. Dethier (Eds.) Rates of chemical weathering of rocks and minerals, pages 61-81. Academy Press

Huang, W.H. and Kiang, W.C. 1972. Laboratory dissolution of plagioclase feldspars in water and organic acids at room temperature. American Mineralogist, 57: 1849-1859.

Krauskopf, K.B. 1967. Introduction to Geochemistry. McGraw-Hill Inc. New York, 721 pp.

Lundegårdh, P.H. & Laufeld, S. 1984. Norstedts stora stenbok Mineral-bergarter-fossil. 376 p. Norstedts, Stockholm.

Lundström, U. 1990. Laboratory and lysimeter studies of chemical weathering. Phil. Trans. R. Soc. Lond. A

Lundström, U and Öhman, L.O. 1990. Dissolution of feldspars in the presence of natural organic solutes. Journal of Soil Science, 41

McFarlane, MJ and Bowden, JB 1992. Mobilisation of aluminium in the weathering profiles of the African surface in Malawi. Earth Surface Processes and Landforms 17: 789-805. (Concerning iron-rich laterites, aluminium and silica).

Martini, LP and Chesworth, WP (Eds.) 1992. Weathering, soils and paleosols. A most useful book, containing chapters on alteration products etc. and the concentration of metals by weathering.

Nickel, E. 1973. Experimental dissolution of light and heavy minerals in comparison with weathering and intrastitial solution. Contributions in Sedimentology 1, 1-68.

Ollier, C. 1984. Weathering. 2nd edn. This classical book contains a short description of chemical weathering processes.

Olsson, M and Melkerud, P.-A. 1991. Determination of weathering rates based on geochemical properties of the soil. Geol. Survey of Finland, Special Paper no 9.

Rosén, K (Editor): 1991. Chemical weathering under field conditions. Report from a Nordic seminar, 27-28 September 1990, Wik, Uppsala. Reports in Forest Ecology and Forest Soils. Department of Forest Soils Swedish University of Agricultural Sciences. 185 p. Report 63.

Sverdrup,H.U. 1990. The kinetics of base cation release due to chemical weathering. Lund University Press, 246 pp.

Swoboda-Colberg, NG and Drever, J. 1993. Mineral dissolution rates in plot-scale field and laboratorie experiments. Chemical Geology 105:51-69. Shows experimentally that dissolution rates in the laboratory are higher than those in field. (se weathering sid 196)

Troedsson & Nykvist. 1973. Marklära och markvård. Almqvist & Wiksell, Stockholm. 402.

Wasklewics 1994. Importance of environment on the order of mineral weathering in oliving (olivine?) basalts, Hawaii. Earth Surface Processes and Landforms 19, 715-34. Mineral susceptibility to weathering may vary with the nature of the biochemical environment.

Webster, JG. 1986. The solubility of gold and silver in the system Au-Ag-S-O_2-H_2O at 25° and 1 atm. Geochimica et Cosmochimica Acta 50, 1837-45. This paper develops the view that the solubility of gold (and silver) in other than acid solutions may be due to complex formation by sulphur-bearing ligands. Precipitation of gold occurs when the combined gold-silver complex breaks down.

Wells, A.F. 1984. Structural inorganic chemistry, 5th edition. This large reference book (over 1000 pages) is an excellent source book which provides a wealth of structural data for solid compounds).

Yatsu, E. 1988. The nature of weathering. An introduction.

Appendix 1 List of internal reports (excel files).

These internal reports (excel files) can be obtained from Dr. Gunnar Ch Borg, address, see the title page! Some diagrams based on the Laser-ablation MS measurements are also electronically available, like some photos.

Internal report 2001:12_1

In this internal report the different measurements, *i.e.* the yield (%) of the different elements versus the different extraction methods are collected. It is the isotopes, which are measured by the ICP method. The yield is then calculated as percent of the content of investigated standard samples.

Due to interference and other disturbances the measurements of the different isotopes of the same element can be differently reliable. A critical examination has been performed, and the apparent faulty results have been omitted. This internal report shows the not omitted values.

Internal report 2001:12_2

Internal report 2001:12_2 is based on the same information as 2001:12_1. The highest value of each isotope (yield in %) investigated is marked grey, and some of the highest values are given, and the rest of the values are omitted. This makes it easier to see the most efficient combinations.

Internal report 2001:12_3

In Internal report 2001:12_3 the same values as in Internal report 2001:12_1 are sorted after mineral/bedrock type. So it is possible to study which extraction method which is most efficient (yield in %) for a certain element and standard sample.

Internal report 2001:12_4

The same values as in Internal report 2001:12_3, but in the same way as in Internal report 2001:12_2 only the highest values are given.

Internal report 2001:12_5

The content (g/tonne) of different elements of the standard samples used.

Internal report 2001:12_6

The same values as in Internal report 2001:12_1, but calculated as yield (g/tonne) standard sample instead of yield (%). The values are organised after the different standard samples.

Internal report 2001:12_7

The same as Internal report 2001:12_6, but only the highest values are presented.