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**The analytical methods and the precision of the element
determinations used in the regional bedrock geochemistry
in the Tampere–Hämeenlinna area, southern Finland**

by Harry Sandström



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THE ANALYTICAL METHODS AND THE PRECISION OF THE
ELEMENT DETERMINATIONS USED IN THE REGIONAL BEDROCK
GEOCHEMISTRY IN THE TAMPERE-HÄMEENLINNA AREA,
SOUTHWESTERN FINLAND

by

HARRY SANDSTRÖM

with 11 figures and 5 tables

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The analytical methods applied in a pilot project investigating the regional geochemistry of bedrock are described. From comparison of duplicate samples, the sampling, analytical and system precisions are estimated for every element and every method. On the basis of the accuracy and precision data, an analytical and quality control scheme is proposed for the final project phase. It is recommended that the XRF technique relying on pressed pellets and a fundamental parameter method should be adopted as the core technique. However, lanthanoids, U and Th should be analysed by ICP-MS technique after acid digestion and fusion. Because of the better sensitivity, aqua regia leach (+/- mercury co-precipitation) followed by GAAS determination is recommended for precious (Au, Ag, Pd) and semi-metals (As, Bi, Sb, Se), even though this method is based on partial leach.

Key words (GeoRef Thesaurus, AGI): geochemical surveys, bedrock, sampling, chemical analysis, methods, accuracy, precision, quality control, Tampere, Hämeenlinna, Finland

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PREFACE

The bedrock of Finland, which is mainly Precambrian in age, is on average covered by some 7 metres of Quaternary sediments, such that only 3 % of the surface area is exposed. Because till, the most abundant material in the overburden, was derived from bedrock it generally corresponds compositionally to bedrock, though because of mixing and transport, till analysis only provides an overall view. On the other hand, the degree of exposure makes representative sampling of bedrock a real challenge.

A rock geochemistry research program was established in 1991 by the geochemistry department of Geological Survey of Finland. The final decision to start the research program was preceded by intensive discussions on the need, on the content, and on the methods of the program throughout most of the whole 1980's. Essential support to the program was given by Prof. G. Govett in his reports in 1986 and 1988, when he was evaluating the scientific achievements and role of the geochemistry department. The rock geochemistry program started and took shape rapidly following his second evaluation report. Raimo Lahtinen made the first preliminary project proposal in 1988, and a working group consisting of Pekka Lestinen (chairman), R. Lahtinen and Esko Korkiakoski was established in the department in order to prepare a plan for the whole research program. Their proposal was finalized already by the end of 1988. The essential content of this proposal was a pilot study project for the years 1989–1990. Because this kind of research program was quite unique even from an

international viewpoint, it was natural to commence with a pilot study more thorough than usual. These publications were collected from the results of the pilot study, processing the data, and their practical applications. The research program began very soon after the results of pilot study were available, and the field work phase of the research program has already been completed.

The main emphasis of the pilot phase was to study the representativeness of sampling, selecting the correct sampling grid, determining the amount of samples needed, and selecting the analytical methods. All these more or less technical aspects were reported in an internal report in 1991.

One of the main principles of the rock geochemistry research program has been the use of the most modern analytical techniques, which make possible, in addition to ordinary major element analysis the obtaining of high quality data for minor and trace elements. In addition to geochemical data, petrophysical parameters of the samples are determined. The public domain data bank covering the whole country, which will be available on completion of the program, thus offers an exceptionally broad and high quality source of data for application and interpretation in bedrock geochemistry studies.

The aim of the rock research program was determined 'to collect geochemical data concentrated in trace elements from the area of the whole country, to produce background data for interpretations of regional till geochemistry data, to classify the rock types, and to clarify the metallogeny of the bedrock.

Geochemical changes pertaining to the crustal evolution will be studied, too'.

These issues of the GSF Bulletin are concerned with application of the data and provide examples of potential ways of using the data. Recently it has also been realized that the data are valuable in other quite unforeseen applications, such as in evaluation of water

quality in drilled wells. The final results of the research program are planned to be published as soon as possible for the benefit not only of researchers in Finland but also in other countries interested in problems of Archean and Proterozoic bedrock as well as for those studying regional health and environmental problems.

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Reijo Salminen

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INTRODUCTION

The Geological Survey of Finland has launched a regional Rock Geochemistry Research Project (RGRP) which eventually will cover the whole country. Together with the existing regional geochemical data for till, the regional geochemical data for bedrock, based on systematic sampling, will form an invaluable geochemical data bank of the Finnish bedrock and overburden. The analytical scheme proposed for the Rock Geochemistry Research Project is comprehensive, covering the major components as well as about 40 minor and trace elements. It is estimated that the sample pretreatment and analytical costs will make up about 30% of the total costs of the project. Because of the unique nature of the project, special attention must be paid to the quality assurance of the whole data acqui-

sition process, including sampling, sample pretreatment and analysis. Because the project is scheduled to run for nine years (1991–1999) and will utilize analytical methods reaching sub ppb concentration levels, and because even small deviations in background levels may influence the overall geochemical conclusions, the control of precision and drift is more important than accuracy. For this reason, a quality control system has been tailor-designed for the project with special emphasis paid to precision and drift control both within batches and between batches. In order to test and optimize the proposed sampling method, the data acquisition, and the methods of analysis and interpretation, a pilot project was implemented in the Tampere–Hämeenlinna area.

STUDY AREA AND SAMPLING STRATEGY

The study area is situated in southern Finland, in the central part of the Fennoscandian shield. The region lies entirely within the Svecofennian domain (see Figure 1). This area was chosen for the pilot study because 1:100 000 scale bedrock and low altitude aeromagnetic maps are available for the area. Added to this, considerable geochemical data are available on the overburden, and some interesting base and precious metal anomalies have been indicated. The geology of the target area is described by Lahtinen (1996). The study area covers approximately 9600 km² and the total number of sampling sites is 358.

The sampling plan was based on the existing 1:100 000 bedrock maps, where the rock

types were divided into main groups of granitoids, mafic plutonics, felsic volcanics and gneisses, mafic volcanics and amphibolites, sedimentary rocks and "other" including all other rock types (e.g. metasomatic rocks). The occurrence of these rock types was calculated in 100 km² squares as percentages. If the areal distribution exceeded 5% one sample was taken, and if it exceeded 20% for volcanics and mafic plutonics or 50% for granitoids and sedimentary rocks, two samples were taken. The sampling sites were chosen to include all the main rock types and were as evenly distributed as possible in one 1:100 000 map sheet. A more detailed description of the sampling strategy is presented by Lahtinen (1996).

From each site, four subsamples were collected with a small-scale percussion drill (sample diameter 2.5 cm and length 15–20 cm) or occasionally with a hammer instead. The actual sampling area varied from 10-cm-wide turbidite beds to approximately 2 m² for homogeneous granites. A composite sampling strategy was used for <5 cm veined migmatites. In all cases, the visible weathered cover of the samples was removed. The four subsamples were combined into a single sample in the laboratory for analysis. For granitoid samples, a total volume of approximately 300 cm³ was equivalent to 900 g.

To control the representativeness of the collected sample for the particular rock type, on average every tenth sampling site was sam-

pled in duplicate. The duplicate sample, subsequently referred to as the duplicate outcrop sample, was taken from the same outcrop, about 1–2 metres from the original sample. Again, each sample comprised four subsamples. The distance between the original and duplicate samples was chosen so as to be less than the location accuracy in the field. The duplicate outcrop sample was selected so that it represented the same rock type as the original sample. Veins, inclusions and aggregates were avoided as far as possible. As a control on the homogeneity of the whole geological formation, in about 40 cases, another duplicate sample was taken from an outcrop of similar lithology about 200–1000 m away. These samples are subsequently referred to as

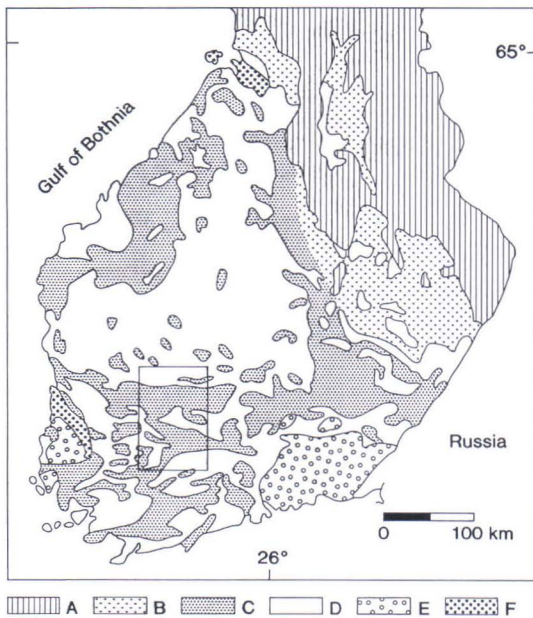


Fig. 1. The simplified geological map of southern Finland after Simonen (1980). The rectangle masks the study area. A. Archaean rocks; B. Karelian schists; C. Svecofennian schists, gneisses and migmatites; D. Svecofennian plutonic rocks; E. rapakivi granites; F. Jotnian sedimentary rocks.

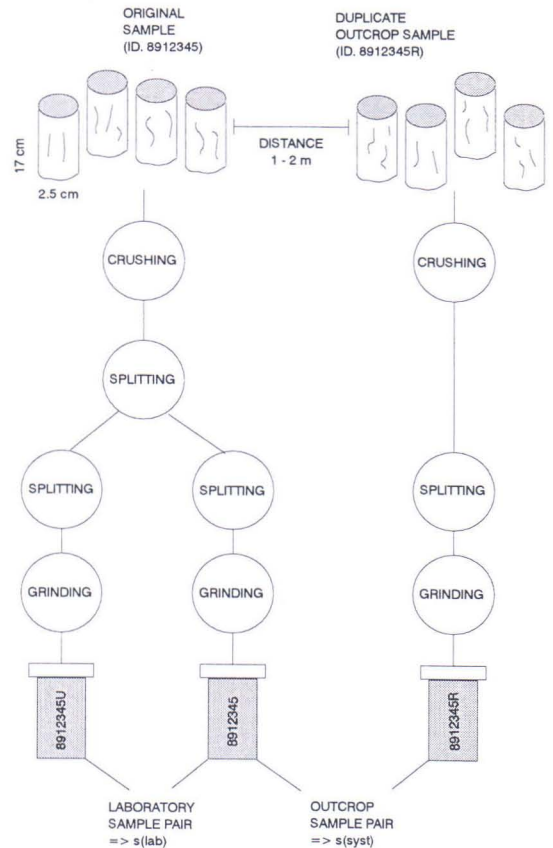


Fig. 2. Scheme showing generation of the duplicate samples.

duplicate formation samples. The analytical results for these duplicate outcrop and formation samples were used in evaluating the sam-

pling precision and formation homogeneity, as described below (see the section "Analytical and sampling precision" and Fig. 2).

METHODS AND INSTRUMENTATION

Sample pretreatment

The following equipment was used for sample pretreatment in the laboratory:

- Jaw crusher, Retsch BK1, with iron-manganese plates
- Riffle splitter, 12 pcs of 2 cm riffles made of stainless steel
- Vibrating mill, Herzog HSM 100P, with carbon steel grinding vessel
- Hydraulic presser, Herzog HTP40

The sample was crushed to <5 mm with the jaw crusher. With the riffle splitter, about 200 g of the crushed sample was separated and

ground in a carbon steel grinding vessel in a vibrating disc mill, to grain size <60 µm. A carbon steel grinding vessel was chosen to avoid the cobalt and tungsten contamination likely with a tungsten carbide grinding vessel. The pulverized sample was stored for analysis in a 60-ml plastic tube.

Duplicate laboratory samples were prepared for the laboratory quality control. After crushing, the original samples of the duplicate outcrop sample pairs were split with a riffle splitter into two portions. The split portions were submitted to the same pretreatment and analytical process as all other samples (see section "Analytical and sampling precision" and Fig. 2).

Chemical analysis

The instrumentation and short descriptions of the methods used at the GSF are presented below. Acid digestion followed by analysis by inductively coupled plasma atomic emission (ICP-AES) method was included in the programme to provide reference information for the existing till geochemical data obtained by aqua regia digestion method. Graphite furnace atomic absorption (GAAS) methods based on partial leach, were used for precious and semi-metals and some other elements because of the superior sensitivity. Flame atomic absorption (FAAS) determination of iron was included when it was found that the carbon steel grinding vessel used in the X-ray fluorescence (XRF) method caused significant iron con-

tamination (see section "Analytical accuracy" below). Instrumental neutron activation analysis (INAA) was subcontracted to the Technical Research Centre of Finland (Rosenberg et al. 1982). Commercial laboratory services (X-Ray Laboratories Ltd) were also used for elements not routinely determined at the GSF.

XRF analysis

The powdered sample (7 g, approx. <60 µm) was mixed with 210 mg binder wax (Hoechst-Wachs C) and ground in a high frequency vibrating mill (1500 r/min) in a hardened carbon steel vessel for two and a half minutes (Note! The original method involves

a tungsten carbide grinding vessel in order to obtain fine powder, $<10\ \mu\text{m}$). The powder was pressed on a wax base at 20 tonnes pressure for 20 seconds. The intensities of the characteristic X-ray lines were measured with a sequential XRF instrument and concentrations were calculated with a fundamental parameter method, RRFPO (Ala-Vainio 1986). A Philips PW1480 sequential wavelength dispersive spectrometer was used, with a 100kW generator, side window 3 kW Rh-tube, and PX-1, PE, GE-C (curved), LIF200, and LIF220 crystals.

GAAS determination of Au, Pd, Te

The pulverized sample (1 g) was digested with aqua regia at room temperature overnight, and co-precipitated with mercury, in the presence of SnCl_2 as reducing agent. The precipitate was dissolved in aqua regia and diluted to two millilitres, and elements were determined by graphite furnace atomic absorption spectrometry (GAAS). A Perkin Elmer PE3030 instrument with Zeeman background corrector was used to determine Au and Te, and a Perkin Elmer PE2280 instrument was employed for Pd. A detailed description of the method is presented by Kontas et al. (1990).

GAAS determination of As, Ag, Bi, Sb, Se

The sample (0.5 g) was digested for one hour with aqua regia at 90°C , diluted to 15 ml and analysed for As and Ag by GAAS. For Se, Bi and Sb determination the sample was then subjected to reducing co-precipitation with mercury, with NaBH_4 as reducing agent, and the precipitate was dissolved in aqua regia. GAAS determinations were carried out with a Perkin Elmer PE3030 instrument with Zeeman background corrector. The described procedure is a modification of the method reported by Niskavaara et al. (1990). The reducing agent in the original method, SnCl_2 ,

was replaced by NaBH_4 to ensure the coprecipitation of Sb and Bi (Niskavaara et al. 1992)

ICP-AES analysis

The powdered sample (150 mg) was digested in a glass test tube with 3 ml aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) for one hour at 90°C . It was then diluted to 15 ml. ICP-AES determinations were made with a Jarrell Ash Atomcomp Series 8000 instrument with 34 fixed element channels.

FAAS determination of Fe

The powdered sample (500 mg) was digested overnight in a teflon beaker with 20 ml aqua regia, 20 ml hydrofluoric acid and 5 ml perchloric acid and then evaporated on a hot plate to dryness. The residue was dissolved in hydrochloric-nitric acid mixture (0.5 and 10 ml, respectively) and diluted to 50 ml.

Determinations of C and F

Total carbon was determined with a Leco CR12 carbon analyser by igniting the sample (0.5 g) at 1370°C in oxygen flow. Carbon was determined as CO_2 using an infrared detector. Calibration was based on natural reference samples.

For fluoride determination the sample (100 mg) was fused with 2 g of sodium hydroxide in a nickel crucible in a muffle furnace (600°C) for 20 minutes, with the melt mixed after ten minutes. Fifty ml of deionized water was poured into the crucible. The mixture was warmed at 70°C for one hour and then let stand overnight at room temperature. It was filtered and diluted to 100 ml, and the fluoride was measured with an ion selective electrode, with TISAB III buffer used to adjust the ionic strength of the sample solutions.

ANALYTICAL ACCURACY

The total accuracy study is not relevant for the ICP-AES and GAAS determinations, which were based on partial leach. However, international reference samples introduced by

Table 1. XRF determination of elements (wt%) in international reference samples SY-2, SY-3, Br and MA-N.

Component	SY-2		SY-3		Br		MA-N	
	XRF	reference	XRF	reference	XRF	reference	XRF	reference
Na ₂ O	4.42	4.31	4.19	4.12	3.17	3.05	5.90	5.84
MgO	2.43	2.69	2.42	2.67	13.35	13.28	0.02	0.04
Al ₂ O ₃	12.19	12.04	11.81	11.75	10.04	10.20	17.72	17.62
SiO ₂	58.67	60.05	59.11	59.62	37.59	38.20	66.41	66.6
P ₂ O ₅	0.46	0.43	0.57	0.54	1.10	1.04	1.53	1.39
S	0.019	0.016	0.055	0.051	0.039	0.039	0.01	0.01
Cl	0.021	0.140	0.019	0.015	0.040	0.035	0.021	0.014
K ₂ O	4.43	4.44	4.25	4.23	1.37	1.4	3.18	3.18
CaO	7.89	7.96	8.32	8.26	13.57	13.8	0.59	0.59
TiO ₂	0.13	0.14	0.14	0.15	2.62	2.6	0.01	0.01
V	0.0052	0.005	0.0056	0.005	0.0337	0.0235	0.0006	0.00046
Cr	0.0038	0.0009	0.0036	0.0011	0.0366	0.038	0.0026	0.0003
MnO	0.31	0.32	0.33	0.32	0.20	0.20	0.04	0.04
Fe ₂ O ₃	6.05	6.31	6.40	6.49	12.65	12.88	0.56	0.47
Ni	0.0014	0.00099	0.0010	0.0011	0.0269	0.026	0.0010	0.0003
Cu	0.0000	0.00052	0.0011	0.0017	0.0077	0.0072	0.0133	0.014
Zn	0.0266	0.0248	0.0267	0.0244	0.0176	0.016	0.0246	0.022
Rb	0.0207	0.0217	0.0198	0.0206	0.0043	0.0047	0.3518	0.36
Sr	0.0274	0.0271	0.0308	0.0302	0.1367	0.132	0.0088	0.0084
Y	0.0125	0.0128	0.0725	0.0718	0.0030	0.003	0.0043	0.0001
Zr	0.0316	0.028	0.0367	0.032	0.0304	0.025	0.0026	0.0027
Nb	0.0028	0.0029	0.0164	0.0148	0.0117	0.0098	0.0227	0.0173
Ba	0.0441	0.046	0.0432	0.045	0.1005	0.105	0.0042	0.0042
La	0.0074	0.0075	0.1283	0.134	0.0086	0.0082	0.0000	0.00004
Ce	0.0163	0.0175	0.2240	0.223	0.0152	0.0151	0.0001	-
Pb	0.0118	0.0085	0.0183	0.0133	0.0022	0.0008	0.0039	0.0029
Th	0.0339	0.0379	0.0877	0.1003	0.0011	0.0011	0.0001	0.0001

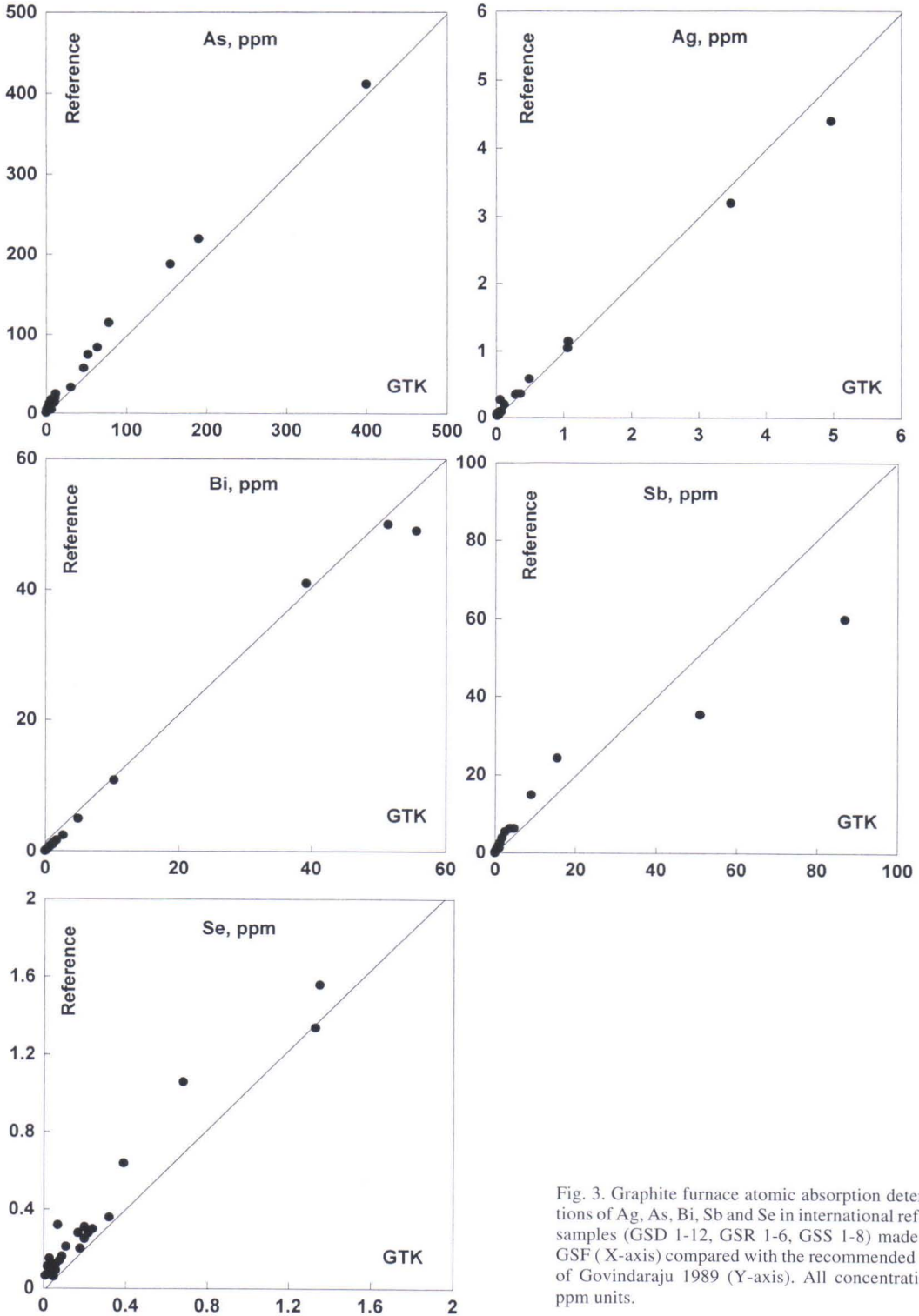


Fig. 3. Graphite furnace atomic absorption determinations of Ag, As, Bi, Sb and Se in international reference samples (GSD 1-12, GSR 1-6, GSS 1-8) made at the GSF (X-axis) compared with the recommended values of Govindaraju 1989 (Y-axis). All concentrations in ppm units.

Table 2. Elemental contamination estimated by analysing a quartz sample, ground in a tungsten carbide (n=2) and a carbon steel grinding vessel (n=10). All figures in wt%.

Component	Steel	Tungsten carbide	Error
Na ₂ O	0.00	0.00	0.00
MgO	0.0073	0.0085	-0.0012
Al ₂ O ₃	0.1522	0.1150	0.0372
SiO ₂	92.93	98.16	-5.23
P ₂ O ₅	0.0028	0.0000	0.0028
S	0.0028	0.0000	0.0028
Cl	0.0032	0.0074	-0.0042
K ₂ O	0.0093	0.0210	-0.0117
CaO	0.0185	0.0125	0.0060
TiO ₂	0.0026	0.0031	-0.0005
V	0.0011	0.0004	0.0007
Cr	0.0065	0.0026	0.0039
MnO	0.0459	0.0053	0.0407
Fe ₂ O ₃	6.84	0.05	6.79
Ni	0.0029	0.0011	0.0019
Cu	0.0024	0.0000	0.0024
Zn	0.0008	0.0018	-0.0009
Rb	0.0002	0.0000	0.0002
Sr	0.0000	0.0000	0.0000
Y	0.0000	0.0000	0.0000
Zr	0.0000	0.0000	0.0000

the Institute of Geophysical and Geochemical Exploration, IGGE (Langfang, Hebei, China), were analysed as a check on the GAAS method. The results for these stream sediments

(GSD 1–12), soils (GSR 1–8) and rock samples (GSR 1–6) are presented in Figure 3 and compared with the values recommended by Govindaraju (1989). As can be seen, arsenic, antimony and selenium are only partially dissolved by aqua regia attack, while Bi is almost totally dissolved. The acid digestion procedures were used to obtain reference values for the existing till geochemical data.

The accuracy of the XRF method was approved by analysing four international reference samples: syenite SY-2, syenite SY-3, basalt Br and granite MA-N. The results together with the reference values (Govindaraju 1989) are presented in Table 1. Note that the results for the reference samples are based on sample preparates that were ground in a tungsten carbide vessel, whereas our samples were ground in a carbon steel vessel (see above). As can be seen for the quartz sample in Table 2, the contamination from the steel vessel is significant. Due to the dilution of the sample with iron, there was a greater than five per cent decrease in the silicon concentration, expressed as SiO₂. For other major components the decrease was within normal analytical precision at the concentration level of the components in quartz. Elemental contamination from the steel grinding vessel was observed for Cu, Cr and Ni. In six randomly chosen routine samples from the batch, analysed after steel and tungsten carbide grinding, the decrease in SiO₂ concentration varied between 1 and 4%, and the contamination for Cu, Cr, and Ni was less than 5 ppm on average. For the interpretation of iron, the decision was made to use FAAS rather than XRF results.

ANALYTICAL AND SAMPLING PRECISION

The overall variance of the analytical system can be expressed as

$$s_{\text{sys}}^2 = s_{\text{sa}}^2 + s_{\text{lab}}^2 \quad (1)$$

where s_{sa}^2 refers to the sample variance, caused by sample heterogeneity and sampling errors, and s_{lab}^2 refers to the laboratory variance, caused by errors in sample pretreatment and analysis. The laboratory variance can further be divided into subvariances to estimate, for example, sample preparation and instrument variances. Thus $s_{\text{lab}}^2 = s_{\text{prep}}^2 + s_{\text{ins}}^2$.

The standard deviation, s , is the square root of the variance, and can be further divided into subdeviations. The relative standard deviation (s_r , coefficient of variation) is expressed as follows:

$$s_r = \frac{s}{\bar{x}} * 100\% \quad (2)$$

where \bar{x} is the mean of the measurements.

The precision (P) takes into account the confidence limits and is related to the relative standard deviation as follows:

$$P_{1-x} = t_{(f),0x} * s_r \quad (3)$$

where x is the risk in percentage; $t_{(f),0x}$ is the t-function value with f degrees of freedom ($f = n - 1$, where n is the number of measurements) and $x\%$ risk; and s_r is the relative standard deviation ($= s/\bar{x}$). For 95% confidence limit and when the number of measurements exceeds 30, the formula for precision is

$$P_{.95} = 2 * s_r \quad (4)$$

The accepted procedure for estimating the precision of an analytical method is to analyse a reference sample (or a monitoring sample selected from the batch) several times and calculate the standard deviation:

$$s = \sqrt{\left(\frac{\sum (x_i - \bar{x})^2}{n-1} \right)} \quad (5)$$

where x_i is the single measurement, \bar{x} is the mean of the measurements and n is the number of the measurements (ISO 5725-1986). The standard deviation, calculated as above, gives a quantitative estimate of the repeatability of the method because the test conditions are stabilized (same operator, same instruments etc.) and the time scale is short. In long-term projects like ours, the reproducibility of the method is usually more informative. One way to obtain information on the long-term stability of a method is to analyse the same reference or monitoring sample in different batches, and prepare a so-called \bar{x} -chart control (Chemistry Quality Assurance Handbook). This method was included in our work, but with recognition of its drawbacks. Prominent among these drawbacks is the fact that the monitoring sample is usually extremely well homogenized and thus not comparable to real samples. In addition, the monitoring sample represents only one matrix and one concentration level of the analyte. Dealing with a wide variety of matrices, as is the case with rock samples, means that the precision estimate based on one sample is not satisfactory.

An alternative way to estimate precision is to utilize paired samples as described by Youden (1951). In this case the precision is a function of the concentration, however, which has to be taken into account in estimating the overall precision. The estimation of precision as a function of concentration is dealt with by Howard and Thompson (1976) and Thompson

(1988) among others. In our work we adopted the simplified procedure for the estimation of precision presented by Minkinen (1976, 1986).

The relative standard deviation is a hyperbolic function of the concentration as follows:

$$s_r = \left(\frac{s_{r0}}{C} + k \right) * 100\% \quad (6)$$

where C is the concentration, s_{r0} is the concentration-independent relative standard deviation (standard deviation of the method at zero concentration) and k is an empirical factor, which can be determined. It is clear that, as the concentration increases, the first term of the sum, in parentheses, approaches zero and the relative standard deviation is expressed as

$$s_r = k * 100\% \quad (7)$$

In practice, when the concentration exceeds the detection limit by five to ten times, the relative standard deviation can be assumed to be constant. Applying formula (5) for two measurements the standard deviation estimate, with one degree of freedom, can be calculated as

$$s_{ir} = \frac{s_i}{\bar{x}} = \frac{\sqrt{(x_{i1} - \bar{x}_i)^2 + (x_{i2} - \bar{x}_i)^2}}{\bar{x}_i} * 100\% \quad (8)$$

where x_{i1} , x_{i2} and \bar{x}_i are the original measurement, the duplicate measurement and the mean, respectively. By substituting d_i for $x_{i1} - x_{i2}$ and d_{ir} for d_i/\bar{x}_i , formula 8 can be rewritten as

$$s_{ir} = \frac{|d_{ir}|}{\sqrt{2}} \quad (9)$$

When n pairs are available and the relative standard deviation is not a function of concentration, the relative standard deviation, with n degrees of freedom, can be calculated as

$$s_r = \sqrt{\frac{\sum d_{ir}^2}{2n}} \quad (10)$$

As noted above, approximately every tenth outcrop was sampled in duplicate. Table 3 shows the distribution (as percentage of occurrence) of rock types in these duplicate samples compared with the distribution of rock types in the overall study. In the laboratory the original member of the outcrop sample pair was split after crushing, as described above. This split sample then formed the laboratory sample pair (U sample). The sample duplication is schematically presented in Figure 2. Forty-five duplicate outcrop samples and 45 laboratory sample pairs were processed in the study, and used to estimate the system precision (P_{syst}) and laboratory precision (P_{lab}), as described below.

Applying formula 9, for every duplicate outcrop sample and laboratory sample pair, $s_{ir(syst)}$ and $s_{ir(lab)}$ were calculated for every element and every method. Because the precision should be only the measure of random errors in the process, the mean of d_{ir} should be zero. Students t-test was used to test that \bar{d}_{ir} was not significantly different from zero (t-

Table 3. The distribution of rock types in duplicate outcrop samples and in the all entire samples of the study.

Rock type	Distribution in duplicate samples, %	Distribution in the overall study, %
granitoids	44.4	41.0
mafic plutonics	13.3	8.4
felsic volcanics and gneisses	2.2	3.8
mafic volcanics and amphibolites	22.2	17.3
sedimentary rocks (including mica gneisses and migmatites)	17.9	29.9

value exceeding 2.14 when $n \geq 15$). The observed systematic error, confirmed by t-test was studied further by plotting d_{ir} vs. analysis time (t) and concentration ($C = \bar{x}_i$). Normally the pairs should be analysed randomly along the batch to include all possible sources of error. However, analysis of the duplicate samples separately at the end of the batch allowed the within-batch smooth or step-like drift to be observed in a plot of d_{ir} vs. time (see Fig. 4). We used this practice for XRF,

ICP-AES and INAA analyses of duplicate laboratory sample pairs. The systematic error confirmed by t-test, was corrected by calculating the mean of d_{ir} , $d_{ir} = f(t)$ or $d_{ir} = f(C)$, when the error was constant, a function of time or a function of concentration, respectively.

To study the standard deviation as a function of concentration, s_{ir} values were plotted against concentration $C (= \bar{x}_i)$. According to formula 6, the standard deviation is either a

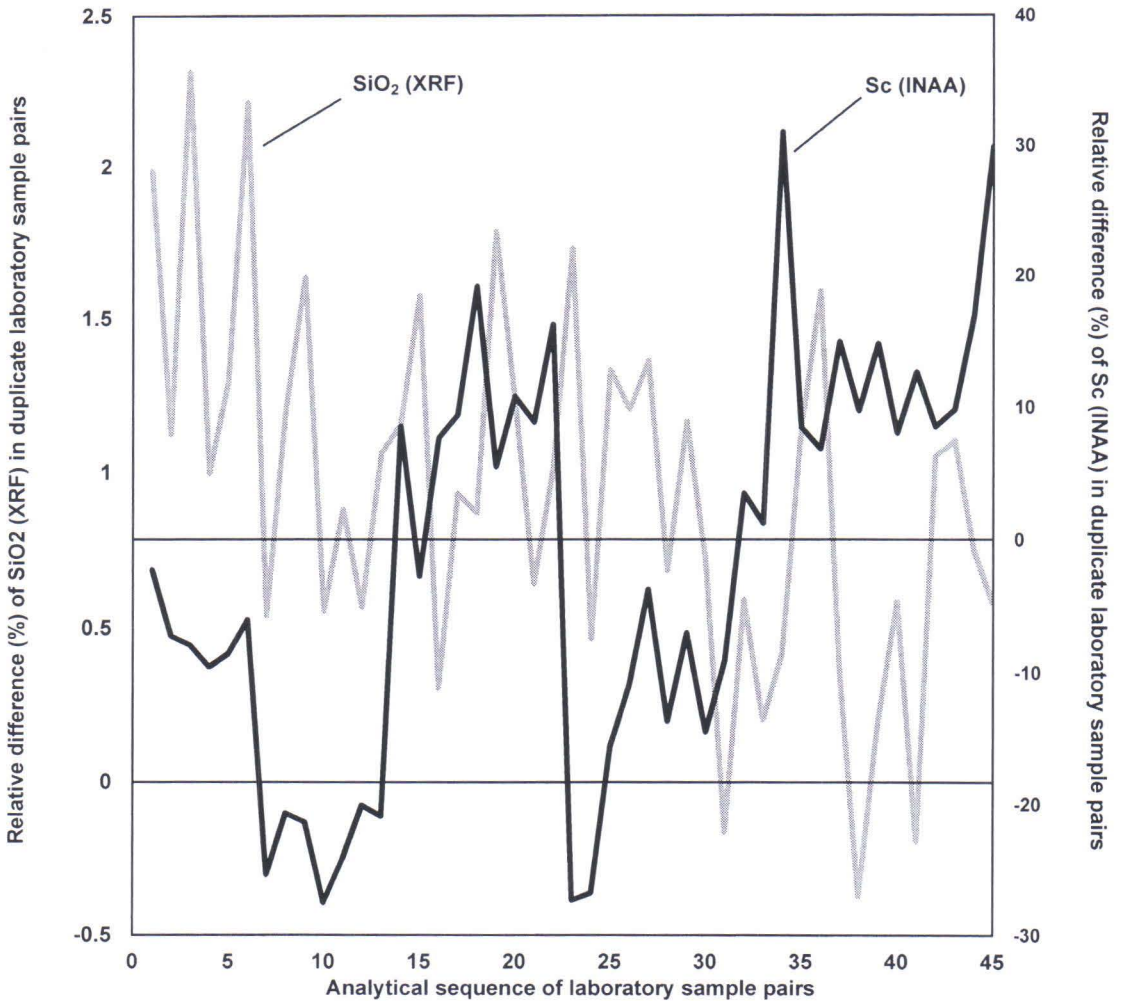


Fig. 4. The relative difference (%) of SiO₂ and Sc in laboratory sample pairs measured by XRF (black line) and by INAA (grey line), respectively, showing two types of in-batch drift of analytical methods.

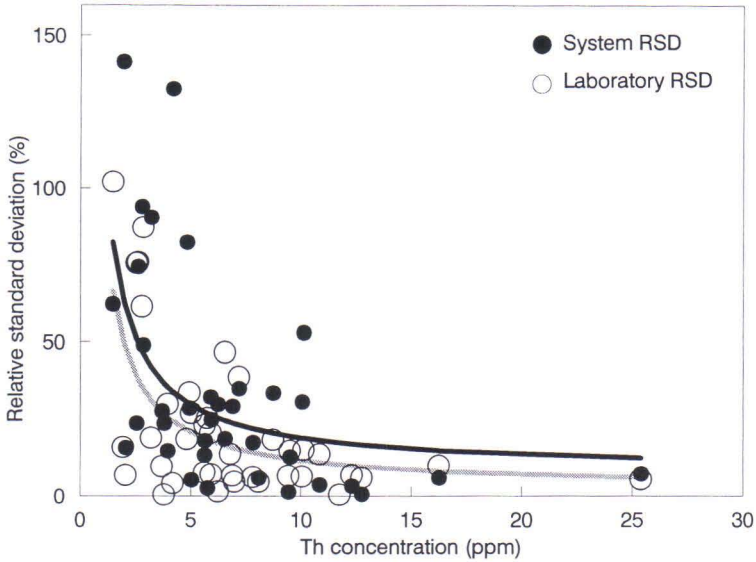


Fig. 5. The relative system (dots and solid line) and laboratory (circles and grey line) standard deviation for Th as a function of Th concentrations in XRF determinations. The hyperbolic fit is calculated by linear regression $1/C$ versus relative standard deviation, where C is concentration.

linear function of $1/C$ ($s = a \times 1/C + k$) or is constant ($s = k$). Using linear regression analysis the parameters of the linear functions $s = f(1/C)$ or $s = \text{constant}$ were calculated. If $s = f(C)$ gave better fit, the parameters of formula 6 were calculated. Figure 5 presents the standard deviation of the XRF determination of Th, where a hyperbolic curve is fitted.

After a correction for possible systematic error, the relative standard deviation for the concentration range where s_r can be regarded as constant was calculated for every element and method, using the formula

$$s_r = \sqrt{\sum s_{ir}^2} \quad (11)$$

The threshold value of the concentration after which the standard deviation can be regarded as constant was estimated visually from s vs C plots. If \bar{x}_i was smaller than the threshold value, the corresponding s_{ir} value in formula 11 was neglected. From the outcrop sample pairs and laboratory sample pairs,

$s_{r(\text{syst})}$ and $s_{r(\text{lab})}$, respectively, can be calculated by formula 11. By applying formula 1, the standard deviation due to the sampling and sample heterogeneity can then be estimated as

$$s_{r(\text{sample})} = \sqrt{s_{r(\text{syst})}^2 - s_{r(\text{lab})}^2} \quad (12)$$

Since the number of the measurements exceeds 30, formula 4 can be used to calculate the corresponding precisions at 95% confidence level. Figures 6–9 summarize the system, laboratory and sample precisions in concentration ranges where the precision can be regarded as constant. The system can be expanded to include the formation heterogeneity (see above “Study area and sampling strategy”) by applying the same procedure as for the outcrop and laboratory sample pairs to the formation sample pairs. This expanded procedure, in which the system precision is calculated in formation scale ($s_{r(\text{form})}$), automatically takes into account sample heterogeneity as well as sampling and laboratory er-

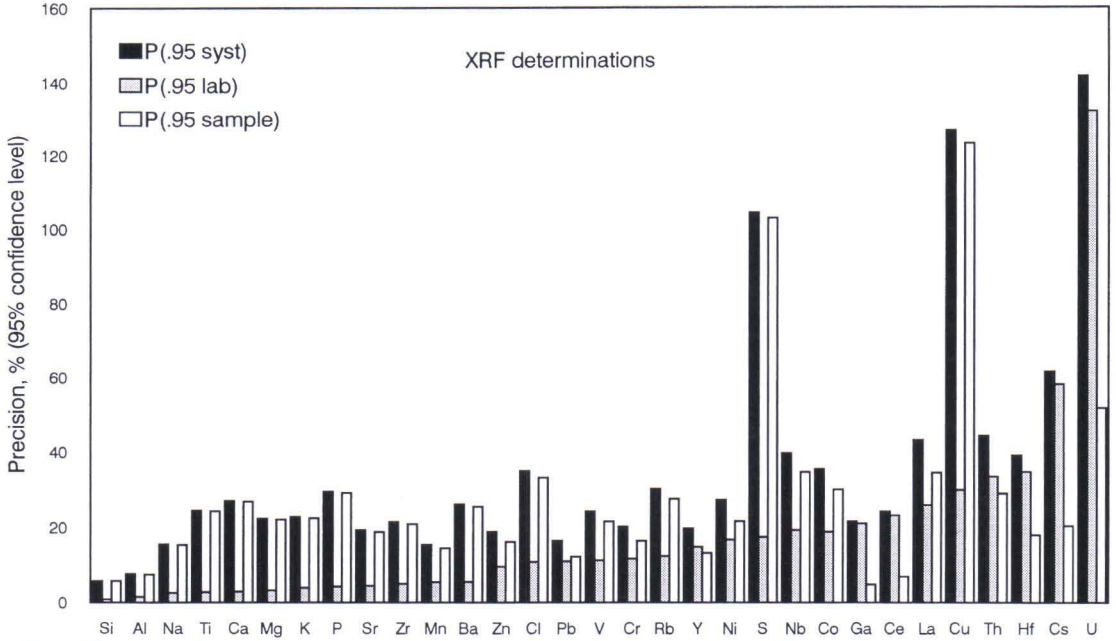


Fig. 6. The system, laboratory and sample precisions of element determinations by XRF, n = 45.

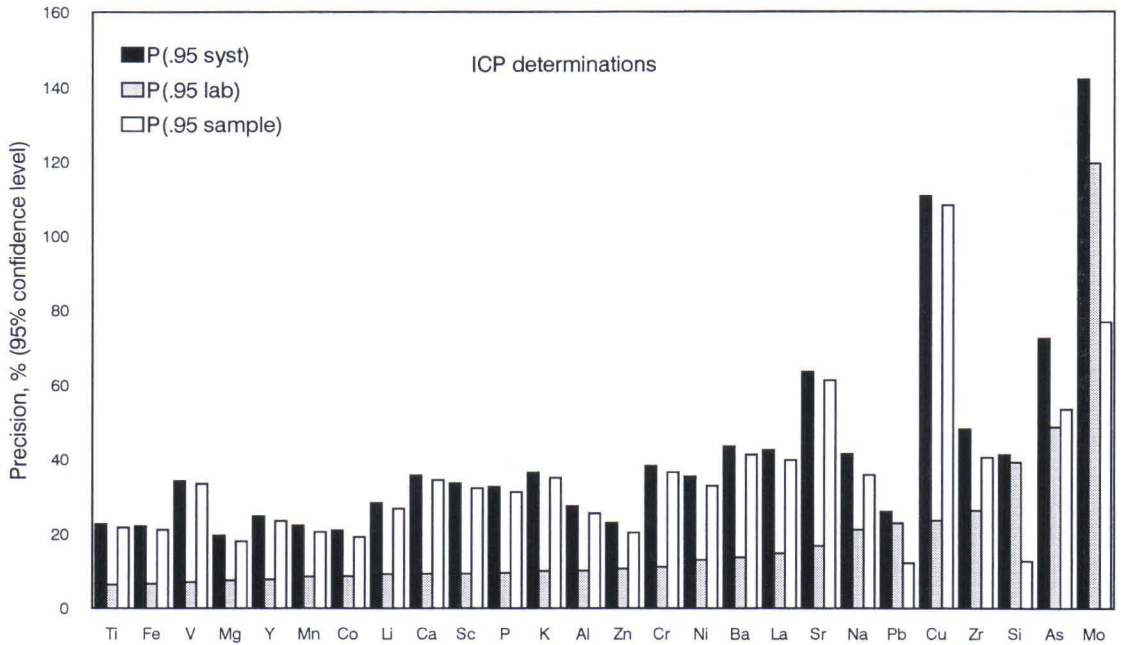


Fig. 7. The system, laboratory and sample precisions of element determinations by ICP-AES (aqua regia leach), n = 45.

rors. Table 4 presents for XRF analysis the relative standard deviations, the threshold concentration value after which the given precision applies, the parameters for formula 6 and the concentration range of the elements in the duplicate sample batch ($\bar{x}_{i(\min)} - \bar{x}_{i(\max)}$). Table 5 gives the same values for the ICP-AES determinations. The system precision in formation scale ($s_{r(\text{form})}$) is also given for selected elements in Tables 4 and 5. By expressing the values of the formation sample pairs as an X-Y plot and using the $P_{.95(\text{syst})}$ as tolerance limits, an average 30% of the measurements can be seen to lie outside the tolerance limits. The fit varies from 18% for silicon to 46% for Nb (see Fig. 10). In regard to chemical composition, an average 70% of the sampled sites can thus be considered to represent the particular

lithological unit in formation scale as well.

In addition to the duplicate samples discussed above, there were 34 sites sampled in duplicate earlier by hammer for petrophysical purposes. The method described above was also applied to these hand specimen sample pairs to calculate the relative standard deviation of the system in outcrop scale. To enable comparison of the system precisions of the adopted sampling strategy and the earlier hand specimen alternative, the system precisions ($s_{r(\text{hspec})}$) for selected elements are included in Table 4. In most cases the relative standard deviation for the hand specimen sampling is considerably worse. Mostly this can be attributed to the hand specimen sampling not being originally designed for geochemical use.

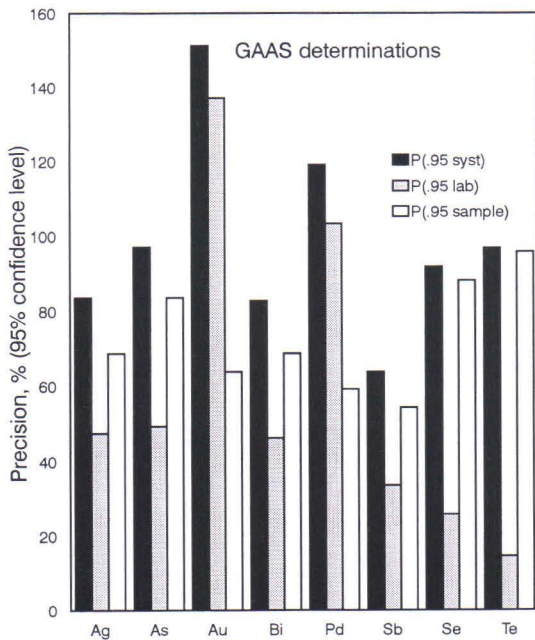


Fig. 8. The system, laboratory and sample precisions of element determinations by GAAS (aqua regia leach), n = 45.

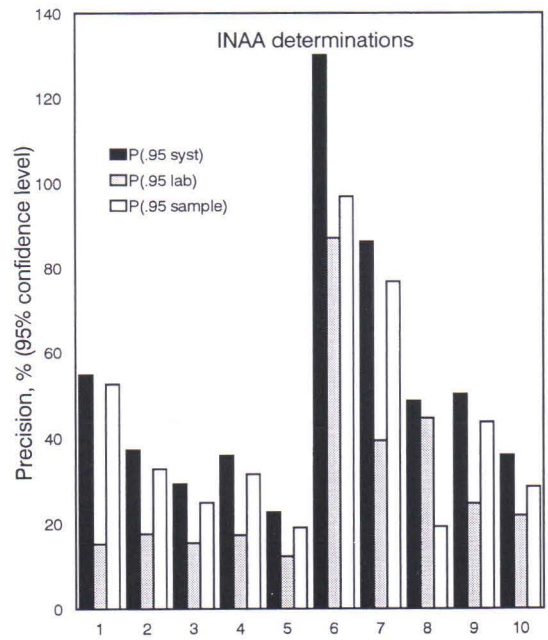


Fig. 9. The system, laboratory and sample precisions of element determinations by INAA, n = 45.

Table 4. The relative standard deviation (%) of the XRF determination of the elements for system ($S_{(sys)}$), laboratory treatment ($S_{(lab)}$) and sampling ($S_{(sample)}$). When the relative standard deviation is a function of concentration (C), the hyperbolic formula is given. Relative standard deviations are given for the system based on hand specimen samples ($S_{(hands)}$), and for the system in regional scale ($S_{(form)}$) and the concentration range of the mean values of the sample pairs.

Component and concentration to which values apply	$S_{(sys)}$ %	$S_{(lab)}$ %	$S_{(sample)}$ %	$S_{(form)}$ %	$S_{(hands)}$ %	Concentration range in duplicate samples, ppm
Al ₂ O ₃	3.77	0.74	3.70	6.43	8.15	13.55–19.85%
Ba	13.04	2.77	12.74			129–1130
CaO	13.52	1.46	13.44	28.51	33.49	0.70–10.50%
Ce	12.07	11.57	3.44			37–121
Cl	17.45	5.38	16.60			35–522
Co > 20 ppm ≤ 20 ppm	17.73 3.45/C + 0.023	9.41 5.585/C - 0.116	15.03			10–53 *
Cr > 66 ppm ≤ 66 ppm	10.05 4.77/C + 0.063	5.83 4.374/C + 0.009	8.19			40–355 **
Cu > 30 ppm ≤ 30 ppm	63.42 2.855/C + 0.056	14.95	61.63	58.74		8–187 *
K ₂ O	11.37	1.96	11.20	24.25	30.9	0.75–5.36%
La	21.56	12.96	17.23			15–62
MgO	11.16	1.62	11.04	31.45		0.28–5.33%
MnO	7.66	2.7	7.17			0.043–0.194%
NaO	7.71	1.25	7.61	15.56		1.68–4.57%
Nb > 10 ppm ≤ 10 ppm	19.83 0.185/C + 0.138	9.62 1.13/C - 0.009	17.34			4–17 *
Ni > 25 ppm ≤ 25 ppm	13.66 2.448/C + 0.050	8.36 3.831/C - 0.028	10.80			16–88
P ₂ O ₅	14.73	2.13	14.58	39.65		0.048–0.434%
Pb > 26 ppm ≤ 26 ppm	8.18 1.688/C + 0.009	5.46 1.837/C - 0.006	6.09			14–48
Rb	15.08	6.16	13.76	21.67	39.17	21–180
S > 100 ppm ≤ 100 ppm	52.2 5.236/C + 0.093	8.71 5.22/C + 0.043	51.47	47.57		41–1455
SiO ₂	2.86	0.42	2.83	4.07	8.49	47.80–71.40%
Sr	9.63	2.25	9.36	30.22	22.92	71–995
Th > 6 ppm ≤ 6 ppm	22.12 1.082/C + 0.0822	16.73 0.934/C + 0.023	14.47	28.76		1–16 *
TiO ₂	12.21	1.37	12.13			0.171–1.410%
V	12.13	5.61	10.75	31.26	21.76	25–327
Y	9.87	7.38	6.55			8–49 *
Zn	9.35	4.74	8.06			41–159
Zr	10.7	2.47	10.41	25.38	38.99	75–389

* Lower end of the range is under the detection limit

** Note! Approximately 30 ppm background level in the analysis method

Table 5. The relative standard deviation (%) of the ICP determination of the elements for system ($s_{(syst)}$), laboratory treatment ($s_{(lab)}$) and sampling ($s_{(sample)}$). When the relative standard deviation is a function of concentration (C), the hyperbolic formula is given. The relative standard deviations are given for the system based on hand specimen samples ($s_{(hands)}$) and for the system in regional scale ($s_{(form)}$), and the concentration range in duplicate field samples are indicated. All concentrations are in ppm units.

Element and concentration to which values apply	$s_{(syst)}$ %	$s_{(lab)}$ %	$s_{(sample)}$ %	$s_{(form)}$ %	Concentration range in duplicate samples
Al	13.71	5.08	12.73		5395–45100
Ba	21.78	6.89	20.66		36–529
Ca	17.82	4.63	17.21		703–19400
Co	10.48	4.27	9.57	30.12	4–31
Cr > 5 ppm	19.1	5.57	18.27		2–132
≤ 5 ppm	$0.638/C + 0.144$	$0.620/C + 0.011$			
Cu	55.35	11.76	54.09	51.09	4–162
Fe	11.03	3.29	10.53		12850–53200
K	18.2	5.01	17.50		2055–22400
La	21.25	7.41	19.92		6–44
Li	14.11	4.58	13.35		9–68
Mg	9.77	3.73	9.03		1745–23350
Mn	11.11	4.25	10.26		147–755
Na	20.75	10.53	17.88		737–4310
Ni > 5 ppm	17.66	6.55	16.40	35.3	2–60
≤ 5 ppm	$0.37/C + 0.125$	$0.42/C + 0.028$			
P	16.27	4.76	15.56	40.53	113–1570
Pb	12.94	11.42	6.08		17–53
Sc	16.77	4.65	16.11		2–19
Sr	31.82	8.4	30.69		5–138
Ti	11.29	3.15	10.84		587–4540
V	17.02	3.48	16.66		9–154
Y	12.35	3.87	11.73		3–24
Zn	11.49	5.34	10.17		14–146
Zr	24.11	13.07	20.26		3–45

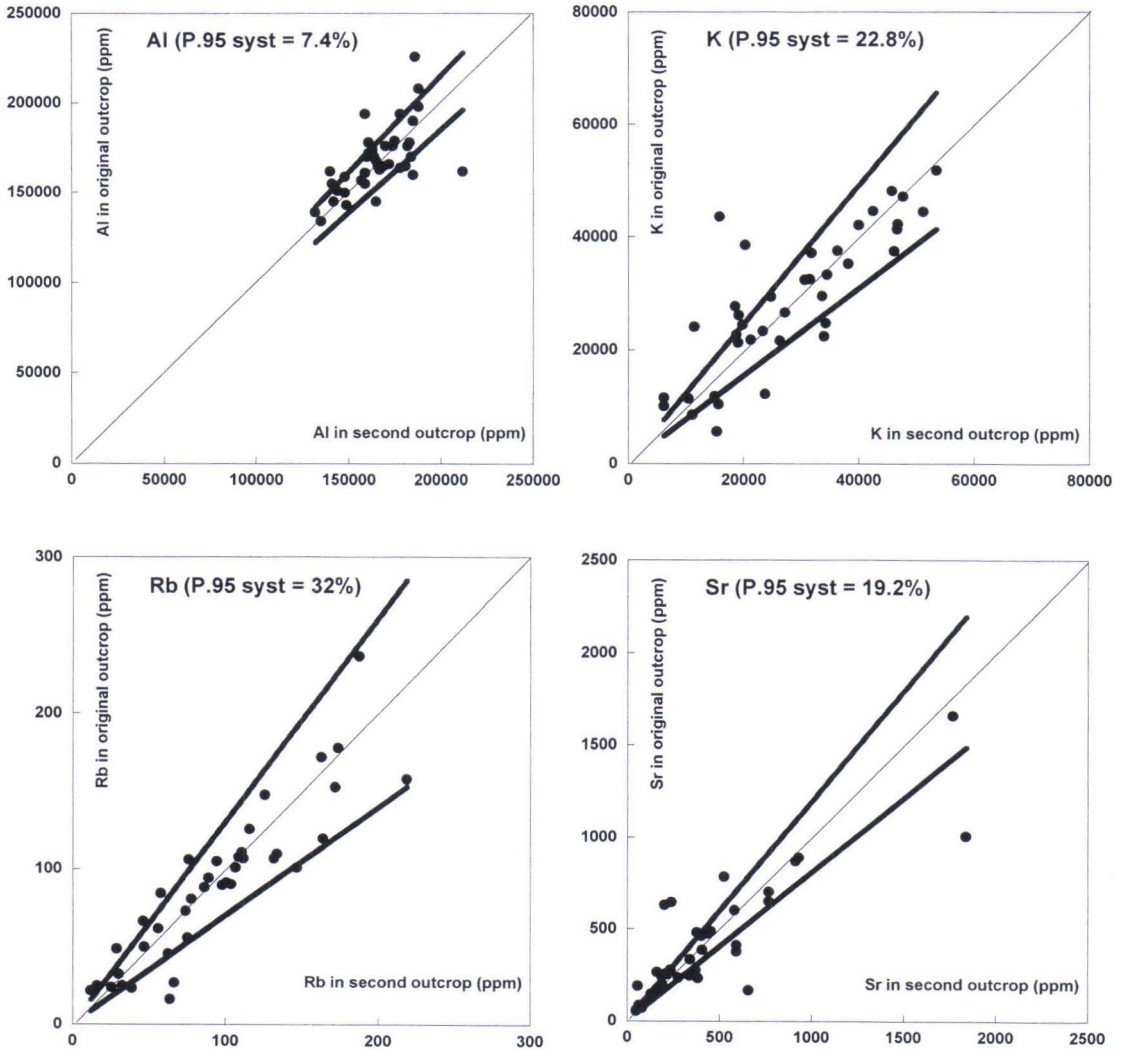


Fig. 10. X-Y plot for determinations of Al, K, Rb, Sr in formation sample pairs. The solid lines represent the system precision at 95% confidence level ($P_{.95(\text{syst})}$) of the elements based on the duplicate outcrop samples.

DISCUSSION

The total concentrations of elements, as provided by XRF, are preferred to partial leach results for the geochemical study of rocks. The XRF method is relatively inexpensive, it provides good element coverage and the sample pretreatment is simple. In addition

the accuracy and precision of the overall XRF method are good. XRF analysis is thus a natural choice as the basic analytical method for the larger project. For some trace elements, nevertheless, the detection limit achieved with XRF is insufficient relative to

the normal background concentrations. For example, the XRF method can be used for Th, Nb, Y only when concentration levels exceed 5 ppm, and in many rock types this is not the case. Moreover, the geochemical interpretation of the results for base metals like Ni, Cu, Pb and Co suffers from too high detection limits. Elements like Cs, Ga, Hf, Sc, Ta, U and REE, excluding La and Ce in anomalously higher concentrations, are seldom measurable by XRF technique. As mentioned above, the XRF method used in this work normally is applied to samples ground to a very fine grain size (<10µm), which is achieved with reasonable grinding time only in a tungsten carbide grinding vessel. In practice, the contaminants from the tungsten carbide vessel, W, Co, and to lesser extent Ta, prevent the analysis of these elements, even though the calculation and correction program includes a contaminant correction option. The carbon steel vessel used in our study in turn causes severe Fe contamination in the samples, which cannot be corrected. Carbon steel vessels also carry contaminants such as Cu, Cr and Mn. For chromium, a base level of about 30 ppm was observed in the XRF results. This is caused by an inadequate background correction in the XRF measuring program and by contamination from the carbon steel grinding vessel.

To analyse those elements that cannot be adequately handled by XRF, an alternative method has to be selected. The instrumental neutron activation method (INAA) used in this study proved suitable for many of the missing elements (Co, Sc, Th, U, Y) The overall precision of INAA for these elements is sufficient (see Fig. 8), though some within-batch drift, as for Sc, was observed. The determination of REE's by INAA is not in practice possible, but the ICP-MS method employed by X-ray Laboratories Ltd. appears adequate.

Although the aqua regia attack comprises only a partial leach, combined with graphite furnace determination it is the best practical

alternative for elements like Au, Ag, Bi and Te. The analytical precision for Ag, Bi and Te is good considering the low concentration range. The reference results (see Fig. 3) show that the analysis of Ag and Bi can be regarded as quantitative. Very few reference results are available for Te and little in general is known about the occurrence of Te in rocks. As a pathfinder element for gold its (Nurmi et al. 1991) occurrence in various rock types in regional scale is nevertheless of great interest. The occurrence of gold as nuggets in geological samples usually leads to poor precision of the determinations. The overall and especially the laboratory precision was also relatively poor in this study. However, the analytical method used for gold has proved to be sensitive (Kontas 1981) and precise enough for geochemical mapping, indicating traceable gold anomalies even in regional scale. The accuracy of gold determinations by graphite furnace atomic absorption spectrometry after aqua regia leach is demonstrated in Figure 11, where GAAS results are compared with INAA results. Arsenic, Se and Sb are only partially dissolved (see Fig. 3), but can clearly be used

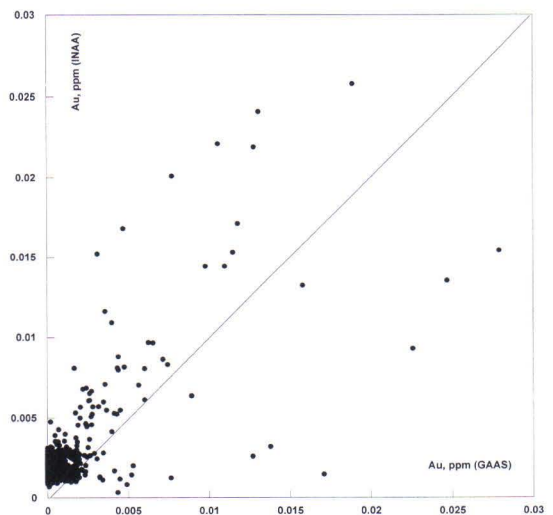


Fig. 11. Comparison of gold values obtained by instrumental neutron activation (INAA) and by graphite furnace atomic absorption technique after aqua regia leach (GAAS).

as indicators of the anomalous areas and rock types because the precision is satisfactory. On the other hand, the precision of the determination of palladium is poor and it cannot really be measured by GAAS method from every rock type.

Excluding Co, Cs, Ga, Hf, U, W and REE's, the system precision of the introduced XRF measuring program for major and minor components is evidently satisfactory, average RSD = 20% at 95% confidence level. The sometimes poor system precision for Cu and S is most likely due to the heterogeneous occurrence of chalcopyrite and other sulphides. The system precision for the partial leach

ICP-AES method is normally adequate, RSD under 30 % at 95% confidence level, except for As, Mo, Sb, Th, U and Yb, for which the detection limit is clearly too high for the concentration levels normally encountered. The sometimes poor system precision for Sr is due to unevenly distributed Sr-bearing carbonate, or more likely to the alteration of plagioclase. The system precision for the precious and semi-metals is relatively poor, especially for gold. However, the concentration levels in this study mostly represent background values of these elements, and one can expect anomalous concentrations to be adequately observed even for gold.

CONCLUSIONS

With the exceptions noted, the XRF method is clearly the method of choice for element determinations in the forthcoming research project. The ICP-MS and ICP-AES methods, based on hydrofluoric and perchloric acid digestion and fusion, will replace INAA for elements excluded from the XRF programme. Because of the better precision, elements like Pb, Th and U, whose background concentrations often are lower than the detection limit of the XRF method, also will be determined by ICP-MS. The method of aqua regia leach and GAAS will be included for precious and semimetals, since there are virtually no alternatives offering the same sensitivity. Despite the poor precision even palladium should be measured, but the interpretation should be focused on ultramafic rocks only. It is further proposed that the aqua regia based ICP-AES determination be included because it can provide information valuable for the interpretation of existing overburden geochemical data. In particular, the solubility of rock types of different mineralogical composition is of great interest. Determinations of As, Mo, Sb,

Th, U and Yb by the ICP-AES method used in this work are virtually useless because these elements normally occur in concentrations below the detection limit of the method.

The results of this pilot study show the necessity of tight quality control. The system of duplicate analysis, of outcrop and laboratory sample pairs, can ensure the control of precision during the several years of the study. When more samples are available the information obtained from the duplicate analyses should be interpreted for specific rock types, and even the mineralogical composition will need to be taken into account in interpreting the results. In addition, a batch of control samples chosen from the first year's samples should be analysed in each succeeding year. Any annual drift will be better controlled in this way than only with the reference samples included in normal laboratory practice. A quartz sample of known concentration should be included in the procedure to control the contamination during the sampling and sample pretreatment.

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