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Report of Investigation 164

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Manual

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GEOLOGIAN TUTKIMUSKESKUS

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Kalevi Rasilainen[1)], Raimo Lahtinen[1)] & Theodore J. Bornhorst[2)]

THE ROCK GEOCHEMICAL DATABASE OF FINLAND MANUAL

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The Rock Geochemical Database of Finland contains chemical data for 6544 bedrock samples throughout Finland. Stratified sampling strategy was used to insure that all lithologies are well represented in the database. Major and trace elements were analysed by XRF, ICP-MS, ICP-AES and GFAAS methods. To assess the quality of the chemical concentration data, precision and analytical drift were estimated using 375 duplicate sample pairs. The lowest reliable concentration for each element and analytical method was determined using the precision estimates. In addition to the chemical concentrations, the database contains the geographic location and several geological attributes for each sample.

Key words: (GeoRef Thesaurus, AGI): bedrock, rocks, geochemistry, data bases, chemical analysis, quality control, Precambrian, manuals, Finland

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Suomen kalliogeokemian tietokanta sisältää kemiallista tietoa 6544 kallioperänäytteestä eri puolilta Suomea. Näytteenottostrategia valittiin varmistamaan se, että kaikki kivilajiseurueet ovat hyvin edustettuna tietokannassa. Pää- ja hivenalkuaineet analysoitiin XRF-, ICP-MS-, ICP-AES- ja GFAAS-menetelmillä. Kemiallisten alkuainepitoisuuksien laadun arvioimiseksi analyysitulosten tarkkuus ja analyyttinen tasonvaihtelu laskettiin käyttäen 375 toistonäyteparia. Pienin luotettava konsentraatio määritettiin jokaiselle alkuaineelle ja analyysimenetelmälle arvioitujen tarkkuuksien avulla. Kemiallisten pitoisuuksien lisäksi tietokanta sisältää paikkatiedon ja useita geologisia määreitä jokaiselle näytteelle.

Asiasanat: (GeoRef Thesaurus, AGI): kallioperä, kivilajit, geokemia, tietokannat, kemiallinen analyysi, laadunvalvonta, prekambri, käsikirjat, Suomi

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CONTENTS

INTRODUCTION

The Precambrian bedrock of Finland is one of the best-mapped Precambrian areas in the world. While there are many geochemical studies of bedrock in selected geographic areas from around Finland, there is no consistent geochemical database that covers the bedrock of all of Finland. The Geological Survey of Finland undertook a major project in the 1990's to obtain regional geochemical data for various rock types from throughout the country. The objective of this project was to produce a high quality and internally consistent geochemical data set for bedrock covering the whole Finland.

Prior to the project, a pilot study was performed in 1989 to develop sampling and analytical methods (Lahtinen 1996, Lahtinen & Korhonen 1996, Lahtinen & Lestinen 1996, Lestinen et al. 1996, Sandström 1996). Following the completion of the pilot study, field sampling of bedrock throughout Finland commenced in 1990 and was finished 1995. The publication of the Rock Geochemical Database of Finland is the culmination of a decade-long effort.

The database contains chemical data for use in the study of various geological themes including the classification of rocks into tectonic and genetic groups, clarification of the metallogenic provinces, crustal evolution and origin, and the interpretation of the already existing national-scale till geochemical data. Furthermore, the rock geochemical data can be used outside the field of classical geology, for example in medical and environmental applications.

The database is available through the web pages of the Geological Survey of Finland.

URL: http://www.gtk.fi/publ/RGDB/.

FIELD SAMPLING

Samples of bedrock were collected throughout Finland (Fig. 1) using the strategy and techniques described below. The first samples were taken in 1990 and the sampling was completed in 1995. Altogether 6544 samples are included in the database.

Sampling strategy

The sampling strategy was based on a stratified procedure (Lehtonen & Pahkinen 1994) where the number of samples per area depends on the lithological variation seen on geological maps (Figures 1 and 2). Stratified sampling has the advantage of ensuring that the diversity of rock types is well represented within the database. However, the sampling was disproportionate in the sense that the number of samples for any particular rock type in the database does not represent the actual area covered by that rock type. For example, volcanic rocks and mafic plutonic rocks often occur as small lithologic units as compared with large granitoid batholiths and sedimentary units. Thus, the volcanic and mafic plutonic rocks are over-represented in terms of number of samples in the database.

The overall sampling density varied from one sample per 30 km^2 in areas comprised of complex lithology to one sample per 120 km^2 in areas dominated by one homogeneous rock type. The sampling sites were pre-selected by the geologists in charge of the project (Table 21) using 1:100 000 bedrock maps where available; 1:400 000 bedrock maps were used in areas lacking more detailed geologic maps. Since maps of different scales were used in different areas, the stratified sampling procedure was not evenly applied. Rock units in areas sampled using 1:400 000 bedrock maps are less accurately represented in the database than rock units in areas sampled using more detailed 1:100 000 geologic maps. Since the sampling was directed to outcrops only, the availability of outcrops had an effect on the sampling density and areas devoid of outcrops have a lower sampling density.

For approximately every 17th site, a field duplicate sample was taken. These samples were collected to provide information about the outcrop scale heterogeneity of the sampled rock materials. For these same locations, a laboratory duplicate sample was produced and analysed as described below.

Sampling techniques

The samples were collected by a team composed of a geology student and a field assistant. There were altogether 16 teams, but six geology students were responsible for 84 % of observations and sampling (Table 21).

Reconnaissance of each pre-selected sampling area was completed prior to selection of the most suitable specific outcrop area for sampling. Often moss had to be removed in order to provide the most optimal surface area to make observations and collect samples. The recommended optimal outcrop size was 10 m^2, but for 40 % of the sampled sites the size was smaller. The median size of sampled outcrops was 10 m^2 and the inter-quartile range (25 %–75 %) was 6 m^2–30 m^2.

Figure 1. Location of sampling sites for the Rock Geochemical Database of Finland. The distribution of the 6544 sampling sites gives an indication of the lithologic diversity of the bedrock.

At each outcrop, a distinct and homogenous lithologic unit was selected for sampling and the positions for the drill core sub-samples were chosen. Four to six sub-samples were taken depending on the heterogeneity and grain size of the rock material. The sub-samples were placed to clearly represent the unit that was selected for sampling. The spacing between the sub-samples varied according to the nature of the unit sampled from homogenous granitoids and volcanic rocks to more heterogeneous migmatites and finely layered sedimentary rocks. When the rock had layering or banding thicker than 5 cm a single band was selected, in other cases multiple bands were sampled. In addition to the drill core sub-samples for chemical analysis, one oriented drill core sample was taken and stored as a reference sample for each sampling site.

The sampling was done by a portable mini-drill equipped with a diamond bit and water-cooling system. Drilling time of a single core varied from 5 to 30 minutes depending on the rock type. The drill cores were 15 to 20 cm long and 2.5 cm in diameter. Each core was studied and the visibly weathered part of the core was removed. The sample size of four to six drill cores is considered representative for fine- and medium-grained rocks, but heterogeneity due to sampling is possible in coarse-grained rocks. To limit contamination from drilling, new drill bits were first drilled into pure vein quartz. The only clear contamination caused by drilling was Ag. This unfortunately led to the exclusion of Ag results from the database. There was insignificant contamination for Zn (< 1ppm).

The team leader recorded the rock types, their age relationships and primary petrographic, textural and structural features on a standard observation form. The sampled unit was classified as a specific rock type according to a set of standard rock codes. The observed deformation, migmatisation, and alteration were recorded and the sampled outcrop was sketched on the field observation form. The forms were scanned and saved in electronic format (PDF) to be linked with the chemical and other data. A restricted number of the sampling sites were photographed. The geologists in charge undertook field revisions to synchronize the observations made by the different sampling teams.

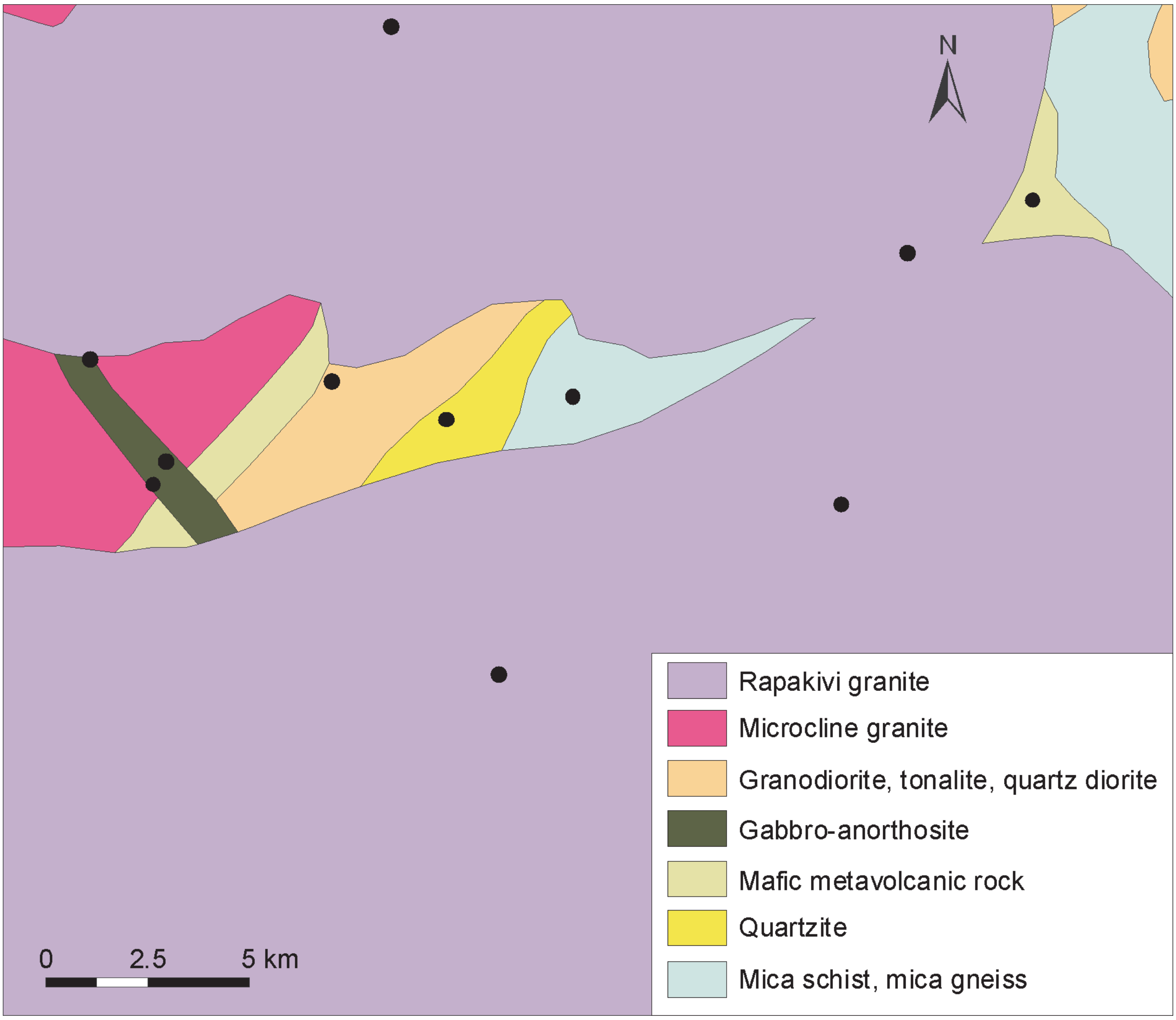

Figure 2. An example of stratified sampling from the northern part of the Wiborg rapakivi granite batholith in southern Finland. The sampling density is low in the area covered by the rapakivi granite and clearly higher in areas where there is more lithological variation. The diversity of the lithologic units is covered by the samples but obviously the number of samples taken from a lithologic unit is not proportional to the area of the unit.

CHEMICAL ANALYSIS

Laboratory sample preparation

Rock samples were crushed to < 5 mm using a jaw crusher with iron-manganese plates (Fig. 3a). The crushed material was split into three portions with a riffle splitter. One portion was stored. From each of the other two portions, about 200 g was separated with a riffle splitter to be pulverised in a ring mill to grain size < 60 µm. One 200 g portion was pulverised with a carbon steel bowl and the other with a tungsten carbide bowl. The pulverised sample material was stored in plastic vials. The pulverising bowls were cleaned after each sample with water and quartz.

Duplicate samples were prepared in the laboratory for quality assurance and control for the same sites where a field duplicate sample was taken (Fig. 3b). For nearly every 17th sampling site, or 5.8 % of the analysed samples, a laboratory duplicate sample was prepared. For those sites, the crushed sample material was split into five portions instead of three. The two additional portions became the laboratory duplicate sample.

All samples have a small erratic amount of iron and manganese contamination from crushing as well as some contamination from pulverizing. However, to minimize the effect of contamination due to pulverizing, the specific pulverizing method was different for different analytical methods. XRF, carbon and fluorine analyses were made using the tungsten carbide pulverised sample material, whereas the carbon

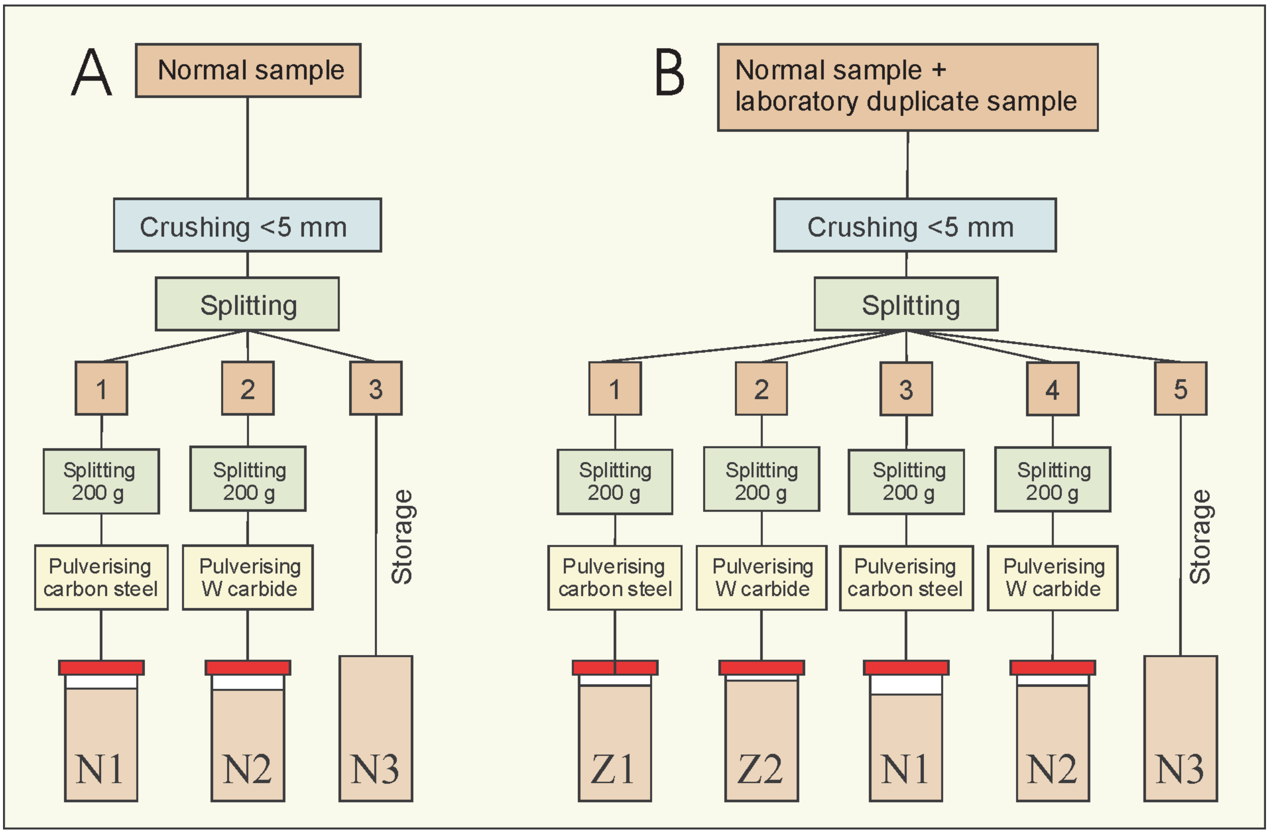

Figure 3. Sample preparation scheme for the Rock Geochemical Database of Finland. A: Only normal field sample prepared for analysis. B: Normal sample and laboratory duplicate sample prepared for analysis.

steel pulverised material was used with the other analytical methods. The cleaning of the pulverising bowls with water and pure quartz after each sample minimized cross-contamination between samples. The elemental concentrations in pure vein quartz samples pulverised by each method are given by Sandström (1996). According to these data, the contamination caused by the pulverising is insignificant for the reported elements.

Analytical methods

All chemical analyses of the samples were performed at the geochemical laboratory of the Geological Survey of Finland between 1992 and 2001. The samples were analysed using X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry with electrochemical atomisation (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS). XRF and ICP-MS analyses were for total element content while ICP-AES and GFAAS analyses were based on aqua regia leach and concentrations determined vary from partial to total. Total carbon was measured with a carbon analyser and total fluorine was analysed potentiometrically after NaOH fusion.

XRF (laboratory method 175X)

Total element XRF analyses were performed using pressed powder pellets. The pressed pellet method used at the GTK geochemical laboratory involved mixing 7 g of pulverized sample material with 210 mg of binder wax. The mixture was ground for two and a half minutes in a high-frequency mill using a tungsten carbide grinding vessel. The mixture was pressed on a wax base using a pressure of 20 t for 20 seconds. The intensities of characteristic X-ray lines were measured with a Philips PW1480 sequential wavelength dispersive spectrometer, using a 100kW generator, side window 3 kW Rh tube and PX-1, PE, curved GE-C, LIF200 and LIF220 crystals. Concentrations were calculated using the fundamental parameter method RRFPO (Ala-Vainio 1986).

ICP-AES (laboratory method 511P)

Partial leach ICP-AES analyses were preformed by digesting 150 mg of the pulverized sample with 3 ml of aqua regia in a glass test tube at 90 °C for one hour. It was then diluted to 15 ml, mixed thoroughly, left to settle and centrifuged. The solution was used for the ICP-AES determinations with a JarrellAsh Atomcomp Series 8000 instrument using fixed channels for 34 elements. Optimum instrumental running parameters were used: RF-power 950W, plasma gas flow 18 l/min, coolant gas flow 0.5 l/min, observation high 12 mm, variable nebuliser pressure, Cu/Mo intensity ratio 0.90 ± 0.2, and 10 ppm Cu standard intensity at 15 000–20 000 cps. Aqua regia leach dissolves sulphides, some oxides, and some silicates. Mineral phases such as barite, zircon, monazite, sphene, chromite, gahnite, ilmenite, rutile, and cassiterite are hardly dissolved at all. This method is considered to yield partial concentrations for the elements determined. If the sample is fine-grained enough the base metals will be generally, but not always, completely dissolved. The method is described by Niskavaara (1995).

GFAAS (laboratory method 511U)

Partial leach GFAAS analyses were performed by digesting 0.15 g of pulverised sample with aqua regia at 90 °C for one hour and subsequently diluting to 15 ml. Arsenic and Ag were analysed by GFAAS. The sample was then subjected to reducing co-precipitation with mercury using $NaBH_4$ as a reducing agent. The precipitate was dissolved in aqua regia and Se, Bi and Sb were determined by GFAAS. A Perkin-Elmer PE3030 instrument was used with a Zeeman background corrector. The effectiveness of the aqua regia dissolution is the same as described for the ICP-AES method. The method is described by Niskavaara and Kontas (1990). The original published method was modified by replacing $SnCl_2$ with $NaBH_4$ as the reducing agent to better ensure the co-precipitation of Sb and Bi.

GFAAS (laboratory method 521U)

Partial leach GFAAS analyses were performed by digesting 5 g of pulverised sample with aqua regia at room temperature overnight and then co-precipitating with mercury using $SnCl_2$ as a reducing reagent. The precipitate was dissolved with aqua regia and diluted to two millilitres. Gold, Te and Pd were determined by GFAAS using a Perkin Elmer PE3030 instrument with a Zeeman background corrector (Au, Te) and a Perkin Elmer PE2280 instrument (Pd). The effectiveness of the aqua regia dissolution is similar to that described for the ICP-AES method. The method is described by Kontas et al. (1990).

ICP-MS (laboratory method 308M)

Total element ICP-MS analyses were preformed by mixing 0.2 g of pulverised sample with 10 ml of 40 % hydrofluoric acid and 4 ml of 70 % perchloric acid in a Teflon dish. After evaporation on a hot plate, the residue was dissolved in 20 ml of 8 mol/l nitric acid and 1 ml of 30 % hydrogen peroxide. The solution was filtered and the filtrate was saved. The filter was ashed in a platinum crucible. The residue was fused with 0.2 g of lithium metaborate and 0.02 g of sodium perborate and then dissolved in 5 ml of 0.8 mol/l nitric acid. This solution was added to the filtrate and the combined solution was made up to 100 ml (1.8 mol/l nitric acid). The ICP-MS determinations were performed with a Perkin-Elmer Sciex Elan 5000 instrument using normal resolution and external calibration. All concentrations were determined by one measurement from one dilution of the sample. The acid dissolution followed by fusion used for this method effectively digest most refractory minerals. However, the major disadvantage of all fusion methods is the introduction of large amounts of total dissolved solids, which necessitates increased dilution and may cause some trace element concentrations in the solution to become too low for quantitative analysis (Jarvis & Jarvis 1992). The method is described by Rautiainen et al. (1996).

C analysis (laboratory methods 811L, 816L)

Carbon analyses were performed using a Leco CR-12 carbon analyser instrument. In total carbon analysis (811L), 0.5 g of the powdered sample was placed into a ceramic combustion boat. The boat was placed into the furnace and carbon was oxidised to carbon dioxide in an oxygen atmosphere at 1370 °C. The carbon dioxide was driven with oxygen carrier gas through an infrared cell, where carbon dioxide absorbs energy at a specific wavelength. This wavelength was selectively passed through a filter into an infrared sensor, which converts the energy level to carbon dioxide concentration. The method is described by Saikkonen and Rautiainen (1990).

Non-carbonate carbon was determined when total carbon exceeded 0.05 % by removing the carbonate carbon from the sample by chemical volatilisation. In this procedure (816L), 0.5 g of powdered sample was weighted into a ceramic combustion boat. The sample was moistened with water and mixed with about 4 ml of HCl (6 mol/l) to dissolve the carbonate carbon. The sample was evaporated dry on a sand bath at about 120 °C. The HCl treatment was repeated twice, followed by washing with water 10 times to remove any remaining acid. The sample was dried in an oven at 100 °C overnight, after which non-carbonate carbon was determined in the same manner as total carbon. The amount of carbonate carbon was calculated from $C_{tot}–C_{noncarb}$ and it is expressed in the database as CO_2.

F analysis (laboratory method 707I)

Total fluorine analysis was preformed by fusing 100 mg of pulverised sample with 2 grams of sodium hydroxide in a nickel crucible in a muffle furnace at 600 °C for 20 minutes. The melt was mixed after 10 minutes in the furnace. After the fusion, 50 ml of deionised water was added into the crucible. The mixture was warmed at 70 °C for one hour and then let sit overnight at room temperature. After filtering the mixture was made up to 100 ml and fluoride was determined with an ion selective electrode using TISAB III buffer to adjust the ionic strength of the sample solution. The method is described by Fabbri and Donati (1981).

QUALITY ASSURANCE AND CONTROL

The geochemical laboratory quality assurance and control included the analysis of two internal quality control samples (granite QC-1 and peridotite QC-2) every day or once for each analysis batch. In addition to these control samples, certified reference materials and in-house reference samples were analysed periodically to provide information on the quality of the measurement data. At the time the chemical analyses for this database were made, reliable reference values for aqua regia soluble elements were available for only three certified reference materials (Niskavaara 1995), which made it difficult to estimate the accuracy of the partial dissolution methods (ICP-AES, GFAAS). The quality assurance protocol and analytical quality control procedure of the laboratory for the ICP analyses are described by Niskavaara (1995).

In addition to the normal quality assurance and control procedures followed by the geochemical laboratory, a laboratory duplicate sample was made and analysed chemically for 381 locations. Six of these were later eliminated due to erroneous results and the remaining 375 samples were used to study data quality. The laboratory duplicate samples include uncertainty due to sample heterogeneity, sample preparation and analytical measurements and thus provide the most realistic estimate of the quality of the data. The laboratory duplicate samples were used to quantify the precision of the concentration data reported by the laboratory and establish the lowest reliable concentration for each element. The laboratory duplicate samples were also used to investigate analytical drift.

Precision

Precision can be defined as a measure of mutual agreement among a series of individual measurements. There are several estimators of precision, which generally represent the spread of a measurement data distribution. This distribution can be derived from either repeated measurements of the same sample or measurements of pairs of different samples. For this database, the precision was estimated from the spread of the concentration data derived from sample pairs composed of the laboratory duplicate sample and the corresponding normal sample (Fig. 3b). Estimated this way, the precision includes the reproducibility uncertainty of the analytical method as well as uncertainty due to sample preparation and sample heterogeneity. The precision also includes analytical drift when the time between the measurements of a paired sample is long enough.

The measured concentration of an element can be expressed as:

$$\begin{aligned} C_{N,i} &= T_i + e_{N,i} \\ C_{Z,i} &= T_i + e_{Z,i} \end{aligned} \tag{1}$$

where $C_{N,i}$ and $C_{Z,i}$ are the measured concentrations of the normal (N) and laboratory duplicate (Z) sample in sample pair i, T_i is the true (unknown) concentration and $e_{N,i}$ and $e_{Z,i}$ are the errors between the measured and true values. The errors are assumed to be generated by random processes, which are independent from sample to sample. An estimate of the error term for each *N-Z* sample pair is defined as:

$$e_i = \frac{1}{\sqrt{2}}\left(C_{N,i} - C_{Z,i}\right) \tag{2}$$

The factor 1/√2 is included because the error term for both the normal and laboratory duplicate sample is assumed to come from the same distribution. Estimating the precision is equivalent to estimating the spread of the error terms. For this database, the modified median absolute difference (M.MAD) approach (Randles & Wolfe 1979, Sirois & Vet 1999) was used to estimate the spread of the error terms. This non-parametric estimator was selected because it minimizes the effects of extreme values. It is defined as:

$$M.MAD(e) = \frac{1}{0.6745} Median\left(\left|e_i - Median(e_i)\right|\right) \tag{3}$$

where the coefficient (1/0.6745) is included to ensure that the modified median absolute deviation is a consistent estimator of the standard deviation of e, if the distribution of e is normal.

The non-parametric coefficient of variation (relative standard deviation) is defined as:

$$CoV = \frac{M.MAD}{Median\left(\overline{C_i}\right)} * 100\% \tag{4}$$

where $\overline{C_i}$ is the average of the measured concentrations of the normal (N) and laboratory duplicate (Z) sample in a sample pair:

$$\overline{C_i} = \frac{C_{N,i} + C_{Z,i}}{2} \tag{5}$$

Precision is then defined as:

$$P_{1-x} = t_{n-1,x} * CoV \tag{6}$$

where x is the probability of error, n is the number of *N-Z* sample pairs and t is the coefficient of Student's t-distribution (Minkkinen 1986). Hence, precision is associated with a confidence level. In this article, a confidence level of 95 % is used.

The precision was estimated for each element and analytical method. At low concentrations near the detection limit, the precision of an analytical method is generally poorer than at higher concentrations. The estimated precisions were used to define the limit of lowest reliable concentration as described below. The precision was then estimated for a few fixed concentration intervals above the lowest reliable concentration. These values are reported in Tables 1–7. The precision estimate is also given for concentrations below the lowest reliable concentration for several ore metals.

The precision for the major elements is generally better than 5 %. When the lowest concentration ranges are excluded, the median precision for all of the trace elements is 13.5 %. The precision is better than 10 % for 14 trace elements and worse than 30 % for 10 trace elements. For concentrations just above the lowest reliable concentration, the median precision for the trace elements is 26 %. It should be noted that the precision values estimated here using sample pairs are likely to be higher than those reported for other large databases where precision estimates are based solely on reproducibility (see Discussion).

Lowest reliable concentration

The estimated precision values are typically very poor at the lowest concentrations reported by the laboratory, which indicates that the low concentration values are unreliable. With increasing concentration, the precision gradually becomes better. This underlines the need to define a limit above which the concentration data can be considered quantitatively reliable.

The simplest and unfortunately common way to define the limit of the lowest reliable concentration is to use the detection limit reported by the laboratory. The detection limit is usually defined as a threshold below which measured values do not differ significantly from a blank signal, at a specified level of probability (Currie 1968, Keith et al. 1983). This means that the precision of measurements near the detection limit can be so poor that measured concentration values above the detection limit really cannot be considered reliable. The limit of quantification is commonly used as the threshold above which the reported concentration values can be regarded reliable and as a way to avoid erroneously reporting truly valid concentrations as being below the detection limit. The quantification limit is generally computed as 10 times the standard deviation of a background signal (Jenner 1996), which results in a threshold about three times the detection limit (Hesel 2005), depending on how the detection limit is defined. Measured values above the quantification limit can be considered reliable with high probability.

The detection limits reported by the geochemical laboratory for the elements analysed by the various analytical methods are shown in Tables 1–7. For the XRF method, the detection limit depends on the matrix of the sample and can therefore vary from sample to sample. The XRF detection limits are experimental and determined by analysing more than 30 certified international reference samples and pure quartz. The detection limit is the lowest value where relative error for several samples is 100 % or less (M. Hagel-Brunnström, personal communication 2007). For the carbon analyses methods (811L and 816L), the detection limit is defined as three times the standard deviation of the reagent blank value (Saikkonen and Rautiainen 1990). For the other methods, the laboratory detection limit is calculated as the mean value of reagent blank measurements plus six times its standard deviation, and expressed as concentrations in the sample, taking into account the dilution factor (M. Hagel-Brunnström, personal communication 2007).

For this study, the geochemical laboratory of the Geological Survey of Finland made an exception to their normal procedure and reported all measured concentration values regardless of the laboratory detection limit. This made it possible to use the actual measurement values to determine a realistic threshold for reliable concentrations. Plotting the reported concentration of an element in a normal sample against its reported concentration in the corresponding laboratory duplicate sample is a visual means of estimating the quality of the measured concentration values and the concentration level below which the data are no longer reliable (Fig. 4). Plots of all available (normal – laboratory duplicate) sample pairs indicate that for some elements, the lowest reliable concentration is higher than the laboratory detection limit, whereas for other elements, the opposite is true.

The estimated precision values should contain all possible sources of uncertainty from sample preparation and heterogeneity to analysis in the laboratory. Hence, trimming of the sample set was not done as the anomalous differences in concentration between the paired normal and laboratory duplicate samples might well represent real sources of uncertainty, which are in fact present in the database. The nugget effect, caused by the existence of some elements in only a few grains of material in the sample, is one possible source of excess scatter in the paired normal and laboratory duplicate sample set data. Gold is perhaps the most prominent example of such behaviour. A few erratic values for some elements (e.g., Zr, Nb) and increasing scatter for other elements at higher concentrations (Nd, Sm, Ta, U, Y, Zr; Table 7) for the ICP-MS method may be caused by a nugget-like effect. This effect is probably a combined result of the occurrence of coarse accessory minerals and small sample weight (200 mg) producing scatter. Since the nugget effect cannot be confidently identified, no attempt was made to eliminate sample pairs affected by it.

To determine the lowest concentration that can be regarded as reliable, the normal and laboratory duplicate sample paired data was ordered according

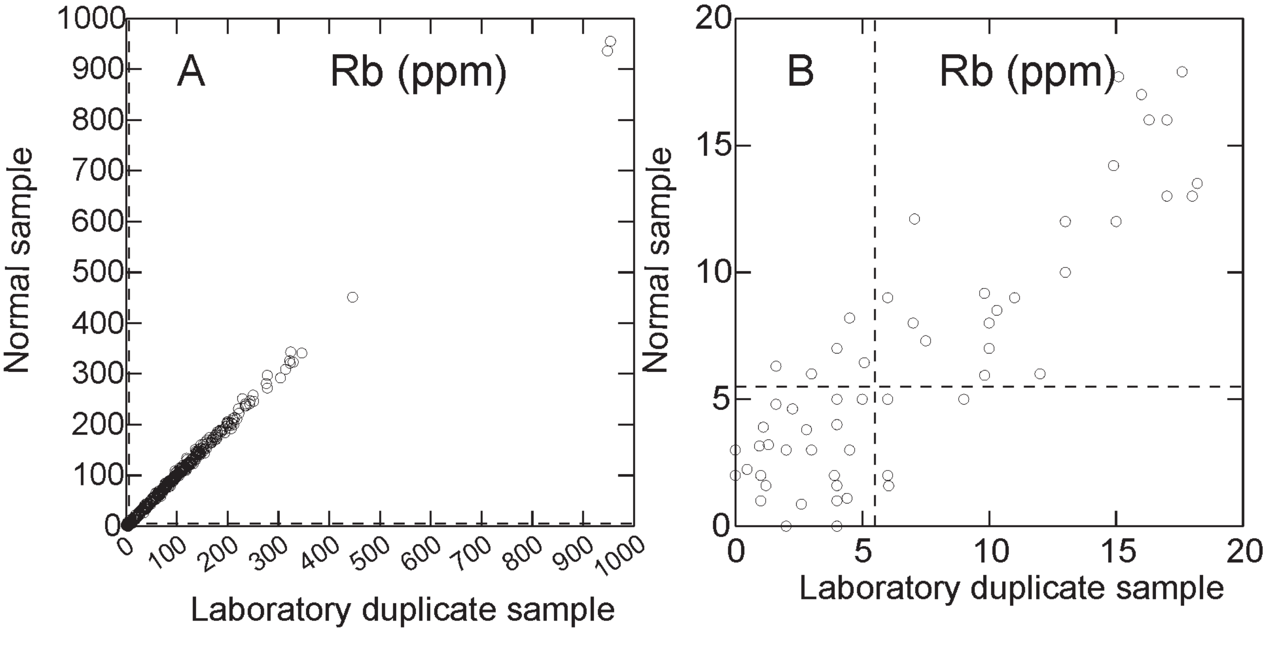

Figure 4. Plot of concentration in the normal sample against and concentration in the laboratory duplicate sample for Rb (XRF), used to visualise the quality of the concentration data. The lowest reliable concentration (see text) is shown as a dashed line. A: The whole data range, B: Low concentrations.

to increasing mean value concentration in the sample pair. The precision was then calculated for a moving window through the data. Plots of the moving window data confirm that the precision is poor at the lowest concentrations and becomes better with increasing concentration. The lowest reliable concentration was defined as the minimum concentration value in the moving window when the precision calculated for the window (at the 95 % confidence level) becomes better than or equal to 50 % (Fig. 5).

The precision was studied using 10, 20, and 30 sample moving windows through the normal and laboratory duplicate sample paired data. A window width of 20 samples proved to be a good compromise between the rather large difference of precision values between consecutive 10-sample windows and the larger range of concentration values covered by each 30-sample window. For most elements and analytical methods, the lowest reliable concentration was defined by the 20-sample moving window. For some elements, the precision was better than 50 % beginning from the lowest mean value concentration in the paired data for a 20-sample moving window. In such cases progressively smaller window widths of 10, 5 and 3 samples were used until the lowest reliable concentration value was found. For a few elements, the precision was better than 50 % beginning from the lowest mean concentration even when using a 3-sample moving window. In those cases, the lowest reliable concentration could not be defined and it was assumed to be the same as the laboratory detection limit or the lowest mean concentration in the paired data, whichever was smaller. The lowest reliable concentration (LRC) values are given in Tables 1–7.

It must be noted that the lowest reliable concentration determined this way is based solely on the paired normal and laboratory duplicate sample data and includes sources of uncertainty such as sample heterogeneity and sample preparation in addition to analysis method uncertainty. Thus, it is a realistic estimate and in many cases, it is higher than the laboratory assigned detection limit.

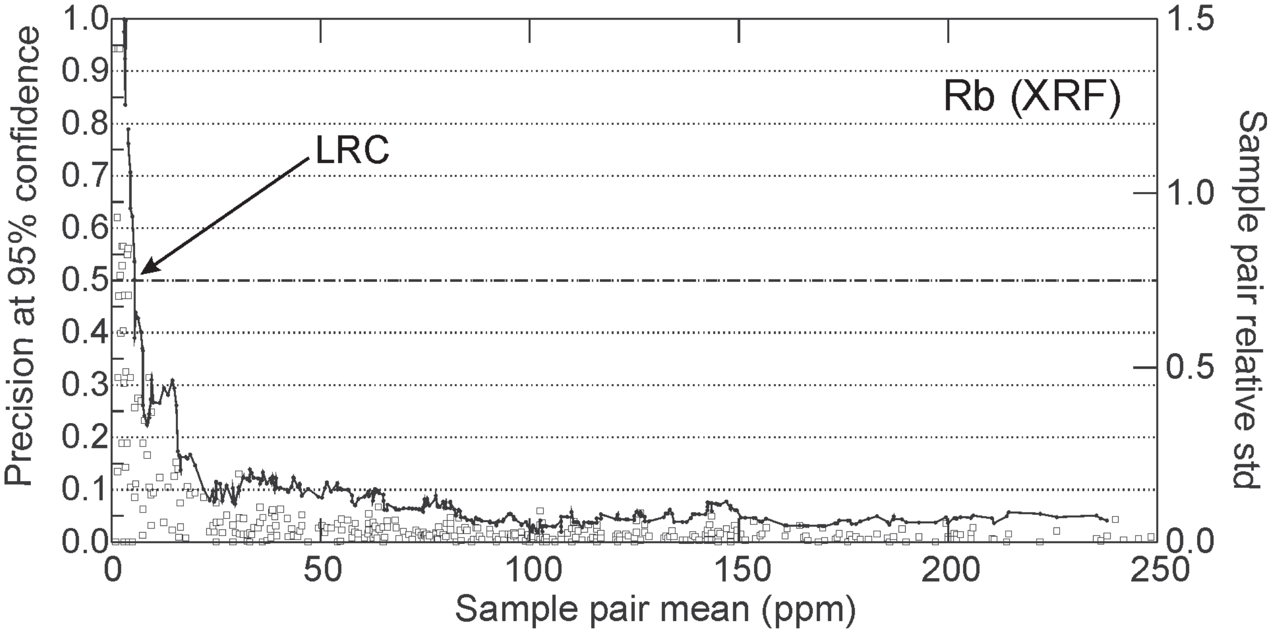

Figure 5. Estimated precision for Rb (XRF) concentration at 95 % confidence level in a 20-sample moving window through the normal and laboratory duplicate sample pair data. The precision is calculated using the M.MAD method (see text) and the value for each 20-sample window is plotted against the lowest sample pair concentration mean value in the window. The lowest reliable concentration (LRC) is defined as the concentration at which the precision becomes less of equal to 50 % as the sample pair mean concentration increases. Sample pair relative standard deviation values are plotted as grey circles.

Table 1. Major elements analysed by pressed powder pellet and XRF method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (%)	LRC (%)	Precision at 95% conf. level			Data range (%)
				Precision (%)	Range (%)	N of sample pairs	
SiO_2	175X	0.02	=DL	2	[11.75–50.00]	58	11.75–96.05
				1	(50.00–96.05]	317	
TiO_2	175X	0.005	=DL	5	[0.01–0.35]	108	0.01–2.91
				3	(0.35–2.91]	267	
Al_2O_3	175X	0.02	=DL	3	[0.92–10.00]	23	0.92–28.80
				1	(10.00–28.80]	352	
FeO	175X	0.01	=DL	3	[0.39–4.00]	153	0.39–16.00
				2	(4.00–9.00]	157	
				4	(9.00–16.00]	65	
MnO	175X	0.004	0.012	12	[0.012–0.05]	106	0.008–0.37
				6	(0.05–0.10]	135	
				4	(0.10–0.37]	126	
MgO	175X	0.03	0.09	5	[0.09–2.00]	173	0.03–38.35
				3	(2.00–5.00]	126	
				2	(5.00–38.35]	70	
CaO	175X	0.004	=DL	4	[0.01–1.00]	41	0.01–31.15
				3	(1.00–2.00]	81	
				2	(2.00–31.15]	253	
Na_2O	175X	0.08	0.05	4	[0.05–1.00]	16	0.01–6.64
				2	(1.00–6.64]	346	
K_2O	175X	0.004	0.003	2	[0.003–2.00]	138	0.002–6.97
				3	(2.00–6.97]	235	
P_2O_5	175X	0.01	0.024	16	[0.024–0.05]	31	0.001–1.27
				8	(0.05–0.10]	92	
				6	(0.10–1.27]	222	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
Precision: Estimated precision
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 2. Trace elements analysed by pressed powder pellet and XRF method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (ppm)	LRC (ppm)	Precision at 95% conf. level			Data range (ppm)
				Precision (%)	Range (ppm)	N of sample pairs	
Ba	175X	20	21	29	[21–100]	34	16–5261
				7	(100–200]	33	
				4	(200–5261]	301	
Cl	175X	60	45	30*	[45–100]	120	17–4650
				27	(100–200]	105	
				13	(200–4650]	99	
Cr	175X	30	19	30	[19–25]	43	9.5–5308
				19	(25 –50]	70	
				8	(50–5308]	184	
Cu	175X	20	17	35	[17–30]	54	0.5–629.5
				15	(30–629.5]	122	
Ga	175X	20	10	36	[10–20]	41	2–65.45
				18	(20–65.45]	324	
Mo	175X	10	2.6*	39	[2.6–13.4]	10	0.001–13.4
Nb	175X	10	7	32	[7–13]	120	1–82
				20	(13–82]	115	
Ni	175X	20	14	29	[14–30]	69	0.12–2518
				15	(30–100]	119	
				9	(100–2518]	46	
Pb	175X	30	14	26*	[14 –20]	73	9–102
				16	(20–40]	240	
				13	(40–102]	39	
Rb	175X	10	5.5	31	[5.5–25]	39	1–955
				10	(25–70]	85	
				5	(70–955]	224	
S	175X	60	70	40	[70–200]	44	1.19–16800
				20	(200–300]	24	
				12	(300–16800]	122	
Sr	175X	10	4	20	[4–50]	28	3–4932
				6	(50–100]	22	
				3	(100–4932]	324	
V	175X	30	6	46	[6–25]	46	2.5–580
				18	(25–50]	64	
				6	(50–580]	258	
Y	175X	10	2.8	42	[2.8–10]	68	0.24–126
				21	(10–30]	217	
				12	(30–126]	71	
Zn	175X	20	4	22	[4–30]	33	1–341
				11	(30–70]	91	
				8	(70–341]	246	
Zr	175X	10	6	35	[6–25]	15	0.65–804
				5	(25–804]	356	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
Precision: Estimated precision
*: Drift dominates precision, see text.
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 3. Carbon and F analyses. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (%)	LRC (%)	Precision at 95% conf. level			Data range (%)
				Precision (%)	Range (%)	N of sample pairs	
C_{tot}	811L	0.01	0.05	48	[0.045–0.08]	36	0.001–10.6
				17	(0.08–10.6]	56	
$C_{noncarb}$	816L	0.02	0.05*	–	–	–	–
F	707I	0.01	0.055	32	[0.055–0.07]	78	0.01–1.51
				17	(0.07–0.10]	67	
				16	(0.10–1.51]	55	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
*$C_{non-carb}$: No duplicate analyses performed, hence LRC asssumed to be same as for C_{tot}.
Precision: Estimated precision
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 4. Elements analysed by aqua regia digestion and ICP-AES method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (ppm)	LRC (ppm)	Precision at 95% conf. level			Data range (ppm)
				Precision (%)	Range (ppm)	N of sample pairs	
Al	511P	15	1100	10*	[1100–95600]	373	1000–95600
B	511P	5	4.5	50	[4.5–23.15]	19	0.034–23.15
Ba	511P	1	10	15* 10 7	[10–50] (50–100] (100–1060]	89 86 179	3.6–1060
Ca	511P	50	=DL	12* 14	[100–5000] (5000–246500]	230 145	100–246500
Co	511P	1	0.9	12 8	[0.9–5.0] (5.0–114]	73 288	0.5–114
Cr	511P	1	5	14* 7 16	[5–30] (30–175] (175–2235]	162 134 28	1.7–2235
Cu	511P	1	3	21 10	[3–13] (13–576]	122 210	0.85–576
Fe	511P	50	2300	10*	[2300–103650]	372	1300–103650
K	511P	200	100	31 8 5	[100–1500] (1500–6000] (6000–30500]	74 107 194	100–30500
La	511P	1	1.3	10* 14	[1.3–40] (40–206]	283 68	0.03–206
Li	511P	1	3.5	11* 7	[3.5–5.0] (5.0–395]	11 327	0.7–395
Mg	511P	50	=DL	10* 8	[100–5000] (5000 249000]	120 255	100–249000
Mn	511P	1	50	16 12 9	[50–100] (100–300] (300–1165]	22 166 183	8.7–1165
Mo	511P	2	2.6	47	[2.6–14.5]	18	0.08–14.5
Na	511P	100	150	32* 12	[100–2000] (2000–12150]	337 30	100–12150
Ni	511P	3	3.5	19 10 7	[3.5–10] (10–30] (30–2240]	120 101 122	1.5–2240
P	511P	50	6	13 7	[6–200] (200–4975]	87 287	5–4975
Pb	511P	10	8.7	38	[8.7–46]	75	0.18–46
S	511P	20	14.3	28 14	[14.3–300] (300–16700]	182 131	3.9–16700
Sc	511P	0.5	0.4	13* 6	[0.4–8] (8–26.5]	287 74	0.09–26.5
Sr	511P	1	1.2	15* 12	[1.2–40] (40–622]	328 39	0.38–622
Th	511P	6	5.6	20* 15	(5.6–15] (15–66.5]	167 94	0.06–66.5
Ti	511P	2	=DL	9 7	[6.1–2000] (2000–7535]	210 165	6.1–7535
V	511P	1	0.6	15 8 6	[0.6–10] (10–90] (90–339]	54 225 91	0.17–339
Y	511P	0.5	0.15	15* 12	[0.15–6] (6–101.2]	181 194	0.15–101.2
Zn	511P	1	2	8 6	[2–40] (40–324]	134 235	0.2–324

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
Precision: Estimated precision
 *: Drift dominates precision, see text.
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 5. Elements analysed by aqua regia digestion and GFAAS method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (ppm)	LRC (ppm)	Precision at 95% conf. level			Data range (ppm)
				Precision (%)	Range (ppm)	N of sample pairs	
As	511U	0.2	3*	42	[0.075–1.0]	191	0.075–498
				60	(1.0–3.0]	141	
				50	(3.0–498]	43	
Bi	511U	0.02	0.04	42	[0.04–0.07]	47	0.004–11.345
				34	(0.07–0.2]	69	
				38	(0.2–11.345]	45	
Se	511U	0.03	0.055	34	[0.055–0.2]	92	0.004–2.64
				18	(0.2–2.64]	53	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
As: Precision not stable, LRC assumed to be 3 ppm.
Precision: Estimated precision
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 6. Elements analysed by aqua regia leach and GFAAS method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (ppb)	LRC (ppb)	Precision at 95% conf. level			Data range (ppb)
				Precision (%)	Range (ppb)	N of sample pairs	
Au	521U	0.2	2.5	86	[0.05–0.5]	218	0.05–32
				80	(0.5–1.0]	70	
				52	(1.0–2.5]	57	
				50	[2.5–15]	26	
Pd	521U	1	5	127	[0.05–5)	331	0.05–28
				49	[5–10]	20	
				18	(10–28]	11	
Te	521U	2	5	136	[0.5–5)	221	0.5–131
				40	[5–20]	93	
				35	(20–131]	53	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
Precision: Estimated precision
Pd: Precision below the LRC calculated using standard deviations instead of M.MAD.
Te: Precision may be over 50% for some intervals at concentrations > 5 ppb.
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Table 7. Elements analysed by total digestion and ICP-MS method. Detection limits reported by the geochemical laboratory and estimates of the lowest reliable concentration and precision.

Element	Method	DL (ppm)	LRC (ppm)	Precision at 95% conf. level			Data range (ppm)
				Precision (%)	Range (ppm)	N of sample pairs	
Ce	308M	0.15	0.22	9	[0.22–75]	264	0.22–483
				16	(75–483]	110	
Co	308M	0.5	2	31	[2–5]	53	0.36–134
				21	(5–20]	172	
				10	(20–134]	120	
Dy	308M	0.1	0.55	30	[0.55–1]	26	0.04–20.8
				14	(1–5]	257	
				12	(5–20.8]	70	
Er	308M	0.15	0.3	32	[0.3–0.5]	28	0.025–14.55
				15	(0.5–14.55]	325	
Eu	308M	0.1	0.09	25*	[0.09 –0.5]	52	0.005–7.49
				15	(0.5–7.49]	316	
Gd	308M	0.15	0.5	22	[0.5–2.0]	65	0.005–23.3
				12	(2.0–23.3]	303	
Hf	308M	0.5	0.12	26	[0.12–2.0]	67	0.06–15.85
				19	(2.0–15.85]	304	
Ho	308M	0.1	0.09	28	[0.09–0.2]	33	0.005–4.39
				14	(0.2–4.39]	325	
La	308M	0.1	0.55	30	[0.55–5.0]	30	0.095–239
				12	(5.0–239]	337	
Lu	308M	0.1	0.03	28	[0.03–0.12]	81	0.01–3.66
				17	(0.12–3.66]	283	
Nb	308M	0.2	0.16	13	[0.16–2.0]	41	0.096–64.85
				10	(2.0–64.85]	331	
Nd	308M	0.2	0.2	23	[0.2–5.0]	25	0.18–209
				9	(5.0–30]	213	
				13	(30–209]	134	
Pr	308M	0.1	0.74	9	[0.74–8.0]	219	0.02–58.8
				15	(8.0–58.8]	135	
Rb	308M	0.2	0.6	15	[0.6–15]	47	0.07–926
				7	(15–926]	317	
Sc	308M	0.3	2.8	29	[2.8–5]	47	0.39–74.35
				14	(5–30]	228	
				11	(30–74.35]	60	
Sm	308M	0.2	0.5	16	[0.5–2]	63	0.09–30
				12	(2–7]	231	
				15	(7–30]	72	
Ta	308M	0.2	0.06	26	[0.06–0.4]	130	0.002–12.5
				13	(0.4–1]	164	
				15	(1–12.5]	60	
Tb	308M	0.1	0.08	11*	[0.08–1]	307	0.005–2.73
				14	(1–2.73]	59	
Th	308M	0.5	0.13	18	[0.13–48.5]	364	0.04–48.5
Ti	308M	10	=DL	12*	[59.8–18000]	374	59.8–18000
Tm	308M	0.1	0.03	32	[0.03–0.1]	59	0.005–2.89
				17	(0.1–2.89]	306	
U	308M	0.2	0.08	35	[0.08–0.2]	23	0.004–13.2
				22	(0.2–3]	253	
				25	(3–13.2]	82	
V	308M	0.5	2	21	[2–10]	37	0.31–517
				9	(10–200]	276	
				6	(200–517]	52	
Y	308M	0.1	=DL	11	[0.17–10]	90	0.17–119
				6	(10–20]	95	
				12	(20–119]	189	
Yb	308M	0.15	0.22	27	[0.22–1]	99	0.07–23.7
				17	(1–3]	212	
				14	(3–23.7]	51	
Zr	308M	0.5	3	18	[3–100]	99	0.91–649
				16	(100–200]	190	
				24	(200–649]	84	

DL: Detection limit reported by the geochemical laboratory
LRC: Estimated lowest reliable concentration
Precision: Estimated precision
*: Drift dominates precision, see text.
Range: Concentration range for which the precision was estimated
N of sample pairs: Number of sample pairs used in the precision estimate
Data range: Range of sample pair mean concentration data

Analytical drift

Drift is defined here as a systematic change with time in the concentration values of an element measured repeatedly from the same sample with the same method. Drift can result in differences between groups of samples that are not real. For the Rock Geochemical Database of Finland, samples from different areas were analysed at different times, which makes the consideration of drift especially important when comparing data from different geographic locations.

The drift was estimated using the paired normal and laboratory duplicate samples. The laboratory duplicate samples were analysed in batches after the corresponding normal samples. The time between the corresponding analyses varies, but it is long enough to enable the use of the sample pairs to determine the drift. Only samples with concentration equal or greater than the lowest reliable concentration were used to estimate the drift.

The relative error for each sample pair can be defined as:

$$re_i = \frac{\left(C_{N,i} - C_{Z,i}\right)}{\overline{C_i}} \qquad (7)$$

where $C_{N,i}$ and $C_{Z,i}$ are the measured concentrations of the normal (*N*) and laboratory duplicate (*Z*) sample and $\overline{C_i}$ is the average of $C_{N,i}$ and $C_{Z,i}$ in sample pair *i*. Plotting the relative error of an element concentration for each sample pair sorted by the time of analysis of the normal sample gives a visual estimate of the analytical drift (Fig. 6). In these plots, the amount or level of drift at a specific time is expressed as the positive or negative displacement of the average relative error from zero at that time.

The maximum absolute drift is given by the difference between the maximum and minimum drift levels (levels of relative error). A moving median through the paired normal and laboratory duplicate sample data was used to smooth the local variation in the data and estimate the drift levels for each element. Several window widths from two to 30 were tested. Small window widths are sensitive to variations caused by just a few samples, whereas wider windows tend to smooth local variations and give a better estimate of the changes in the drift level. The difference between the maximum and minimum drift levels decreases with increasing window width. The decrease is rapid at small window widths and becomes slower at larger window widths. The maximum absolute drift was estimated for each element using a 20-sample moving median.

Drift is a component of the total precision reported here. The changes in level of drift with time are not abrupt, but gradual. This makes it practically impossible to separate the drift component from the total precision estimates. Those elements, for which the drift component dominates the precision, are noted in Tables 1–7. For these elements, it is especially important to carefully consider the precision when making comparisons.

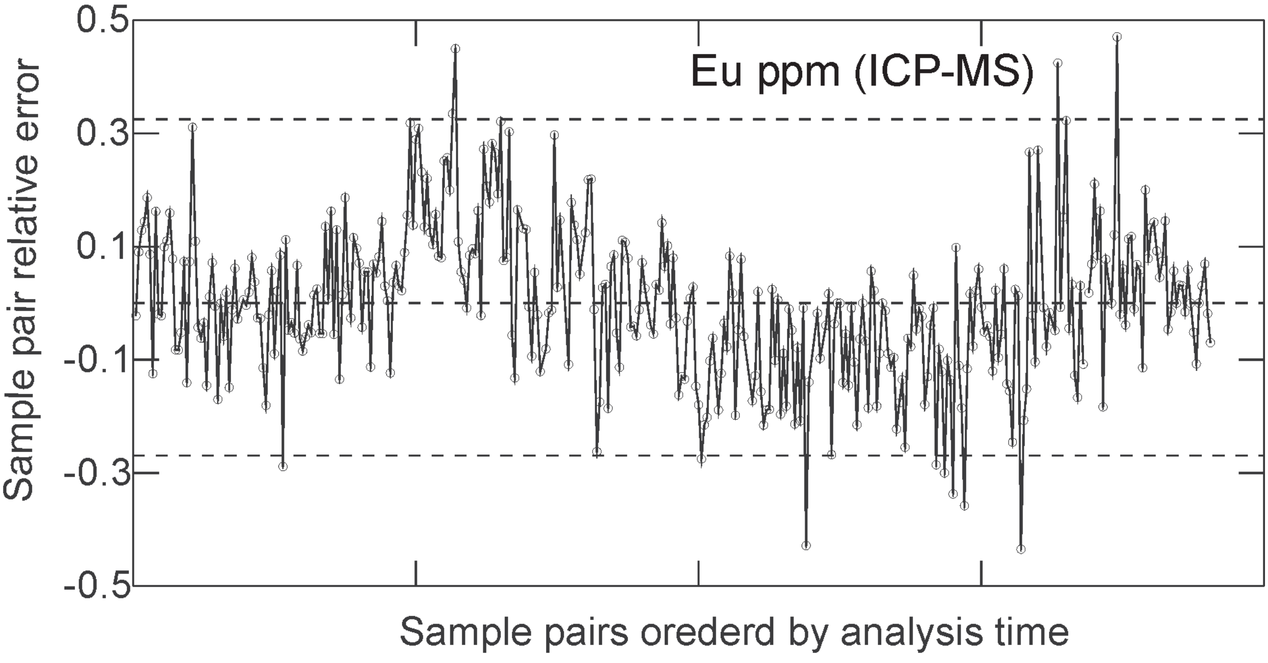

Figure 6. Relative error of Eu (ICP-MS) concentration for each normal sample – laboratory duplicate sample pair sorted by the time of analysis of the normal sample. Drift is indicated by the positive or negative displacement of the level of the relative error from zero.

Accuracy

Accuracy is used here to describe the correctness of the data, i.e., how near the measured value is to the true value. According to the quality assurance protocol of the geochemical laboratory, certified reference materials and other in-house reference samples are measured regularly to monitor the accuracy of the measured concentration data. Measurement values reported by the laboratory for certified reference materials are given in Tables 8–11 for the XRF and ICP-MS methods. Table 12 shows the measurement results of two in-house reference materials for carbon analysis. For the methods utilising aqua regia partial dissolution (ICP-AES, GFAAS), no reliable reference values for certified reference rock materials existed at the time of analysis. However, according to tests reported by Niskavaara (1995), the measured concentrations of several elements (Co, Cu, Fe, Mn, Mo, P, Pb, S, Th and Zn) differ on average less than 10 % from the recommended total values when analysed by the ICP-AES method. For the fluorine analyses, no accuracy data was available.

In Tables 8–12, the method value is the arithmetic mean of the repeated measurements of the certified reference sample and the uncertainty value of the method (u_r) is the standard deviation the method value. The standard deviation represents the spread of a measurement data distribution, and is used as an estimate of precision. The combined standard uncertainty contains the effects of both accuracy and precision and is expressed according to the law of propagation of uncertainty (Taylor & Kuyatt 1994) as:

$$u_c(y) = \sqrt{u_r^2 + \Delta^2} \qquad (8)$$

where Δ stands for method error and is given by the difference between the method value and the reference value. The expanded uncertainty estimates the combined standard uncertainty interval at a required confidence level:

$$U = k * u_c(y) \qquad (9)$$

The coverage factor k equals 2 in Tables 8–12 and hence the confidence level is 95 %. The relative uncertainty is the expanded uncertainty expressed as a percentage of the concentration. The uncertainty of the reference value has not been taken into consideration in the estimation of the combined standard uncertainty.

The proportion of accuracy in the relative uncertainty values reported for the reference samples (Tables 8–11) is on average 0.7 for the XRF analyses and 0.3 for the ICP-MS analyses. For some elements, there is a large difference between the relative uncertainty values for the two reference samples analysed by the same method (e.g., MgO and Y for XRF and Co, Er, Eu, La and Tb for ICP-MS). In these cases, the proportion of the accuracy component in the related uncertainty is much larger for the larger related uncertainty value. The only exceptions to this are Y and Co.

The poor combined uncertainty values for XRF determined Cl, Nb, Pb and S are dominated by the accuracy component. The especially poor values for S might be explained by airborne contamination on the surface of the pressed powder pellet over time, since the same pellet had been used for control analyses for several years (M. Hagel-Brunnström, personal communication 2007). This contamination is not believed to affect fresh samples. However, there is a group of less than 60 samples in the database, for which sulphur concentration determined by the XRF method (120–1300 ppm) is 2–138 times higher than the sulphur concentration determined by the ICP-AES method (<14–400 ppm). The reason for the discrepancy between the XRF and ICP-AES results for these samples is unknown.

The certified reference samples reported in Tables 8–12 do not cover the whole range of concentrations in the database, and for some elements, the concentrations in the reference samples are extremely high and out of the range of normal values appearing in the database. Since the expanded uncertainty (including both accuracy and precision components) depends on the concentration, the reference samples do not give a full picture of the accuracy and precision of the XRF and ICP-MS methods throughout the concentration ranges for all the elements in the database. However, the data gives a general idea of the trustworthiness of the analytical results and indicates that the accuracy of the XRF and ICP-MS methods is similar to that reported by other chemical laboratories.

The accuracy of the analytical results can be roughly inferred from comparison of elemental analyses by two different analytical methods. XRF can be compared to ICP-MS for six elements within the database: Nb, Rb, Ti, V, Y and Zr. Both methods produce total element concentrations. However, if minerals are not completely dissolved then ICP-MS concentrations should be less than XRF concentrations. In addition, the two methods would not correspond with each other if there were problems in the accuracy of the analytical results.

Linear regression using the XRF concentration as the dependent variable and the ICP-MS concentration as the independent variable was used to estimate the correspondence of the two analytical methods. Linear correlation between the results of the two methods is good and the slopes of the regression lines indicate

Table 8. Determination of elements by pressed powder pellet and XRF method in certified reference material SY-3, syenite CCRMP, Canada.

	Method value Bull. 393	Method value $\overline{X}$ (%)	Reference value $\overline{R}$ (%)	Uncertainty value of the method u_r	Combined standard uncertainty $u_c(y)$	Expanded uncertainty *U*	Relative uncertainty U_r (%)
SiO_2	59.11	59.44	59.68	0.162	0.287	0.574	1.0
TiO_2	0.14	0.14	0.15	0.003	0.006	0.013	8.9
Al_2O_3	11.81	12.22	11.76	0.062	0.467	0.935	7.6
Fe_2O_3	6.40	6.36	6.49	0.063	0.141	0.283	4.4
MnO	0.33	0.32	0.32	0.004	0.004	0.009	2.7
MgO	2.42	2.39	2.67	0.021	0.280	0.560	23
CaO	8.32	8.05	8.25	0.043	0.204	0.408	5.1
Na_2O	4.19	4.35	4.12	0.029	0.229	0.459	11
K_2O	4.25	4.15	4.23	0.023	0.081	0.161	3.9
P_2O_5	0.57	0.62	0.54	0.005	0.078	0.157	25
Ba	0.0432	0.0451	0.0450	0.0009	0.0009	0.0017	3.9
Cl	0.0190	0.0366	0.0150	0.0014	0.0216	0.0432	118
Cr	0.0036	0.0022	*0.0011*				
Cu	0.0011	0.0020	0.0017				
Ga		0.0035	0.0027	0.0003	0.0008	0.0016	48
Mo		0.0000	*0.0001*				
Nb	0.0164	0.0210	0.0148	0.0002	0.0062	0.0125	59
Ni	0.0010	0.0017	0.0011				
Pb	0.0183	0.0179	0.0133	0.0003	0.0046	0.0093	52
Rb	0.0198	0.0203	0.0206	0.0003	0.0004	0.0009	4.4
S	0.0550	0.1015	0.0510	0.0017	0.0506	0.1011	100
Sr	0.0308	0.0316	0.0302	0.0004	0.0015	0.0030	9.4
V	0.0056	0.0051	0.0050	0.0004	0.0005	0.0009	18
Y	0.0725	0.0709	0.0718	0.0006	0.0011	0.0022	3.1
Zn	0.0267	0.0259	0.0244	0.0005	0.0015	0.0031	12
Zr	0.0367	0.0373	0.0320	0.0004	0.0053	0.0107	29

Number of measurements: 36.
The time of analysis: 07.05.1996–08.10.1996.
Method value Bull. 393 is the measured value published by Sandström (1995).
Reference values are based on Govindaraju (1994). Numbers in italics are informative values.
Explanation of the columns is given in the text.
Uncertainty values were not calculated when the reference value was lower than the laboratory detection limit.

Table 9. Determination of elements by pressed powder pellet and XRF method in certified reference material BR, CRPG basalt, France.

	Method value Bull. 393	Method value $\overline{X}$ (%)	Reference value $\overline{R}$ (%)	Uncertainty value of the method u_r	Combined standard uncertainty $u_c(y)$	Expanded uncertainty U	Relative uncertainty U_r (%)
SiO_2	37.59	37.95	38.20	0.088	0.266	0.531	1.4
TiO_2	2.62	2.64	2.60	0.025	0.044	0.089	3.4
Al_2O_3	10.04	10.44	10.20	0.057	0.244	0.487	4.7
Fe_2O_3	12.65	12.63	12.88	0.132	0.281	0.562	4.4
MnO	0.20	0.19	0.20	0.002	0.007	0.014	7.3
MgO	13.35	13.41	13.28	0.094	0.162	0.324	2.4
CaO	13.57	13.18	13.80	0.059	0.622	1.244	9.4
Na_2O	3.17	3.34	3.05	0.023	0.293	0.587	18
K_2O	1.37	1.33	1.40	0.007	0.071	0.141	11
P_2O_5	1.10	1.16	1.04	0.010	0.117	0.234	20
Ba	0.1005	0.1019	0.1050	0.0013	0.0033	0.007	6.6
Cl	0.0400	0.0562	0.0350	0.0009	0.0212	0.042	76
Cr	0.0366	0.0356	0.0380	0.0006	0.0025	0.005	14
Cu	0.0077	0.0077	0.0072	0.0004	0.0006	0.001	16
Ga		0.0023	0.0019				
Mo		0.0000	0.00024				
Nb	0.0117	0.0117	0.0098	0.0002	0.0019	0.004	33
Ni	0.0269	0.0280	0.0260	0.0007	0.0021	0.004	15
Pb	0.0022	0.0019	0.0005				
Rb	0.0043	0.0049	0.0047	0.0003	0.0003	0.001	13
S	0.0390	0.0824	0.0390	0.0013	0.0435	0.087	105
Sr	0.1367	0.1362	0.1320	0.0010	0.0043	0.009	6.3
V	0.0337	0.0288	0.0235	0.0014	0.0055	0.011	38
Y	0.0030	0.0027	0.0030	0.0002	0.0004	0.001	27
Zn	0.0176	0.0172	0.0160	0.0004	0.0013	0.003	15
Zr	0.0304	0.0300	0.0260	0.0009	0.0041	0.008	27

Number of measurements: 36.
The time of analysis: 07.05.1996–08.10.1996.
Method value Bull. 393 is the measured value published by Sandström (1995).
Reference values are based on Govindaraju (1994).
Explanation of the columns is given in the text.
Uncertainty values were not calculated when the reference value was lower than the laboratory detection limit.

Table 10. Determination of elements by total digestion and ICP-MS method in certified reference material SY-2, CCRMP syenite, Canada.

	Method value $\overline{X}$ (%)	Reference value $\overline{R}$ (%)	Uncertainty value of the method u_r	Combined standard uncertainty $u_c(y)$	Expanded uncertainty U	Relative uncertainty U_r (%)
Ce	157	175	7.16	19.4	38.7	25
Co	8.29	8.6	2.73	2.74	5.49	66
Dy	19.6	18	1.03	1.87	3.73	19
Er	14.6	12.4	0.74	2.32	4.64	32
Eu	2.36	2.42	0.13	0.15	0.29	12
Gd	17.2	17	1.24	1.26	2.52	15
Hf	8.01	7.7	0.58	0.66	1.32	17
Ho	4.45	3.8	0.22	0.69	1.38	31
La	67.3	75	4.65	8.99	18.0	27
Lu	2.77	2.7	0.15	0.16	0.33	12
Nb	28.4	29	1.32	1.44	2.88	10
Nd	74.6	73	3.63	3.97	7.95	11
Pr	19.5	18.8	0.91	1.16	2.32	12
Rb	212	217	9.38	10.7	21.4	10
Sc	6.98	7.0	0.67	0.67	1.34	19
Sm	15.5	16.1	0.81	0.99	1.98	13
Ta	1.73	2.01	0.14	0.31	0.62	36
Tb	3.00	2.5	0.16	0.52	1.05	35
Th	349	379	24.1	38.8	77.6	22
Ti	787	899	57.4	126	252	32
Tm	2.36	2.1	0.12	0.29	0.58	25
U	249	284	19.8	40.5	81.1	33
V	49.3	50	2.80	2.88	5.76	12
Y	136	128	6.28	9.81	19.6	14
Yb	17.2	*17*	0.87	0.88	1.77	10
Zr	282	280	15.1	15.2	30.4	11

Number of measurements: 327.
The time of analysis: 21.02.1995–02.02.2000.
Reference values are based on Govindaraju (1994). Figures in italics are informative values.
Explanation of the columns is given in the text.

Table 11. Determination of elements by total digestion and ICP-MS method in certified reference material SDC-1, USGS mica schist, USA.

	Method value $\overline{X}$ (%)	Reference value $\overline{R}$ (%)	Uncertainty value of the method u_r	Combined standard uncertainty $u_c(y)$	Expanded uncertainty U	Relative uncertainty U_r (%)
Ce	87.3	93	4.01	6.94	13.9	16
Co	17.1	17.9	1.33	1.56	3.12	18
Dy	6.42	6.7	0.38	0.47	0.95	15
Er	3.98	4.1	0.23	0.26	0.52	13
Eu	1.52	1.71	0.09	0.21	0.42	27
Gd	7.42	7.2	0.66	0.70	1.40	19
Hf	7.54	8.3	0.85	1.14	2.27	30
Ho	1.32	1.5	0.07	0.19	0.39	29
La	41.0	42	2.04	2.27	4.53	11
Lu	0.59	0.53	0.04	0.07	0.15	25
Nb	17.6	18	0.84	0.92	1.83	10
Nd	40.2	40	2.05	2.07	4.13	10
Pr	10.5	9.8	0.51	0.88	1.75	17
Rb	119	127	5.17	9.74	19.5	16
Sc	15.9	17	1.09	1.51	3.03	19
Sm	7.88	8.2	0.46	0.56	1.12	14
Ta	1.13	1.21	0.07	0.11	0.22	20
Tb	1.14	1.18	0.07	0.08	0.17	15
Th	10.9	12.1	0.78	1.42	2.84	26
Ti	5689	6054	349	506	1012	18
Tm	0.60	0.65	0.04	0.07	0.13	22
U	2.60	3.14	0.25	0.60	1.19	46
V	94.3	102	4.58	8.92	17.8	19
Y	39.6	40	1.96	2.00	4.00	10
Yb	3.99	4	0.25	0.25	0.50	13
Zr	289	290	27.0	27.0	54.1	19

Number of measurements: 341.
The time of analysis: 21.02.1995–02.02.2000.
Reference values are based on Govindaraju (1994).
Explanation of the columns is given in the text.

Table 12. Determination of carbon in two in-house reference materials.

Reference material	Method value $\overline{X}$ (%)	Reference value $\overline{R}$ (%)	Uncertainty value of the method u_r	Combined standard uncertainty $u_c(y)$	Expanded uncertainty U	Relative uncertainty U_r (%)
RS 91	0.448	0.448	0.010	0.01	0.02	4.4
$CaCO_3$	12.07	12.0	0.152	0.17	0.33	2.8

RS 91: Phyllite from Karungi, Finland. Number of measurements 59.
$CaCO_3$: Calcium carbonate (J.T. Baker pro analysi). Number of measurements 67.
The time of analysis: 13.03.1998–02.12.1998.
Explanation of the columns is given in the text.

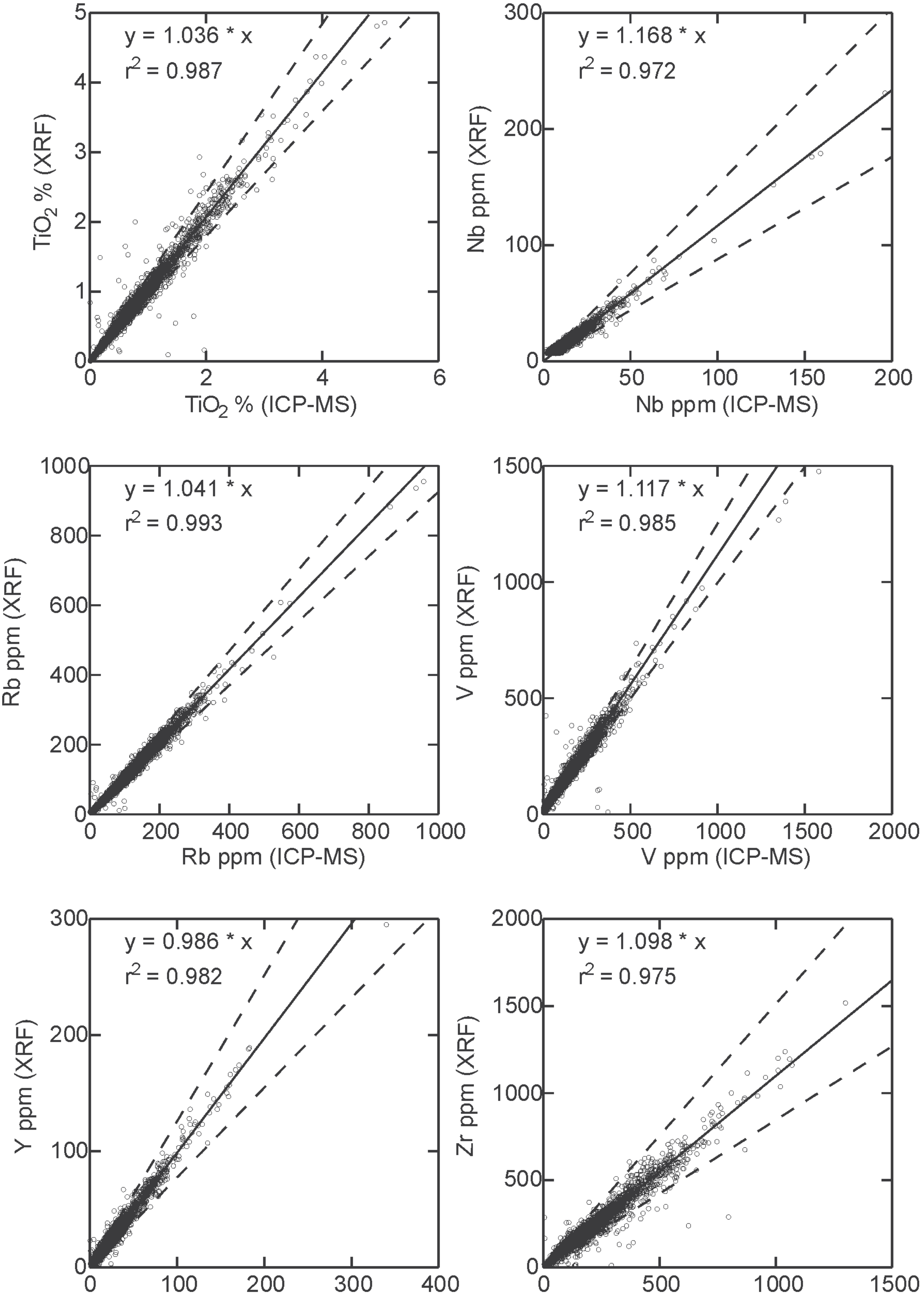

Figure 7. Comparison between XRF and ICP-MS analyses for elements that were analysed by both analytical methods. Linear regression of the XRF values based on the ICP-MS values is shown by the solid line and the equation is given on each figure. The dashed lines show the precision estimated using duplicate sample pairs (Tables 1, 2 and 7). Pearson correlation coefficients are also shown below the regression equations.

that the concentrations yielded by the two methods are very similar for all the six elements (Fig. 7). Most of the variation around the regression line is within the estimated precision of the concentration values at higher concentrations. However, at lower concentrations, the variation around the regression line is slightly larger than the precision of the concentration values. For Ti, Rb and Y, the XRF results are on average within a few percent of the ICP-MS results, but for Nb, V and Zr, the XRF concentrations are on average 10–17 % higher than the ICP-MS results. The accuracy of Nb and Zr concentrations is very good and that of V is quite good for the ICP-MS method, whereas the accuracy of these elements is much poorer for the XRF method (Tables 8–11). Hence, the linear regression results indicate that the XRF results for these elements are systematically somewhat higher than the correct values.

DATABASE CONTENTS

The Rock Geochemical Database of Finland contains the concentration of a wide variety of elements in 6544 rock samples taken from the bedrock throughout Finland. Depending on the analytical method, the concentrations are either total or partial determinations of the actual amount of the element in the rock. The variable names used in the database for the various elements provide the name of the analysed element and the analytical method e.g., NI_XRF is Ni analysed by the XRF method, EU_ICPMS is Eu analysed by the ICP-MS method and so on. The concentration unit, laboratory detection limit, lowest reliable concentration, and estimate of precision are given in Tables 1–7 for each element and analytical method. All concentration values that are below the lowest reliable concentration are listed in the database as "<LRC", where LRC is the numeric value of the lowest reliable concentration for the element and analytical method in question. This convention is selected to prevent the unintentional use of uncertain values in calculations. It is up to the user to choose how to use the "<LCR" values. Statistical techniques to analyze censored data are discussed by Helsel (2005).

In addition to elemental concentrations, a variety of other attributes of the samples are included in the database (Table 13). The variables that describe these attributes are listed below and in supplemental Tables (14–21). Character variables have '$' as the last character in their name.

The variable LABNUM provides a unique laboratory sample number for each different sampling location. The value of LABNUM functions as a link to the PDF file containing the scanned field observation form.

The variables XCOORD and YCOORD provide the exact geographic location of the bedrock sample in the rectangular grid-coordinates of the Finnish Uniform Coordinate System (YKJ). The system is defined by the following parameters: Ellipsoid = International 1924, Zone = 3, Central meridian = 27, False easting = 3500000, Scale factor at central meridian = 1.000, Zone width = country wide.

The variables MAP100$ and MAP20$ provide the index number for the 1:100 000 and 1:20 000 scale geologic maps of Finland.

The original field rock names in Finnish are given in the variable FNAME$. The various field names were unified after the fieldwork. The variable ROCKTYPE$ gives the unified rock names.

The variable GROUP provides the major rock group for each sample: sedimentary, volcanic, plutonic or dyke (Table 14). Various schists and gneisses of uncertain origin, as well as altered and metasomatic rocks and chemical sediments have their own separate classes. A rock was classified as sedimentary if there were visible sedimentary structures, clastic or blastoclastic texture, or if the rock was interbedded in sedimentary strata. A volcanic classification required visible volcanic structures or occurrence as a layer within volcanic strata. Lithologies containing more than 50 % volcanic material were also classified as volcanic, as well as dykes clearly associated with volcanism. A rock was classified as a dyke if, on the outcrop scale, it had clear crosscutting relationship with other rock types, or if it was classified as a dyke on the 1:100 000 or 1:20 000 scale bedrock maps. Plutonic rocks were defined as having clearly intrusive contacts and plutonic or hypabyssal texture. Pegmatitic granites were included in the plutonic group.

The variable COMP provides a classification of each sample based on chemical composition into ultramafic, mafic, intermediate, felsic, alkalic, carbonatitic, or heavy metal rich (Table 14).

The variable SUBGROUP provides a rock name for each sample based on the GROUP and COMP variables. Together the variables GROUP, COMP and SUBGROUP define a systematic three-level classification of all 6544 samples in the database (Table 14).

The variables MINERAL1$, MINERAL2$, MINERAL3$, and MINERAL4$ provide the names of up to four qualifier minerals, in order of decreasing abundance. These minerals are normally not considered as essential constituents of the rock type in question, but are useful as modifiers of the rock names.

Table 13. Database variables. Variable names for the element concentrations are explained in the text. Character variables have '$' as the last character in their name.

Variable name	Description	Values / comments
LABNUM	Laboratory sample number	
XCOORD	Geographic x coordinate	See text for details
YCOORD	Geographic y coordinate	See text for details
MAP100$	1:100 000 scale map index number	
MAP20$	1:20 000 scale map index number	
ROCKTYPE$	Rock name	
FNAME$	Field rock name in Finnish	
GROUP	Rock type group	See Table 14 for details
COMP	Rock group composition	See Table 14 for details
SUBGROUP	Rock type subgroup	See Table 14 for details
MINERAL1$	Additional qualifier mineral 1	Qualifier minerals are listed in order of decreasing abundance from MINERAL1$ to MINERAL4$
MINERAL2$	Additional qualifier mineral 2	
MINERAL3$	Additional qualifier mineral 3	
MINERAL4$	Additional qualifier mineral 4	
OREMIN1$	Ore mineral 1	Ore minerals are listed in order of decreasing abundance from OREMIN1$ to OREMIN4$
OREMIN2$	Ore mineral 2	
OREMIN3$	Ore mineral 3	
OREMIN4$	Ore mineral 4	
AVERGRSIZE	Average grain size	See Table 15 for details
MAXGRSIZE	Maximum grain size	See Table 15 for details
METAM	Metamorphic grade	See Table 16 for details
MIGMAT	Degree of migmatisation	See Table 17 for details
DEFORM	Degree of deformation	See Table 18 for details
ALTER	Degree of alteration	See Table 19 for details
UNIT	Lithologic unit of the sample on the 1:1 000 000 scale bedrock map of Finland	See text and the 1:1 000 000 bedrock map for unit codes
AGEGROUP	Apparent age classification of samples	See Table 20 for details
DUPLICATE$	Field duplicate sample indicator	D: field duplicate sample taken
SAMPLER$	Initials of person responsible for observation/sampling	See Table 21 for details
SAMDATE$	Sampling date	Format: DDMMYY
SAMTYPE$	Sampled material type	P: outcrop, R: block field, L: boulder
SAMAREA	Size of outcrop/sampled area	Size in square meters
SAMDEVICE$	Sampling device	P: portable drill, L: hammer
THINSECT$	Thin section index	1: thin section made

The variables OREMIN1$, OREMIN2$, OREMIN3$, and OREMIN4$ provide the names of up to four ore minerals possibly present in the sample, in order of decreasing abundance.

The variables AVERGRSIZE and MAXGRSIZE provide the estimated average and maximum grain size of the sample from field observation grouped into six size classes (Table 15).

The variable METAM provides an estimate of the degree of metamorphism based on mineral assemblages observed in the field (Table 16).

The variable MIGMAT provides an estimate of the degree of migmatisation from field observations (Table 17). Where possible, sampling of mylonitic material was avoided.

The variable DEFORM provides an estimate of the degree of deformation based on the textures observed in the field (Table 18).

The variable ALTER provides an estimate of the degree of alteration from field observations (Table 19). Late alteration processes associated with brittle deformation were recorded and sampling was aimed at the least altered materials.

The variable UNIT provides the assignment of each sample to one of the lithologic units shown on the 1:1 000 000 scale bedrock map of Finland (Korsman et al. 1997). The scale of the 1:1 000 000 bedrock map prohibits fine details to be shown. Hence, many samples that fall within a certain lithologic unit on the map actually belong to another lithologic unit. In addition, many samples near the boundary between two units fall within the wrong unit due to simplifications that are a necessary part of the 1:1 000 000 scale. All samples were first coded into a lithologic unit by GIS software using the geographic coordinates and the digitized 1:1 000 000 bedrock map of Finland.

Samples near the lithologic contacts and those with rock names not fitting the particular lithologic unit were investigated further. These samples were reassigned when appropriate to the correct lithologic unit using all the observations made from the sampling site along with more detailed 1:100 000 or 1:400 000 scale geological maps and other thematic maps, where available. The numbers provided in the variable UNIT are the lithologic unit code numbers used on the 1:1 000 000 bedrock map of Finland with the following exceptions:

Lithologic unit 28 on the 1:1 000 000 scale map is composed of mica gneisses and mica schists with black schist intercalations. In the area between Vaasa and Kokkola the unit consists also of granite and granodiorite and the granitoid samples from this area have been given a separate lithologic unit code 281. Lithologic unit 39 on the 1:1 000 000 scale map is composed of granite and granodiorite with gneissic inclusions. Around the margins of the large granitic area of unit 39 north of Rovaniemi, there are mica gneisses that have been separated as lithologic unit 391. Seven granitic samples geographically associated with the Lapland greenstone belt were originally mapped as lithologic unit 39 but were reclassified as lithologic unit 501. Some granitic samples in NW Lapland originally mapped as lithologic unit 76 were reclassified as belonging to lithologic unit 39.

The variable AGEGROUP provides age classification for each sample based on the inferences made in the field and from geologic maps (Table 20). The inferred age in the variable AGEGROUP does not always match the age of the assigned lithologic unit as given on the 1:1000 000 scale bedrock map, because variable AGEGROUP was coded based on the 1:100 000 bedrock maps and other more detailed maps used by the field teams.

Table 14. Rock classification used in the database.

GROUP		COMP		SUBGROUP	
1	Sedimentary rock	1	Felsic	0	Other/undetermined
		2	Intermediate	1	Quartz-rich sandstone
				2	Sandstone/quartz-feldspar schist/gneiss
				3	Greywacke/mica schist/mica gneiss
				4	Clay-/siltstone/pelite/mica schist/mica gneiss
				5	Graphite-bearing schist/gneiss
		6	Carbonate rock	0	Other/undetermined
				1	Calcitic limestone
				2	Calcite-dolomite limestone
				3	Dolomite
		7	Heavy metal rich	0	Other/undetermined
				1	Iron formation
2	Volcanic rock	1	Felsic	0	Other/undetermined
		2	Intermediate	1	Lava
		3	Mafic	2	Pyroclastic rock
		4	Ultramafic	3	Epiclastic rock
		5	Alkalic	4	Volcanic dyke rock
		6	Carbonatitic		
3	Dyke rock	1	Felsic	0	Other/undetermined
				1	Pegmatite
				2	Aplite
				3	Quartz-porphyry
		2	Intermediate	0	Other/undetermined
		3	Mafic	0	Other/undetermined
				1	Diabase
		8	Other	0	Other/undetermined
				1	Diabase
4	Plutonic rock	1	Felsic	0	Other/undetermined
				1	Granite
				2	Granodiorite
				3	Tonalite/trondhjemite
				4	Quartz diorite
				5	Quartz monzodiorite/monzodiorite
				6	Quartz monzonite/monzonite
				7	Syenitic rock
				8	Alkali feldspar granitoid

Table 14. Continued.

GROUP		COMP		SUBGROUP	
		2	Intermediate	0	Other/undetermined
				1	Granite
				2	Granodiorite
				3	Tonalite
				4	Quartz diorite
				5	Quartz monzodiorite/monzodiorite
				6	Quartz monzonite/monzonite
				7	Syenitic rock
				8	Alkali feldspar granitoid
		3	Mafic	0	Other/undetermined
				1	Diorite
				2	Gabbro/norite
				3	Anorthosite
		4	Ultramafic	0	Other/undetermined
				1	Peridotite
				2	Pyroxenite
				3	Hornblendite
				4	Dunite
				5	Serpentinite
		5	Alkalic	0	Other/undetermined
				1	Alkali granitoid
				2	Alkali syenite
				3	Foid-bearing syenite
				4	Foid-bearing monzonite/monzodiorite/monzogabbro
				5	Foid-bearing diorite/gabbro
				6	Foid syenite/monzosyenite
				7	Foid monzodiorite/gabbro, foid diorite/gabbro
				8	Foidolite
				9	Ultramafic rock
		6	Carbonatitic	0	Other/undetermined
				1	Calsitic carbonatite
				2	Dolomitic carbonatite
				3	Ferroan carbonatite
				4	Sodic carbonatite
5	Schist, gneiss, amphibolite, skarn rock	1	Felsic	0	Other/undetermined
		2	Intermediate	1	Sedimentary
		3	Mafic	2	Volcanic
		4	Ultramafic	3	Plutonic
		5	Alkalic		
		6	Carbonatitic		
6	Metasomatic rock, chemical sediment	1	Felsic	0	Other/undetermined
				1	Chert,quartz rock
				2	Sericite schist
				3	Cordierite-sillimanite schist/gneiss
				4	Cordierite rock etc.
		2	Intermediate	0	Other/undetermined
		3	Mafic	1	Cordierite/anthophyllite/hypersthene gneiss
				2	Cordierite/anthophyllite/hypersthene rock
		4	Ultramafic	0	Other/undetermined
				1	Soapstone, garbensciefer (feather amphibolite)
				2	Chlorite schist
		5	Alkalic	0	Other/undetermined
				1	Albitite
				2	Unakite
		6	Carbonatitic	0	Other/undetermined
				1	Light coloured skarn
				2	Dark coloured skarn
		7	Heavy metal rich	0	Other/undetermined
				1	Oxide ore
				2	Sulphide ore
7	Other rock				

Table 15. Grain size groupings, based on observation in the field.

AVERGRSIZ MAXGRSIZ	Average grain size Maximum grain size
1	< 0.3 mm
2	0.3–1 mm
3	1–5 mm
4	5–1 mm
5	10–50 mm
6	> 50 mm

Table 16. Degree of metamorphism, based on metamorphic mineral assemblages observed in the field.

METAM	Degree of metamorphism
0	Undetermined
1	Unmetamorphosed
2	Greenschist facies
3	Amphibolite facies
4	Granulite facies

Table 17. Degree of migmatisation, based on observation in the field.

MIGMAT	Degree of migmatisation
0	No migmatisation or veining
1	Occurence of quartz veins
2	Beginning of granitisation and/or incipient melt patches (<5%)
3	Migmatitic area; sampled unit non-migmatized
4	Migmatitic, 5–15% vein material
5	Migmatitic, 15–50% vein material
6	Mylonitic

Table 18. Degree of deformation, based on observation in the field.

DEFORM	Degree of deformation
0	Massive
1	Slightly foliated or schistose
2	Strongly foliated or schistose/gneissose
3	Complexly folded

Table 19. Degree of alteration, based on hand sample observation in the field.

ALTER	Degree of alteration
0	Unaltered
1	Silicified
2	Albitized
3	Skarnified
4	Granitized
5	Fractured
6	Weathered

Table 20. Age of samples divided into groups based on lithologic unit.

AGEGROUP	Age	Comments
0	Undetermined	No age information
1	> 2500 Ma	Archean
2	1600–2500 Ma	Paleoproterozoic in general
3	2300–2500 Ma	Sariolan, Lapponian
4	2000–2300 Ma	Jatulian
5	1950–2000 Ma	Kalevian
6	1850–1950 Ma	Svecofennian
7	1800–1850 Ma	Svecofennian
8	1600–1800 Ma	
9	< 1600 Ma	

The remaining variables include some additional information for each sample. The variable DUPLICATE$ indicates whether a duplicate sample was taken at the sampled location. The variable SAMPLER$ provides the initials of the person responsible for making the observations and taking the sample (Table 21). The variable SAMDATE$ provides the date the sample was collected. The variable SAMTYPE$ provides the nature of the rock from which the sample was collected (Table 13). The variable SAMAREA provides the size of the sampled outcrop in square meters. The variable SAMDEVICE$ provides the device used for collecting the sample (Table 13). The variable THINSECT$ indicates whether a thin section was made. The variable NOTES$ contains updated information concerning the sample received from users of the database.

Table 21. Project personnel during the sampling stage 1990-1995. Initials and number of samples taken are given for those persons, who collected samples in the field.

Person	Task	Initials	No. of samples
Stig Abrahamsson	Assistant/sampling	SHA	55
Alpo Eronen	Assistant/logistics		
Sören Fröjdö	Assistant/sampling	SJF	22
Juha Kauhanen	Assistant/sampling	MJK	155
Esko Korkiakoski	Geologist/planning	EAK	118
Raimo Lahtinen	Geologist/planning/management	RLL	21
Pekka Lestinen	Geologist/planning	PJL	12
Jussi Leveinen	Assistant/sampling	JEL	175
Bo Lindberg	Assistant/sampling	BOL	242
Arto Luttinen	Assistant/sampling	AVL	633
Kari Niiranen	Assistant/sampling	KPN	847
Hannu Ojala	Assistant/sampling	HJO	929
Reijo Puljujärvi	Assistant/logistics		
Mika Räisänen	Assistant/sampling	MHR	1147
Antti Saarelainen	Assistant/sampling	AJS	1480
Reijo Salminen	Management		
Harry Sandström	Chemist/management		
Heimo Savolainen	Assistant/data		
Esko Tamminen	Assistant/sampling	EOT	8
Tuomo Törmänen	Assistant/sampling	TOT	482
Henry Vallius	Geologist	HVV	218

DISCUSSION

The usability of the concentration data depends on the lowest reliable concentration, precision, and accuracy. The first two are important for internal comparisons within the database while all three are important for comparisons with other data.

The lowest reliable concentration and precision were determined using analysis of paired normal and laboratory duplicate samples. This approach was designed to acquire a more realistic estimate of these parameters instead of simply using the detection limit and precision as reported by the laboratory. However, the validity of this approach assumes that the duplicate data set is representative of the whole data set comprising the database. The duplicate data set was generated by producing a laboratory duplicate sample for about every 17th prepared sample. The 375 duplicate samples represent 5.7 % of the sampled locations. The laboratory duplicate samples were analysed in batches along with the rest of the samples. The percentage of samples below the lowest reliable concentration for each element is similar for both the laboratory duplicate data set and the whole database (Table 22). The median difference in the percentage of samples below the lowest reliable concentration between the duplicate data set and the whole database is zero percent units and the maximum difference is 5.1 percent units. There is no systematic pattern in the percentage of concentrations below the lowest reliable concentration between the duplicate data set and the whole database. For some elements, the proportion of concentrations below the lowest reliable concentration is larger for the duplicate data set than for the whole database, whereas for other elements the opposite is true. In addition, the median concentrations of elements are very similar in the duplicate data set and whole database; the average of relative differences in the medians between the two is 3.2 %. On these bases, we are confident that the estimates of lowest reliable concentration and precision are representative of the whole database and define the usability of the concentration data. It must be stressed, however, that the estimates are valid only for the Rock Geochemical Database of Finland, and should not be applied to any other data.

When too many samples are below the lowest reliable concentration, comparisons between samples or groups of samples are difficult. For the whole database, the median number of samples below the lowest reliable concentration for an element is 194, which is three percent of all the samples (Table 22). Fourteen elements have more than 50 % of the samples in the database with concentrations below the lowest reliable concentration. For these elements, estimating the central tendency is problematic. Elements with more than 90 % of their data below the lowest reliable concentration are of very restricted

Table 22. Number of samples with concentration below the lowest reliable concentration (LRC) for the field – laboratory duplicate (N-Z) sample set and the whole database.

				N-Z sample set			Whole database		
Element	Method	LRC		N < LRC	%	N of samples	N < LRC	%	N of samples
SiO_2	XRF	0.02	%	0	0.0	375	0	0.0	6544
TiO_2	XRF	0.005	%	0	0.0	375	9	0.1	6544
Al_2O_3	XRF	0.02	%	0	0.0	375	0	0.0	6544
FeO	XRF	0.01	%	0	0.0	375	0	0.0	6544
MnO	XRF	0.012	%	7	1.9	375	194	3.0	6544
MgO	XRF	0.09	%	7	1.9	375	175	2.7	6544
CaO	XRF	0.004	%	0	0.0	375	0	0.0	6544
Na_2O	XRF	0.05	%	13	3.5	375	150	2.3	6544
K_2O	XRF	0.003	%	2	0.5	375	10	0.2	6544
P_2O_5	XRF	0.024	%	26	6.9	375	456	7.0	6544
Ba	XRF	21	ppm	8	2.1	375	81	1.2	6544
Cl	XRF	45	ppm	61	16.3	375	862	13.2	6544
Cr	XRF	19	ppm	75	20.0	375	1376	21.0	6544
Cu	XRF	17	ppm	190	50.7	375	3539	54.1	6544
Ga	XRF	10	ppm	10	2.7	375	134	2.0	6544
Mo	XRF	2.6	ppm	364	97.1	375	6256	95.6	6544
Nb	XRF	7	ppm	135	36.0	375	2319	35.4	6544
Ni	XRF	14	ppm	140	37.3	375	2635	40.3	6544
Pb	XRF	14	ppm	22	5.9	375	472	7.2	6544
Rb	XRF	5.5	ppm	30	8.0	375	396	6.1	6544
S	XRF	70	ppm	186	49.6	375	3228	49.3	6544
Sr	XRF	4	ppm	2	0.5	375	43	0.7	6544
V	XRF	6	ppm	6	1.6	375	178	2.7	6544
Y	XRF	2.8	ppm	15	4.0	375	264	4.0	6544
Zn	XRF	4	ppm	4	1.1	375	136	2.1	6544
Zr	XRF	6	ppm	3	0.8	375	37	0.6	6544
C_{tot}	LECO	0.05	%	291	77.6	375	5206	79.6	6544
$C_{noncarb}$	LECO	0.05	%	320	85.3	375	5684	86.9	6544
F	ION	0.055	%	184	49.1	375	3566	54.5	6544
Al	ICP-AES	1100	ppm	1	0.3	375	92	1.4	6543
B	ICP-AES	4.5	ppm	348	92.8	375	6032	92.2	6544
Ba	ICP-AES	10	ppm	20	5.3	375	257	3.9	6542
Ca	ICP-AES	50	ppm	0	0.0	375	0	0.0	6542
Co	ICP-AES	0.9	ppm	11	2.9	375	260	4.0	6542
Cr	ICP-AES	5	ppm	50	13.3	375	1004	15.3	6542
Cu	ICP-AES	3	ppm	40	10.7	375	701	10.7	6542
Fe	ICP-AES	2300	ppm	2	0.5	375	52	0.8	6542
K	ICP-AES	100	ppm	0	0.0	375	9	0.1	6542
La	ICP-AES	1.3	ppm	24	6.4	375	308	4.7	6542
Li	ICP-AES	3.5	ppm	35	9.3	375	722	11.0	6542
Mg	ICP-AES	50	ppm	0	0.0	375	3	0.0	6542
Mn	ICP-AES	50	ppm	4	1.1	375	113	1.7	6542
Mo	ICP-AES	2.6	ppm	358	95.5	375	6197	94.7	6544
Na	ICP-AES	150	ppm	8	2.1	375	102	1.6	6542
Ni	ICP-AES	3.5	ppm	28	7.5	375	638	9.8	6542
P	ICP-AES	6	ppm	1	0.3	375	12	0.2	6542
Pb	ICP-AES	8.7	ppm	304	81.1	375	5354	81.8	6544
S	ICP-AES	14.3	ppm	61	16.3	375	1168	17.9	6542
Sc	ICP-AES	0.4	ppm	15	4.0	375	303	4.6	6542
Sr	ICP-AES	1.2	ppm	7	1.9	375	116	1.8	6542
Th	ICP-AES	5.6	ppm	115	30.7	375	2046	31.3	6544
Ti	ICP-AES	2	ppm	0	0.0	375	0	0.0	6542
V	ICP-AES	0.6	ppm	7	1.9	375	124	1.9	6542
Y	ICP-AES	0.15	ppm	1	0.3	375	12	0.2	6542
Zn	ICP-AES	2	ppm	6	1.6	375	194	3.0	6542
As	GFAAS	3	ppm	326	86.9	375	5807	88.7	6544
Bi	GFAAS	0.04	ppm	209	55.7	375	3871	59.2	6544
Se	GFAAS	0.055	ppm	230	61.3	375	4058	62.0	6544

Table 22. Continued.

				N-Z sample set			Whole database	
Element	Method	LRC		N < LRC	%	N of samples	N < LRC	%	N of samples
Au	GFAAS	2.5	ppb	343	91.5	375	6035	92.2	6544
Pd	GFAAS	5	ppb	339	90.4	375	6006	91.8	6544
Te	GFAAS	5	ppb	213	56.8	375	3838	58.6	6544
Ce	ICP-MS	0.22	ppm	0	0.0	374	4	0.1	6541
Co	ICP-MS	2	ppm	28	7.5	374	663	10.1	6541
Dy	ICP-MS	0.55	ppm	21	5.6	374	301	4.6	6541
Er	ICP-MS	0.3	ppm	22	5.9	374	351	5.4	6541
Eu	ICP-MS	0.09	ppm	3	0.8	374	82	1.3	6541
Gd	ICP-MS	0.5	ppm	5	1.3	374	116	1.8	6541
Hf	ICP-MS	0.12	ppm	2	0.5	374	19	0.3	6541
Ho	ICP-MS	0.09	ppm	15	4.0	374	247	3.8	6541
La	ICP-MS	0.55	ppm	6	1.6	374	39	0.6	6541
Lu	ICP-MS	0.03	ppm	7	1.9	374	144	2.2	6541
Nb	ICP-MS	0.16	ppm	1	0.3	374	29	0.4	6541
Nd	ICP-MS	0.2	ppm	1	0.3	374	6	0.1	6541
Pr	ICP-MS	0.74	ppm	19	5.1	374	236	3.6	6541
Rb	ICP-MS	0.6	ppm	9	2.4	374	92	1.4	6541
Sc	ICP-MS	2.8	ppm	42	11.2	374	838	12.8	6541
Sm	ICP-MS	0.5	ppm	10	2.7	374	129	2.0	6541
Ta	ICP-MS	0.06	ppm	18	4.8	374	280	4.3	6541
Tb	ICP-MS	0.08	ppm	8	2.1	374	143	2.2	6541
Th	ICP-MS	0.13	ppm	13	3.5	374	122	1.9	6541
Ti	ICP-MS	10	ppm	0	0.0	374	3	0.0	6541
Tm	ICP-MS	0.03	ppm	8	2.1	374	170	2.6	6541
U	ICP-MS	0.08	ppm	17	4.5	374	212	3.2	6541
V	ICP-MS	2	ppm	9	2.4	374	194	3.0	6541
Y	ICP-MS	2.8	ppm	0	0.0	374	1	0.0	6541
Yb	ICP-MS	0.22	ppm	12	3.2	374	236	3.6	6541
Zr	ICP-MS	3	ppm	1	0.3	374	12	0.2	6541

use. However, since the number of samples below the lowest reliable concentration is not necessarily distributed evenly throughout the database, it is not possible to draw straightforward conclusions on the usability of the data for a particular element within a particular lithologic unit or geographic area.

Analytical precision is a critical parameter for the usability of the concentration data whether internally or externally as compared with other data. The precision should always be taken into consideration when drawing conclusions with regards to individual samples or groups of samples. Because sampling and analysis for samples in the database was mostly done in a systematic manner, one geographic area at the time, there is the possibility of false spatial differences due to analytical drift. Thus, the analytical drift has been studied, as described above, and noted when particularly significant. Since most of the analytical drift is included within the precision estimates it is critical that precision be considered when using this database.

In general, the precision values estimated in this study for the XRF and ICP-MS methods (Tables 1, 2 and 7) are lower than the relative uncertainty values reported by the geochemical laboratory (Tables 8–11), which is understandable since the relative uncertainty includes the effects of both precision and accuracy. Compared with precision values calculated using the method uncertainty values reported by the laboratory (Tables 8–11), the precision values estimated here (Tables 1, 2 and 7) are on average 2.3 times higher for the XRF method and 1.2 times higher for the ICP-MS method. The uncertainty values for the XRF analyses of the reference samples are based on repeated analysis of the same physical pressed powder sample and the uncertainty values for the reference sample ICP-MS analyses are based on repeated dissolution and analysis of portions of the same powdered sample material. On the other hand, the precision estimates in Tables 1, 2 and 7 were calculated using pairs of samples. The latter method includes more variance due to the heterogeneity of the sample material used, the range of compositions covered by the samples and the longer time covered by the analyses of the sample pairs. Considering these differences, the correspondence between the uncertainty values reported by the chemical laboratory and the precision values estimated in this study is good, and the precision values in Tables 1, 2 and 7 can be considered as good descriptors of the reliability of the concentration data.

For some elements, for which the accuracy of the analysis method is very good, the precision value estimated in this report is larger than the combined uncertainty reported by the laboratory. This is because the combined uncertainty in these cases is dominated by the precision component and the precision estimated using the sample pairs is larger than the precision estimated using repeated measurements of the same sample.

In addition to the quality of the concentration data itself, the usability of the database depends on the sampling strategy. While the stratified sampling approach used here has the advantage of good coverage of diverse rock types covering less geographic area, it has the disadvantage that the number of samples for any rock type does not represent the actual area covered by the rock type. Hence, plots simply combining the raw data of several lithologic units might not be representative of the bedrock. Since sampling was more consistent within each lithologic unit, the data should be used only within lithologic units sampled using the same strategy or as grouped according to lithologic unit. Due to the spatially uneven distribution of samples, care must also be used when applying these data for exploration purposes.

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The Rock Geochemical Database of Finland contains chemical data for 6544 bedrock samples throughout Finland. Stratified sampling strategy was used to insure that all lithologies are well represented in the database. Major and trace elements were analysed by XRF, ICP-MS, ICP-AES and GFAAS methods. To assess the quality of the chemical concentration data, precision and analytical drift were estimated using 375 duplicate sample pairs. The lowest reliable concentration for each element and analytical method was determined using the precision estimates. In addition to the chemical concentrations, the database contains the geographic location and several geological attributes for each sample.

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