Variability of XRF and AAS analyses from the Rock Geochemical Laboratory of the Geological Survey of Denmark and Greenland

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Chemical analyses by X-ray fluorescence spectrometry (XRF) and atomic absorption spectrometry (AAS) have been monitored since 1990 by five internal standards. Diagrams of the variability over nine years show that analytical data for major elements, Cr, Cu and V have been stable over the entire period, while data for Ni, Rb and Sr have been stable since 1993. Results for Ba, Zn and Zr have lower precision, but have maintained the same general level. Analysis of international reference material shows that nine of the trace element determinations are accurate or can be adjusted by simple arithmetic to match the recommended values for the reference material.

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Keywords: analysis, analytical methods, geochemical maps, quality control, X-ray fluorescence

The production of geochemical maps for large regions commonly involves the compilation of chemical data obtained over a period of time. In order to base such maps on a consistent data set, it is crucial to monitor chemical data and apply corrections to eliminate any analytical bias that may exist between data sets obtained at different times (Steenfelt 1999). Also in petrologic studies it is common to compare large amounts of chemical data from various sources, and if such data are not carefully controlled analytical biases may be misinterpreted as real differences between the analysed materials. This note presents the results of monitoring of analytical data from one laboratory using internal standards.

The Rock Geochemical Laboratory (RGL) of the Geological Survey of Denmark and Greenland (GEUS), formerly at the Geological Survey of Greenland (GGU), has delivered chemical analyses for geochemical mapping and exploration in Greenland since 1986. Samples of stream sediments and rocks have been analysed by simultaneous X-ray fluorescence spectrometry with a multichannel Philips PW1406 spectrometer on fused samples (using sodium tetraborate as flux) for major elements except sodium and for a short suite of trace elements. Determination of sodium (Na) and copper (Cu) are made by atomic absorption spectrometry (AAS). For details of the methods and instruments see Kystol & Larsen (1999, this volume). Major element analyses from RGL have been monitored by international reference material and have always been very reliable, whereas the quality of the trace element data, except for Cu, has been variable and until now not well documented. The main problem with the use of fused samples for trace element determination is the dilution of the samples by the flux which lowers the concentration of the trace elements and gives poorer counting statistics. The RGL is aware of the problem and stresses to customers that the trace element data are only of reconnaissance character.

Geochemical mapping of Greenland has been undertaken since 1981 and is based on stream sediment samples collected at a density of one sample per 20–50 km^2 (Steenfelt 1993, 1994, 1996). The less than 0.1 mm grain size fractions have been analysed over the years by several methods at a few laboratories besides RGL. In the course of this programme internal standards have been used since 1990 to monitor the quality of analyses from various sources and to detect if there is any bias between data determined by different methods, by the same method determined at different labo-

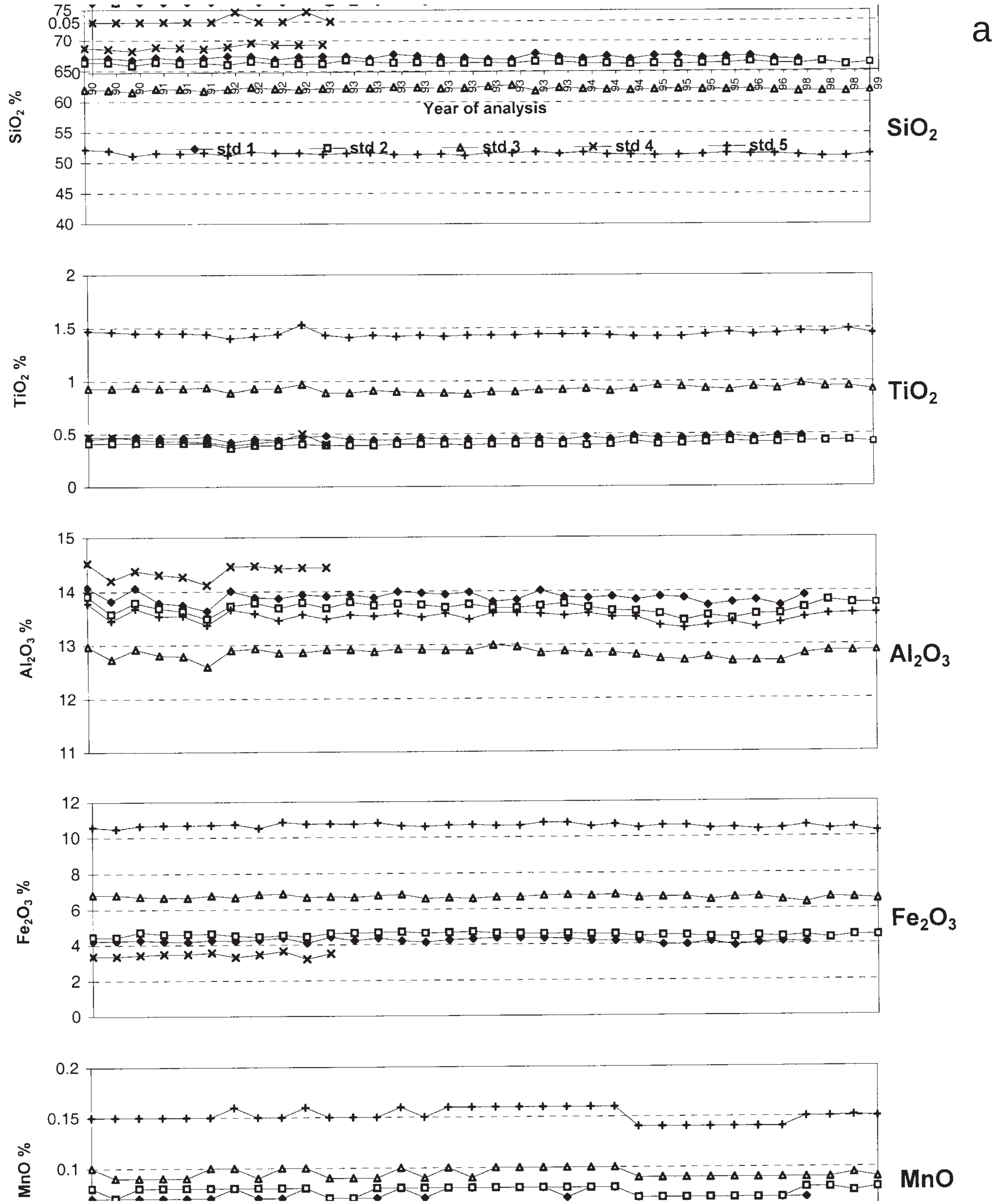

Fig. 1. **a**, **b**: Variability of major element results for five internal standards (std 1–5) in the period 1990 to 1999. The standards are analysed by simultaneous X-ray fluorescence spectrometry on glass discs and atomic absorption spectrometry (for Na) at the Rock Geochemical Laboratory, Geological Survey of Denmark and Greenland. Fe_2O_3 is total iron.

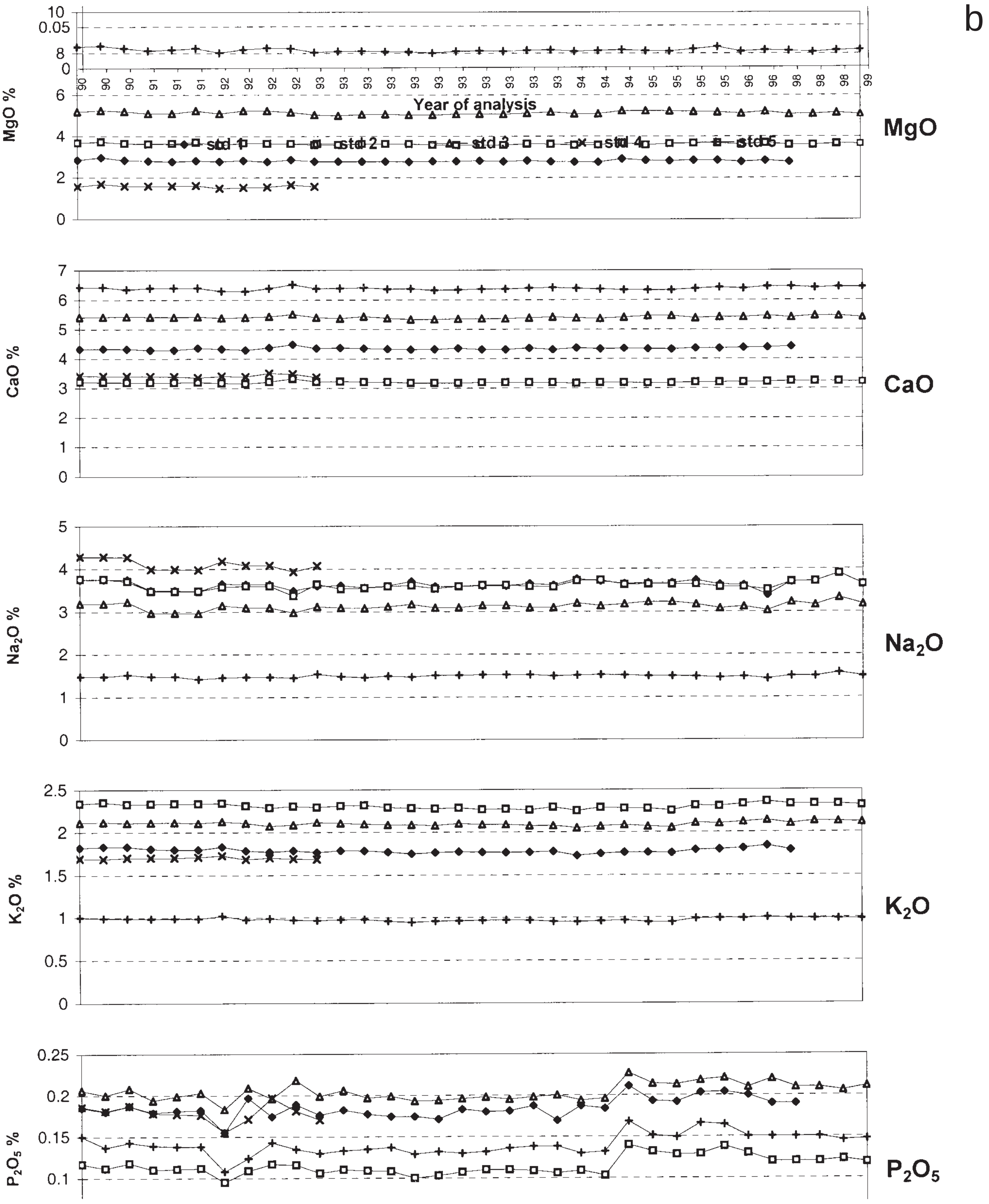

Fig. 1 *(continued)*

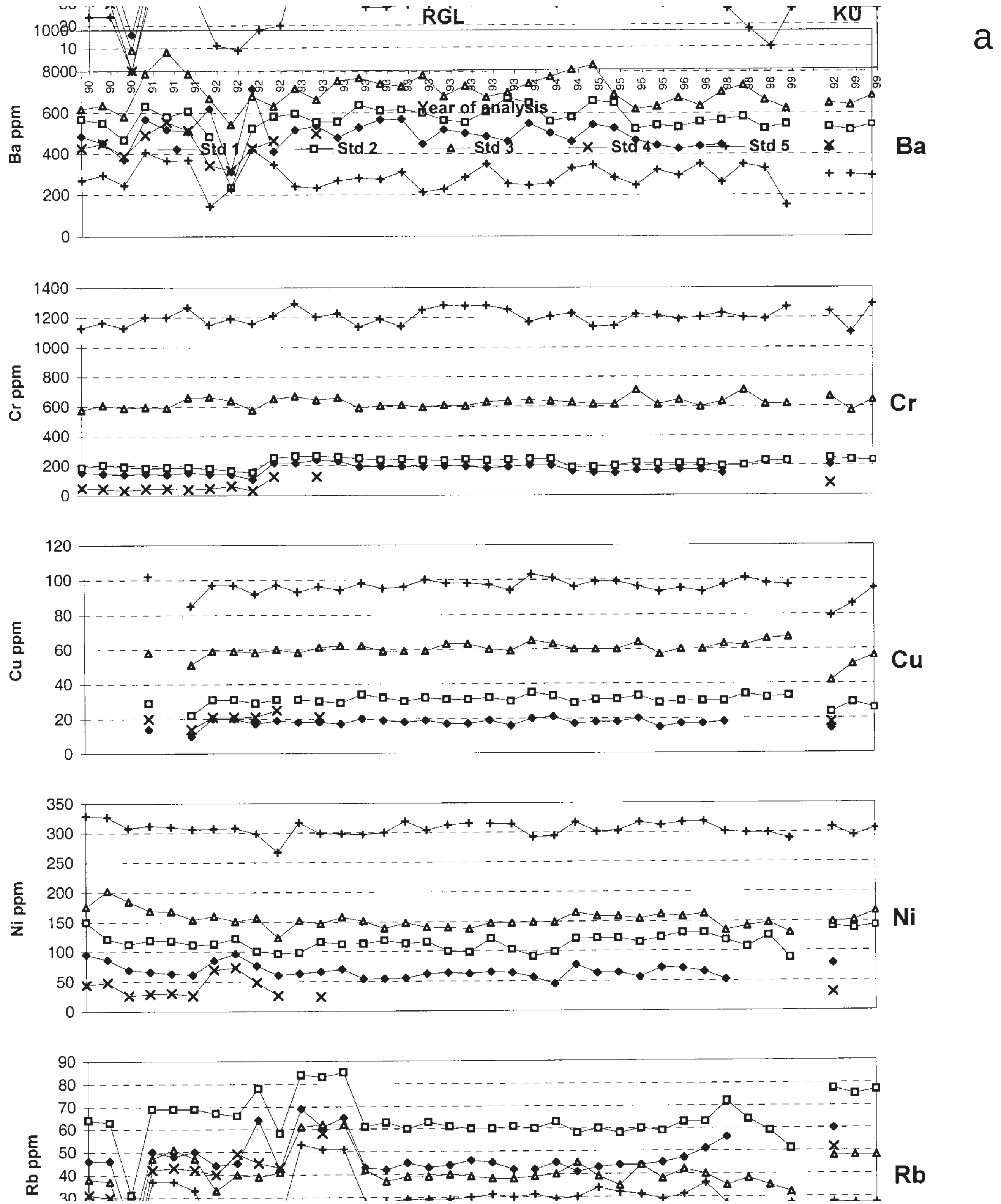

Fig. 2. **a**, **b**: Variability of trace element results for five internal standards (std 1–5) in the period 1990 to 1999. The standards are analysed by simultaneous X-ray fluorescence spectrometry (XRF) on glass discs, and atomic absorption spectrometry (for Cu) at the Rock Geochemical Laboratory (RGL), Geological Survey of Denmark and Greenland, and by sequential XRF on pressed powder pellets by J.C. Bailey, Geological Institute, University of Copenhagen (KU).

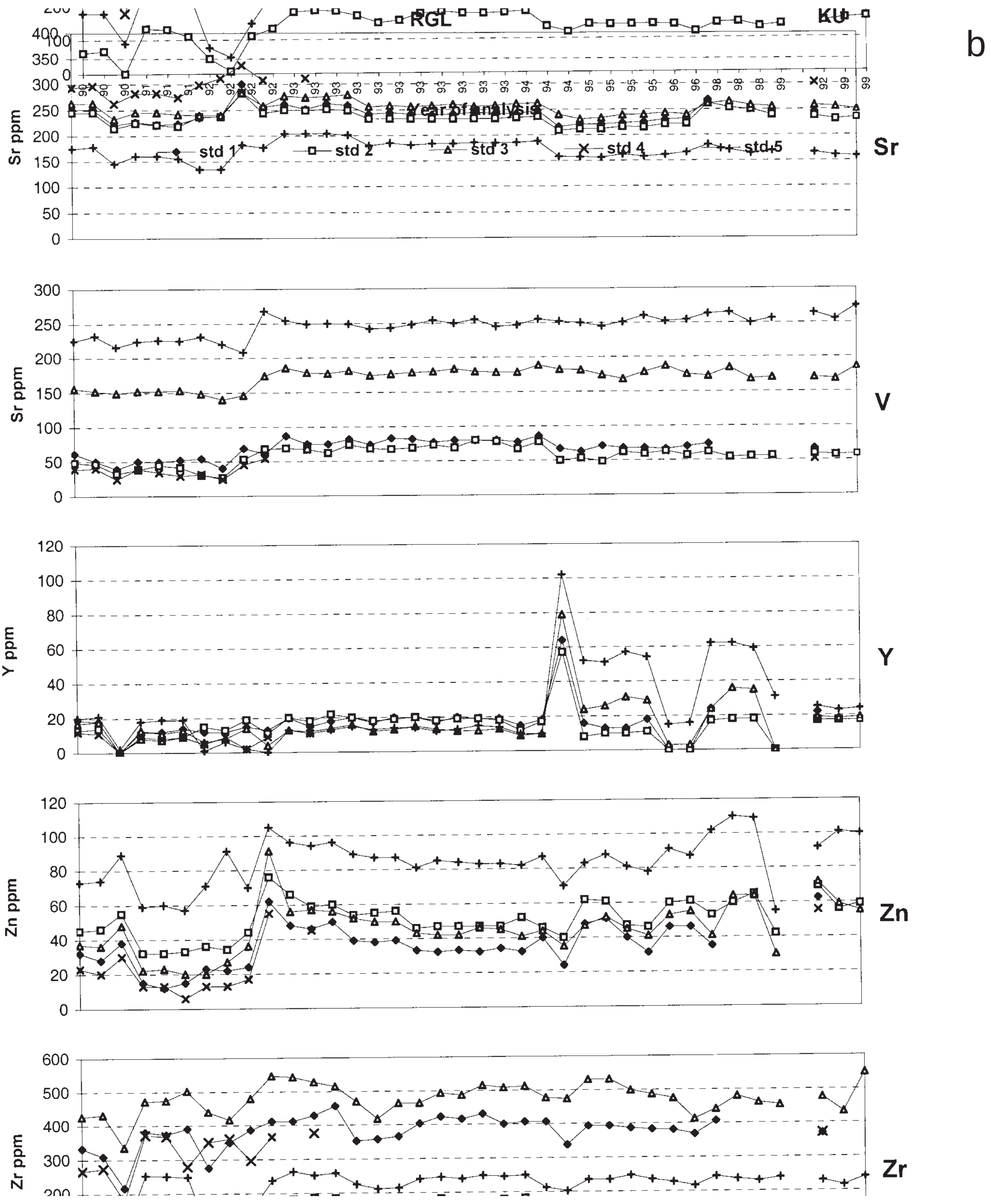

Fig. 2 *(continued)*

Table 1. Chemical analyses of international reference material. Data from RGL and recommended values

	SiO_2		TiO_2		Al_2O_3		Fe_2O_3		MnO		MgO	
	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.
STSD-1	44.83	42.5	0.67	0.8	9.22	9.0	6.46	6.5	0.52	0.5	2.30	2.2
STSD-2	55.13	53.7	0.77	0.8	16.32	16.1	7.52	7.5	0.14	0.1	3.19	3.1
STSD-3	50.94	48.6	0.65	0.7	11.22	10.9	6.19	6.2	0.36	0.3	2.25	2.2
STSD-4	59.83	58.9	0.69	0.8	12.26	12.1	5.62	5.7	0.20	0.2	2.15	2.1
LKSD-1	41.24	40.1	0.50	0.5	7.95	7.8	4.01	4.1	0.09	0.1	1.80	1.7
LKSD-2	59.71	58.9	0.56	0.6	12.25	12.3	6.02	6.2	0.26	0.3	1.73	1.7
LKSD-3	59.86	58.5	0.50	0.5	12.42	12.5	5.81	5.7	0.19	0.2	2.01	2.0
LKSD-4	44.13	41.6	0.35	0.4	5.97	5.9	4.00	4.1	0.07	0.1	0.96	0.9

	CaO		Na_2O		K_2O		P_2O_5		l.o.i.		Sum	
	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.	RGL	Rec.
STSD-1	3.77	3.6	1.88	1.8	1.32	1.2	0.40	0.4	27.85	31.6	99.22	100.1
STSD-2	4.26	4.0	1.81	1.7	2.21	2.1	0.33	0.3	7.59	10.3	99.26	99.7
STSD-3	3.39	3.3	1.65	1.5	1.89	1.8	0.39	0.4	20.31	23.6	99.24	99.5
STSD-4	4.04	4.0	2.80	2.7	1.62	1.6	0.23	0.2	9.53	11.6	98.97	99.9
LKSD-1	10.87	10.8	2.13	2.0	1.16	1.1	0.16	0.2	26.70	29.9	96.61	99.9
LKSD-2	2.25	2.2	1.98	1.9	2.72	2.6	0.30	0.3	11.25	13.6	99.04	100.6
LKSD-3	2.38	2.3	2.41	2.3	2.30	2.2	0.25	0.2	11.23	13.4	99.36	99.8
LKSD-4	1.88	1.8	0.80	0.7	0.87	0.8	0.35	0.3	39.73	43.6	99.11	100.2

Analytical methods at RGL: X-ray fluorescence spectrometry and atomic absorption spectrometry for Na and Cu.
RGL: Rock Geochemical Laboratory of the Geological Survey of Denmark and Greenland.
Rec.: recommended values. l.o.i.: loss on ignition.

ratories or by the same method and laboratory at different times (Steenfelt 1999). The latter is relevant to the aim of this note which is a documentation of the variability of the analytical data delivered by RGL since 1990. The results are of interest to other users of analyses from RGL and to scientists working with analytical quality control.

Internal standards

The internal standards were made from five large samples of stream sediment collected in Greenland in 1989. Four of the streams drain areas of orthogneiss-dominated assemblages with various proportions of supracrustal rocks, whereas the fifth drains Tertiary basalts. Thus the material collected covers the concentration ranges found in most of the stream sediments in West and South Greenland. The samples were dried and sieved and the < 0.1 mm grain size fraction of each was homogenised and split into a large number of 7 g subsamples to serve as internal standards. A set of the five standards has since accompanied every batch of samples submitted for analysis within the geochemical mapping programme. However, standard no. 4 was exhausted during 1993 and no. 1 during 1998.

Variability diagrams

The diagrams in Figs 1, 2 for ten major element oxides and ten trace elements illustrate the temporal variation in the results delivered, i.e. the reproducibility over the nine year period. The analytical data are arranged from left to right in the chronological order they were obtained. The major element results have high reproducibility, whereas some of the trace element results have been fairly variable over time. In cases where the curves are conformable with each other the variation can be ascribed to changes in the analytical conditions, where they are non-conformable the most probable reason for the variation is analytical uncertainty or heterogeneity of the standards. Although RGL sets a recommended lower limit of detection at 50 ppm for the trace elements except Cu (5 ppm), Ba and Y (100 ppm) the customer also receives the values obtained

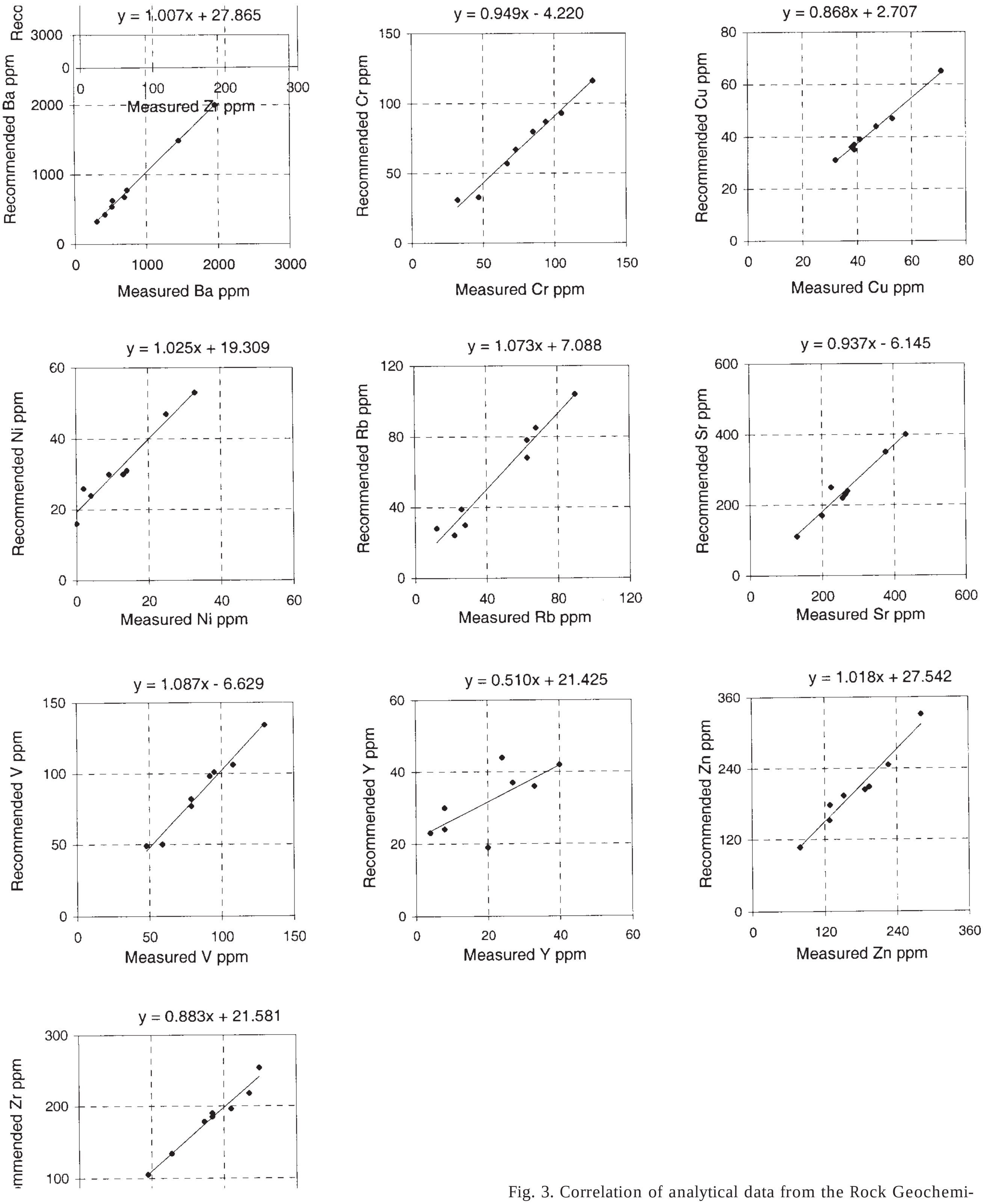

Fig. 3. Correlation of analytical data from the Rock Geochemical Laboratory, Geological Survey of Denmark and Greenland, with recommended values for eight certified international standards (CANMET, STSD 1–4, LKSD 1–4). Determinations of Cu by atomic absorption spectrometry, the others by X-ray fluorescence spectrometry.

below these limits. Therefore it is even possible to examine the quality of the low values.

Results of trace element analysis made on a sequential XRF instrument at the University of Copenhagen using pressed powder pellets and therefore giving more precise determinations are shown for comparison at the right hand side of the diagrams in Fig. 2.

Among the major element results only Al_2O_3 (Fig. 1a) and P_2O_5 (Fig. 1b) display a variability worth observing if results from different periods are to be compared. Trace element diagrams are shown for the elements considered by RGL to be of acceptable quality (Kystol & Larsen 1999, this volume). The remaining trace element data delivered (Nb, Mo, Sn, La and Ce) are totally unreliable at the levels found both in the internal standards and in common rocks. The most reproducible results are those for Cr, Cu and Ni (Fig. 2a), which have been stable throughout the monitored time period. The results for V (Fig. 2b) show a shift in level between 1992 and 1993 but the new level has been maintained since then. The diagram for Sr (Fig. 2b) shows variable results in the beginning of the period followed by more stable results since 1993. However, in the latter period there are three shifts in level, each changing the results 8–9%. There is a good deal of variability for Rb at the beginning and end of the monitored period and three years of good reproducibility in between, even though the concentration of Rb (Fig. 2a) for three of the standards is below the 50 ppm which the laboratory sets as the recommended lower limit of detection (LLD). The results for Ba (Fig. 2a), Zn and Zr (Fig. 2b) are more variable and the curves less conformable than is the case for the other trace elements. This probably reflects a higher degree of analytical uncertainty for these three elements. However, accepting this, the average levels of concentrations measured for each standard appear to have been constant since 1993. The concentrations of Y (Fig. 2b) in the standards are very low compared to the recommended LLD of 100 ppm, and the data delivered from the laboratory are not reliable, although the order of magnitude appears correct until late 1994 by comparison with the data provided by KU. However, as later Y data from RGL have shown erroneous values above 100 ppm, it cannot be recommended to use RGL’s Y data.

Analyses of stream and lake sediment reference material

The accuracy of the RGL analyses has been examined by means of a set of eight internationally certified standards from the Canadian institution CANMET. The CANMET stream sediment standards STSD-1, STSD-2, STSD-3, STSD-4, and lake sediment standards LKSD-1, LKSD-2, LKSD-3, and LKSD-4 (Bowman 1994) were analysed together with the internal standards in 1999 (last data point for RLG analyses in Figs 1, 2). The results for the major elements show very close agreement between measured RGL values and recommended values for the CANMET standards (Table 1). The fact that RGL values for the element oxides are slightly higher than the recommended values is an expected consequence of the lower loss on ignition.

The results for the ten trace elements discussed here are illustrated by scatter diagrams in Fig. 3. All diagrams, except Y, show good correlation between measured and recommended values. The values for Ba, V and Zr are close to recommended values, whereas the other element determinations would need some adjustment to match the recommended level. Because of the linear correlation, such adjustment would only involve simple linear regression.

Concluding remarks

The result of monitoring analyses with internal standards has demonstrated that RGL has had problems keeping the trace element determinations by XRF at constant levels since 1990. For this reason the geochemical mapping programme has preferred to use other trace element analyses whenever possible. On the other hand, the results also show that the reproducibility has been good for certain elements within certain time periods, even at concentration levels close to the recommended lower limit of detection. Furthermore, the variability diagrams demonstrate that some changes are merely a shift in level affecting all standards in the same way, in which case a simple arithmetic calibration can be applied to make data from different periods comparable. In conclusion, monitoring with internal standards has identified element determinations which are generally unreliable, have low precision or are affected by periodic bias. In addition, it has provided a tool for improving the data quality through the possibility for correcting biased results. The correction parameters are found by linear regression of obtained values for the standards of a given set against reference values for each standard. The correction is then applied to the entire batch of samples analysed together with the given set of standards.

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