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Integral Rock Analysis: a new approach in lithogeochemical exploration with use of X-Ray Fluorescence spectrometry

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Abstract

Integral Rock Analysis is a new approach to the acquisition and interpretation of (exploration) geochemical data. An integrated procedure for the rapid and cost-efficient sampling, sample preparation, analysis and statistical treatment of geochemical data is presented. Applicability of the method is discussed on the basis of some examples.

The task of sample preparation is significantly shortened by omitting grinding and homogenization. Flat sections of solid rock-samples, sawn of (small) drill cores, are directly analysed by X-Ray Fluorescence spectrometry (XRF). Analytical results are generally in acceptable agreement with those of conventional methods. Conclusions based on the analysis are not adversely influenced by lower analytical accuracy and precision. Moreover, important additional information with respect to small scale features (mineralogy, texture, alteration processes) is obtained as well. Because the method is non-destructive, the same sections can be investigated by microscope, electron microprobe or X-Ray diffraction. This facilitates the correlation of chemical and mineralogical data and the study of small scale features.

Introduction

Conventional analysis of geological materials requires, depending mainly on grainsize, the collection of relatively large samples which are ground, pulverized and homogenized. A small (representative) sub-sample of the homogeneous powder is prepared for chemical analysis (Fig. 1). For X-Ray Fluorescence analysis (XRF) – in the realm of analytical techniques considered to be rapid and non-destructive – this means the preparation of a pressed powder tablet or the fusion of a glass bead. A separate hand-specimen is generally examined for petrographical description and/or mineralogical determination by X-Ray Diffraction (XRD).

The above described procedure to obtain whole rock geochemical data is often cumbersome, costly and time-consuming. Sample preparation is prone to contamination. Valuable and interesting information regarding the (geological) inhomogeneous element – and mineral-distributions is lost in the various homogenization steps. Still, the quality of the chemical (and mineralogical) analysis may be hampered by insufficient representativity and homogeneity of the sample (e.g. Gy 1982). Correlation of the chemical analysis with the results of mineralogical and petrological investigation is laborious and indirect, because different entities, representative of unequal sized rock volumes, have to be compared.

The Integral Rock Analytical method, at the cost of some loss in analytical quality, can often be

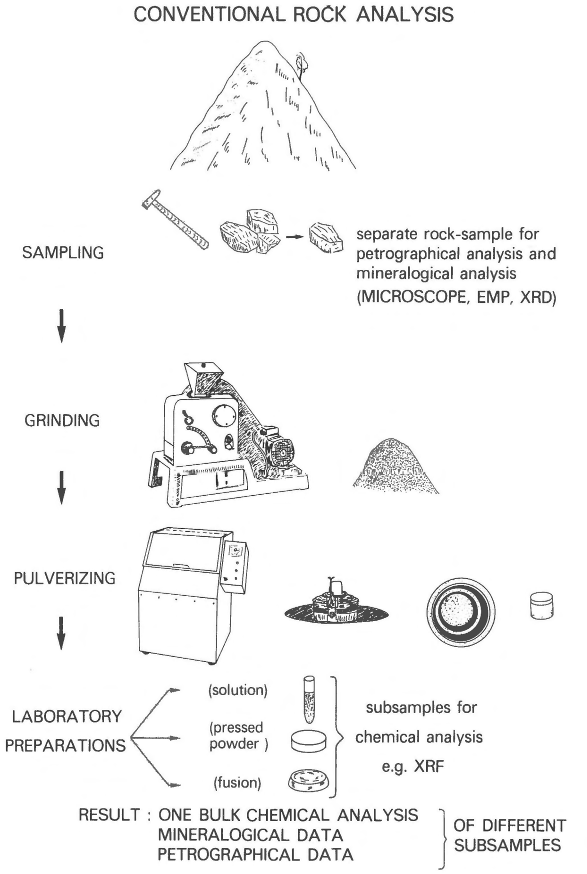


Fig. 1. Schematic representation of conventional sampling and sample preparation.

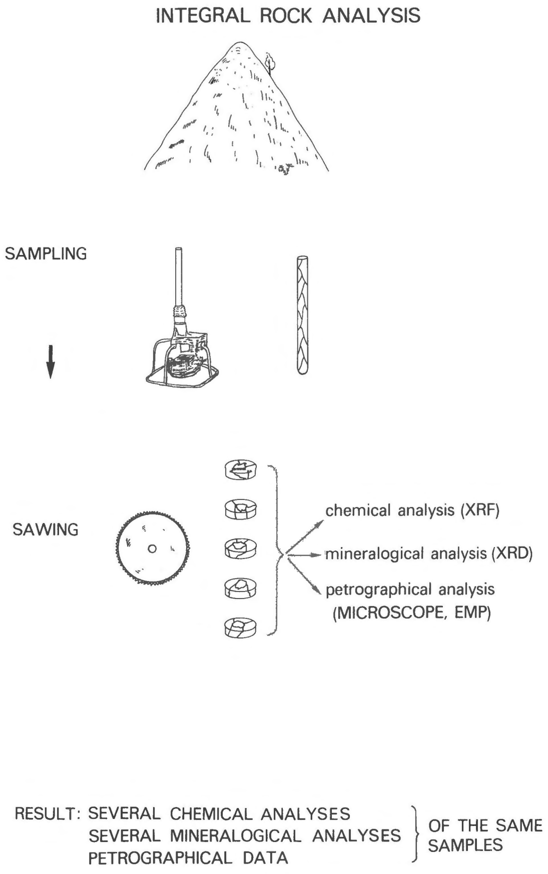


Fig. 2. Schematic representation of sampling and sample preparation following the Integral Rock Analytical method.

applied with similar results and may overcome many of the above difficulties. In contrast to the classical approach in which each step is optimized separately, the method aims to integrally optimize sampling, sample preparation, analysis and interpretation, from economic as well as quality considerations.

Description of the method and techniques used

With Integral Rock Analysis (IRA) flat sections of rock are sawn and directly introduced into the XRF spectrometer (Fig. 2), taking full advantage of the characteristics of X-Ray Fluorescence analysis. The sample preparation step is significantly shorter and cheaper. Possible contamination by grinding and pulverizing is avoided. Because the method is utterly non-destructive, exactly the same samples can subsequently be examined microscopically and submitted to mineralogical analyses by XRD, thus allowing the direct correlation of chemical and mineralogical data. A great advantage is evidently that selection of interesting rock sections can be based on the IRA results. Instead of only one bulkanalysis, several analyses, displaying also the elemental variation and co-variation, are obtained within a relatively small volume of rock.

Several field and laboratory procedures for the easy preparation of rock slices of suitable diameter for the direct introduction into the XRF spectrometer have already been developed and tested. Cores of a suitable diameter (32 mm) are easily collected in the field by means of a small portable drill (Fig. 3). Such a drill typically weighs about 5 kg. A core length of 25 cm requires 5 to 15 minutes of drilling. A full watertank of 20 l (available in backpack construction) is sufficient for 5 to 7 cores. A 25 cm core provides 15 to 20 slices for XRF analysis (on both sides). Slices can also be prepared from drill cores of exploration drilling and hand-specimens. Ideally the XRF apparatus should be adaptable to different core diameters. Cores are cut in slices by ordinary diamond saw to produce flat surfaces. A minimum thickness of ca. 5 mm after sawing is required for infinitely thick samples. Any form of polishing is unnecessary.

Analysis of the rock sections is straightforward and may be compared to the XRF analysis of conventional pressed powder tablets (PPT‘s). Tablets of (international) rock standards are used for calibration. The Rh-Compton method of Feather & Willis (1976) can be used for rapid background and partial matrix correction for many trace elements (K-lines of Ni to Mo, L-lines of Hf to U). For the other elements backgrounds are measured if necessary, no matrix correction procedure has yet been developed. The method would be used to maximum advantage in multi-element analysis with use of a simultaneous spectrometer.

The intensity of the excited radiation exponentionally decreases with depth (Beer‘s Law). This decrease steepens with wavelength. For conventional homogeneous samples the concept of ‘information depth‘ is used to indicate that the effectively analysed volume for e.g. Na is much smaller than that for Zr. However, for all elements the major part of the emitted radiation is produced in the upper layer of a few micrometres. For the heterogeneous IRA sections this means that the analytical result initially represents this upper section only. The average of all analysed sections within one sample, e.g. a small core, is taken to be representative of the sample.

The upper mineral layer is also that part of the sample that may be used for microscopical techniques. Correlation between IRA chemical data and mineralogical composition is therefore expected to be high.

Uni- and multivariate statistical techniques are required for data treatment and interpretation. The detailed data for all analysed sections of each core or sample, as well as averaged data per sample are used in the interpretation. In general a larger number of analyses is made than in the case of a conventional geochemical analysis. (Micro) computer facilities are often needed to handle the large data-set.

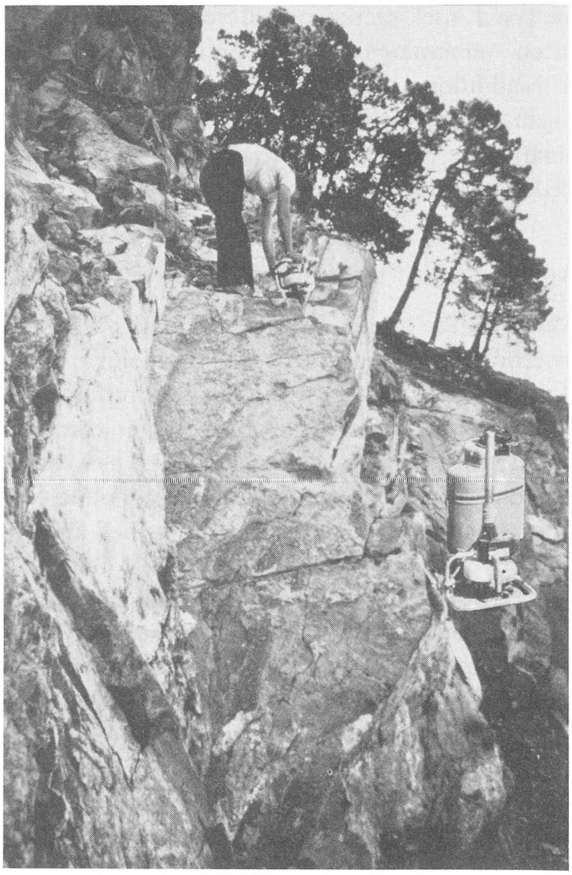


Fig. 3. Photograph, demonstrating the use of a hand-drill (manufacturer: Kupinniemen Konepaja Ky, Finland) in the field.

Standard deviations and correlation coefficients with the IRA method can be computed from extremely local (sample) scale to regional scale. Variation in these parameters from one location to another or from one scale to another may give significant additional information. Correlation patterns e.g. of averaged IRA data (for cores of other sampling units) will tend towards those of data obtained of conventional samples. Correlation patterns using unaveraged IRA data (of the separate analysed rock-sections) will reflect small scale, often mineralogically determined, covariation. This additional small scale information enables the evaluation of the influence of mineralogy and other small scale features on the effects of larger scale processes and vice versa.

Applicability of Integral Rock Analysis

Minimization of sample preparation with XRF has intermittantly been practiced. For geologic materials, which compared to industrial products like cement or ceramics have much larger compositional variation, it is generally applied as a 'quick and dirty' method on the basis of economic considerations. Such techniques as described and applied by amongst others Bowie (1968), Gallagher (1969), Ball et al. (1979), Grout & Gallagher (1980) and Kunzendorf (1972), which in some respects are similar to the XRF part of the IRA method, commonly employ radio-isotope XRF. These instruments have the advantage that they are often portable, but they are less suitable for multi-element analysis and have detection limits several orders higher than conventional instruments (Levinson 1974). They are generally used for a quick semi-quantitative analysis of the heavier element contents only.

Application of minimum sample preparation to unconsolidated material with conventional XRF equipment in exploration geochemistry is reported by Levinson & De Pablo (1975). References to the use in lithogeochemistry are scarce, probably due to the a-priori assumption that results can at best be semi-quantitative.

The IRA project aims to investigate the extent to which the theoretically expected analytical effects are of practical importance in lithogeochemistry.

Requirements of the method are dependent on the type of study. Accurate and precise data are needed in studies concerned with ore grade estimates. However, for many geochemical problems relative values and inter-element relations are of more importance than absolute grades. Levinson (1974) thus stated that in exploration geochemistry, precision is usually more important than accuracy. According to Fletcher (1981) a precision of 10–15% at the 95% confidence level is generally regarded as acceptable for laboratory variability in most exploration programs.

In the literature a number of topics was encountered for which the IRA method may be of special use. Basham et al. (1982), in their study of uranium-bearing accessory minerals and granite fertility, stated that an integrated mineralogical and geochemical procedure is needed to reach confident conclusions. Bowie (1975) claimed that several hundreds of thin sections have to be scanned to detect one single uraninite grain. Therefore IRA, which combines quick chemical scanning opportunities with the possibility of mineralogical study, seems perfectly suited for such an integration. According to Govett (1983) the variance of an element may be of even greater importance than its grade in exploration for ores. With IRA a large number of analyses can be made to gain insight in the distribution and variation of elements on various scales.

The IRA method is envisaged as an additional tool in applied geochemistry and in the study of petrological and mineralogical problems. The dependence on XRF as the analytical technique confines the range of possible elements to be analysed, due to the Auger effect (Bertin 1978), to those with atomic number higher than fluorine.

Analytical and geological research, in a number of application studies covering various rock types like granites, sediments, volcanic rocks associated with massive sulphide deposits (Van Gaans et al., 1985a, 1985b, 1986), is directed towards the effects of the specific IRA sample properties (inhomogeneity, grainsize, rough surface, crystallinity) on the quality of the analysis and towards the usefulness of the expected additional information regarding elemental (co-)variation. Results of conventional studies and petrographical and mineralogical information are used in the evaluation of the chemical IRA data and the final conclusions.

A few examples of our current research program are presented in the sequel.

The Granite of Regoufe

The W-Sn bearing granite of Regoufe, Portugal is a hydrothermally altered, 'specialized' granite of Hercynian age, showing compositional variation. Over 600 rock sections of 59 short drill cores were analysed for 14 elements (Na, Si, P, K, Ca, Ti, Rb, Sr, Zr, Nb, Sn, Cs, Ta and W). No matrix correction was applied.

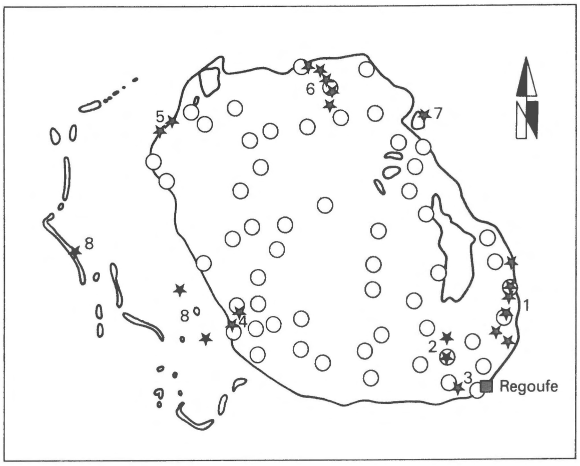
Interest was mainly in the elemental (co)variation over the granite. Comparison with the results of conventional studies was made on this level. Table 1 compares the correlation coefficient matrix for the minor and trace elements of the IRA data (means for the 59 cores) with that of conventionally obtained data (Vriend et al. 1985; Vriend unpubl. data) of different samples. Because of discrepancies between the core- and sample-locations, deviations exist, although the same directional trend is generally indicated.

In general the conclusions of the multi-element Regoufe IRA study (Van Gaans et al. 1985a) are in close agreement with the results of conventional studies (Vriend et al. 1985; Konings et al. in prep.) and are supported by petrographical work of Sluijk (1963). However, sample preparation time was considerably shorter. Additional information was obtained with the new method regarding elemental variance and covariance, especially on the small scale.

The merits of the IRA method are in this respect demonstrated in a study of the chemical variation over the granite-schist contact. A core of approximately 7 cm was drilled across the contact of a schist inclusion with the granite. Profiles for Sn, P, Ti and Nb are shown in Fig. 4. The elements displaying similar trends are indicated. The schist is

Table 1. Comparison of correlation coefficients of IRA data (first line) and conventionally obtained data (second line) for the Regoufe granite (Portugal). IRA data are from Van Gaans et al. 1985a and conventionally obtained data from Vriend et al. 1985. Sample locations for both studies are given in the inset. Open circles indicate conventional geochemical samples; stars indicate drill core locations. Deviations between the two correlation patterns are at least partly due to differences in sample coverage.

	Na	P	K	Ca	Ti	Rb	Sr	Zr	Nb	Sn	Cs	Ta	W
P	.58												
	.59												
K	−.54	−.51											
	−.50	−.48											
Ca	.60	.69	−.36										
	.44	.53	−.41										
Ti	−.68	−.76	.53	−.43									
	−.61	−.85	.60	−.46									
Rb	.28	.60	−.07	.29	−.59								
	.36	.76	−.33	.49	−.81								
Sr	.20	.39	−.14	.37	−.19	.17							
	−.13	−.01	−.00	.29	.04	−.08							
Zr	−.28	−.37	.17	−.23	.58	−.55	.41						
	−.56	−.83	.60	−.43	.96	−.82	.10						
Nb	.37	.61	−.41	.42	−.54	.73	.20	−.54					
	.52	.67	−.57	.52	−.75	.79	−.04	−.77					
Sn	−.15	.30	−.20	.11	−.07	.53	−.09	−.10	.49				
	.16	.64	−.22	.45	−.61	.82	−.03	−.61	.58				
Cs	−.30	.03	.15	−.11	.23	.45	.07	.23	.23	.61			
	−.24	−.15	.31	.10	.23	.21	.01	.25	.01	.36			
Ta	.41	.69	−.45	.44	−.64	.67	.33	−.59	.73	.27	.18		
	.52	.78	−.51	.49	−.84	.89	−.02	−.84	.86	.69	.05		
W	−.19	.13	.04	.06	.22	.25	.02	.23	.33	.64	.52	.01	
	−.13	.15	.03	.05	−.07	.13	−.15	−.12	−.04	.26	−.07	.00	



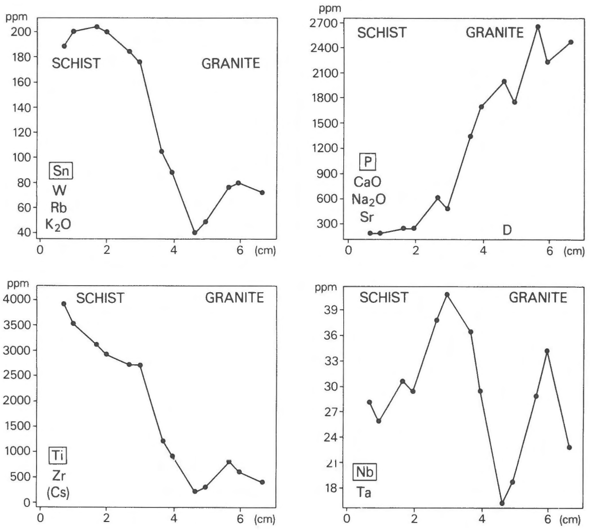


Fig. 4. Element concentration profiles across the contact of a schist-inclusion with granite for Sn, P, Ti and Nb. Elements displaying similar trends are indicated.

rich in W, Sn, Ti, Zr, Rb, Cs and K and poor in P, Ca, Sr and Na compared to the granite and, except for Ti and Zr, also compared to average concentrations for the schist surrounding the granite (Bussink 1984; De Bruijn, personal communication 1985). Relative to average schist values Ti and Zr are low in the schist inclusion. Ta and Nb values are rather variable and higher than average in the schist part of this core.

The sections between 2.5 and 4 cm intercept the contact. Taking this into account the transition is abrupt for most elements. It is thought that the elements, dissolved and transported by hydrothermal fluid(s), are immobilised upon entering the schist. The relative enrichment of the schist inclusion in Sn, W, Ta, Nb (with depletion in Ti, Zr) is in accordance with the mineralization trend observed within the granite (Vriend et al. 1985; Van Gaans et al. 1985a). The schist inclusion appears to be a favourable deposition site for the ore-related elements.

In contrast to the abrupt change in concentration at the contact for the ore-related elements, the changes in Zr, Ti and Na are more gradual. Within the schist inclusion Zr and Ti decrease while Na increases towards the contact. A similar behaviour of these elements is found within the granite, where it is related to albitization and greisenization (Vriend et al. 1985; Van Gaans et al. 1985a). Apparently the influence of these processes decreases rapidly with distance to the granite.

Although the differences between schist and granite, as shown in Fig. 4, may partly reflect the responses to the different matrices, the validity of the above conclusions gives confidence to the correctness of the displayed trends. The greater scatter in the granite part of the profile for most elements is due to the larger grainsize of the granite, which is thus less homogeneous on the scale analysed.

The covariance study of the Regoufe IRA data revealed the effects of the hydrothermal processes on mineralogy and mineral chemistry. For instance, covariance data together with detected anomalous values pointed towards the presence in some analysed sections of specific Nb-Ta trace minerals, which had not been detected before. Tantalo-columbite was subsequently confirmed with electron microprobe data in a rock section selected with the IRA method (Van Gaans et al. 1985a).

Carboniferous sediments of a coal-exploration drilling, Limburg

In the study of the Carboniferous sediments of S.-Limburg, the Netherlands, (ranging from sandstone to carbonaceous shale) an attempt was made to distinguish strata of a sedimentary sequence by their chemistry (chemostratigraphy). Some 700 sections of 80 different lithologic units were analysed for 18 elements (Si, Ti, Al, Fe, Mn, Mg, Ca, P, K, Ba, Cr, Ni, Cu, Zn, Rb, Sr, Y and Zr).

A second point of interest in this study was the conformity of the IRA results with those of conventional methods (Van Gaans et al. 1986). Integral Rock Analytical results of five lithologic units were compared with results of conventional XRF analysis on glass beads and pressed powder tablets made of the same samples (Table 2 and Fig. 5). Despite the wide range of major element compositions (Table 2) causing large matrix effects, conformity between IRA and conventional analyses in

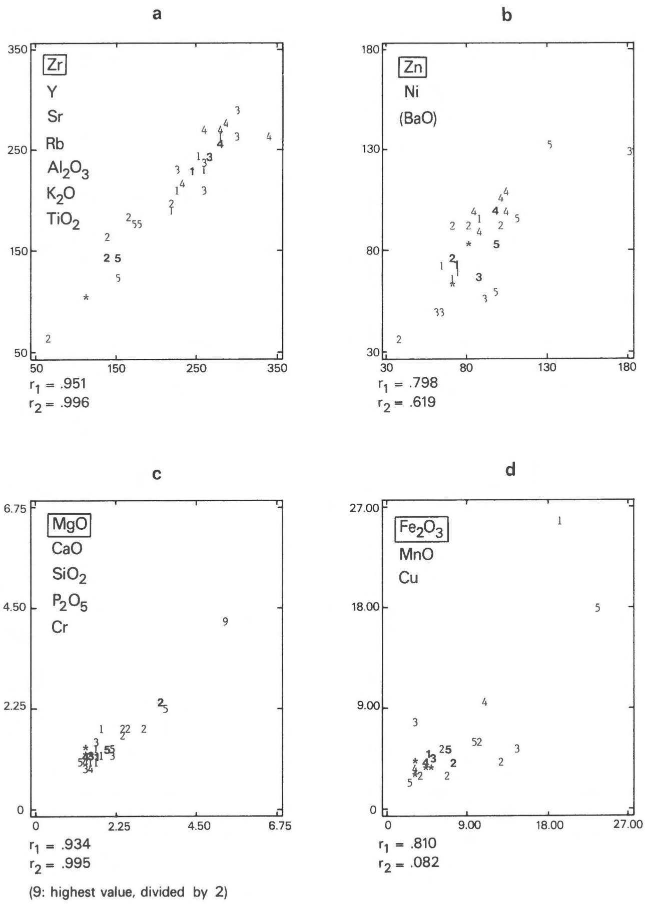


Fig. 5. Comparison of Integral Rock Analysis with conventional XRF Analysis for the Carboniferous sediments of S. Limburg. The mean of in general two IRA sections is plotted against the conventional value. The figures in the plot indicate different lithologic units, * is used for two or more coincident samples. The means per lithologic unit (see Table 1) are indicated by bold figures. (a) Zr as an example of very good conformity; (b) Zn as an example of good average conformity but with more random variation (scatter); (c) MgO as an example of a good linear relationship; (d) Fe_2O_3 as an example of poor accuracy for IRA results. Elements with similar behaviour are indicated. Relations are dependent on the specific rock type studied; different relationships are found in other geochemical environments.

this specific study was satisfactory for most trace and major elements (Table 2 and Fig. 5a, b, c). For MgO, CaO, SiO_2, P_2O_5 and Cr absolute magnitudes of IRA derived concentrations deviated from the conventional result, but data were accurate on a relative basis (Fig. 5c). Only for Fe_2O_3, MnO and Cu IRA results are less accurate (Fig. 5d), probably mainly due to mineralogical factors. The results of the comparative study indicated that the mineralogical effect (De Jongh 1970), c.q. variation in analyte-mineralogy, is of greater influence than variation in bulk chemistry. Laboratory precision (repeated analyses of the same samples) for the IRA analyses about doubled the precision obtained with pressed powder tablets and varied between 3% and 10% at the 95% confidence level for most elements (Van Gaans et al. 1986).

Concerning chemostratigraphy, IRA results showed that the Carboniferous sediments are highly variable, with large differences between as well as within lithologic units. However, major element chemistry allowed the distinction of three chemofacies: a clay-rich facies, a silica-rich facies and a facies dominated by chemical precipitates

Table 2. Comparison of IRA data and conventionally obtained data (XRF on glass beads for SiO_2 to K_2O, XRF on pressed powder tablets for BaO to Zr) for the Carboniferous sediments of S. Limburg. Means of n IRA sections or conventional XRF samples for five lithologic units of the Kemperkoul-1 drillcore are listed. In general for IRA two sections match each conventional sample. Arithmetic means are given for SiO_2, TiO_2, Al_2O_3, K_2O, BaO, Cr, Cu, Rb, Sr, Y and Zr, geometric means for Fe_2O_3, MnO, MgO, CaO, P_2O_5, Ni and Zn. Oxides are in weight percent, trace elements in ppm.

Lithologic unit	1		2		3		4		5	
	IRA	conv	IRA	conv	IRA	conv	IRA	conv	IRA	conv
	n = 10	n = 5	n = 10	n = 5	n = 11	n = 5	n = 10	n = 5	n = 8	n = 5
SiO_2	56.5	60.2	45.1	40.3	55.8	64.0	59.6	64.3	50.0	52.2
TiO_2	.67	.71	.68	.69	.91	.89	.90	.96	.99	.91
Al_2O_3	10.9	10.9	14.1	12.9	15.3	14.7	15.3	16.1	18.7	19.5
Fe_2O_3	5.0	4.9	4.2	7.1	4.6	4.6	4.3	4.4	5.4	6.4
MnO	.11	.15	.10	.19	.08	.09	.09	.08	.05	.08
MgO	1.2	1.7	2.4	3.4	1.2	1.5	1.2	1.4	1.4	1.9
CaO	5.8	5.3	10.6	10.1	1.5	1.5	1.9	1.2	.47	.40
P_2O_5	.09	.11	.07	.10	.09	.10	.08	.13	.06	.10
K_2O	1.9	2.1	2.9	2.7	2.8	2.7	2.7	3.1	3.4	3.6
BaO	.03	.03	.03	.04	.04	.03	.04	.04	.04	.05
Cr	73	98	79	100	99	113	93	111	111	121
Ni	55	53	45	41	54	84	58	69	69	64
Cu	29	25	21	16	29	27	28	29	27	28
Zn	73	72	76	69	68	86	99	95	84	97
Rb	90	91	119	111	137	130	128	143	163	174
Sr	101	106	124	124	125	125	95	102	110	122
Y	33	33	31	31	40	39	41	41	33	35
Zr	229	245	142	139	242	266	259	276	145	153

(carbonates, phosphates, (hydr)oxides). They are roughly related to sedimentary texture. A few single lithologic units have deviating chemical compositions which cannot be described in terms of the above chemofacies. They might be used as chemical marker beds in the correlation of strata. Especially Zn, Ni and Zr signatures appeared relevant (Van Gaans et al. 1986).

Conclusions

Initial results indicate that the IRA method meets the expectations.

The IRA method offers a rapid, low cost procedure that avoids the risk of contamination during sample preparation.

The decrease in representativity in comparison with ordinary bulk samples is counterbalanced by the possibility to study elemental variation and covariation on the centimetre-decimetre scale, important parameters in lithogeochemical investigations. IRA is very suitable for the detailed study of chemical variation across interesting zones (contacts, the weathering zone, mineralized veins).

Some loss in analytical accuracy and precision is incurred, due to the inhomogeneity and the relatively rough surface of the rock section submitted to analysis. Inhomogeneity may result in complex matrix effects, especially for major oxides. Accuracy and precision were found to be within acceptable limits for exploration purposes for many elements. In general, the quality of the IRA analysis is such that valid conclusions regarding the specific geological problem can be drawn.

The direct linkage of the chemical data with the mineralogical composition is possible through XRD, electron microprobe analysis and/or microscopical study of the same section. IRA is a quick chemical scanning method, which provides an easy selection of the analytically most interesting sections from a sequence of flat rock surfaces for further mineralogical, petrographical or chemical investigation. Study of the correlation patterns and standard deviations on different scales helps obtain a better understanding of the underlying mineralogical and geochemical features and processes.

The larger number of analyses partly compensates for the loss in representativity and the greater analytical error. Advantage is taken of the larger surface scanned for the detection of anomalous composition or rare minerals.

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