

Quality assessment and organizational aspects of multi-element analyses of geological material with the IRI-system for routine INAA



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Abstract

Geological research groups at the universities of Amsterdam and Utrecht obtain multi-element concentration data of their samples to a large extent by instrumental neutron activation analysis. At the Interfaculty Reactor Institute (IRI) of the Delft University of Technology, a system for routine INAA has been adapted to be used by laymen (non-specialists in radiochemistry), thus enabling geologists to carry out the analyses themselves. Much attention has been paid in developing the technique to the incorporation of quality control procedures, to ensure that the results reflect a realistic situation. Routinely, about 40–45 elements (including 9 REE) are determined with adequate accuracy. Procedures, performance and organizational aspects are discussed and the application of analytical data to geological problems in the Bergslagen region of central Sweden is briefly illustrated.

Introduction

Instrumental (formerly non-destructive) neutron activation analysis is widely accepted as a very valuable analysis technique for the determination of trace elements in geological material. As early as 1970 a scientific meeting was especially devoted to activation analysis in geochemistry and cosmochemistry (Brunfelt & Steinnes, 1971). During the past two decades an overwhelming amount of papers has been published which deal with further development of this analytical method for geological material, and with the interpretation of the data thus obtained. The radiochemical and/or geochemical aspects have been outlined in several review articles (e.g. Hertogen & Gijbels 1971, Laul 1979, Muecke 1980)).

Many thousands of geological samples are nowadays processed by INAA in experienced laboratories all over the world. In the Netherlands, INAA is carried out at the research reactor establishments in Delft and Petten. Geological (University) research groups have access to the reactor and related facilities of the Interfaculty (formerly Interuniversity) Reactor Institute of the Delft University of Technology. The system for routine INAA at this Institute has, since 1978, been developed and improved as far as availability and ease-of-operation is concerned, to the level of push-button methods and apparatus. As a result, the system can be used by guest-scientists who in general have no knowledge of radiochemistry or nuclear physics. After only a short introductory period, and with the aid of a manual, the guest-scientists are able to start ana-

lyzing on their own. Except for the more efficient use of the reactor, a major advantage of this approach is that interpretation of the analytical results is carried out by the scientists directly involved with the samples. This reduces the risk of not detecting errors, misjudgment, or even the disregarding of relevant data.

For a laboratory, inviting and enabling non-radiochemists to carry-out activation analysis, it is of the utmost importance that accuracy and precision of the results thus obtained reflect a realistic situation. Aspects of the quality controls that are incorporated in the analytical procedure are discussed below.

INAA-procedure and equipment

The basics of INAA are not here discussed; there are excellent textbooks (e.g. De Soete et al. 1972) in which theory, set-ups, advantages and disadvantages and sources of error are extensively treated. The IRI-system for routine INAA has been described in great detail elsewhere (De Bruin et al. 1982, 1984), so only a brief outline is given below.

The analytical system is based on the use of the single comparator method (Girardi et al. 1965) with zinc as a comparator (or standard) element. Analyses of geological material are performed routinely according to a protocol with a initial activation of 7 s at a thermal neutron flux of $1.0 \times 10^{13} \text{ ns}^{-1} \text{ cm}^{-2}$, followed by a decay of 20 minutes and a 5 minute measurement of the induced radioactivity, and a second activation of 1.5 hours at $5.0 \times 10^{12} \text{ ns}^{-1} \text{ cm}^{-2}$, followed by two measurements of 1 hour each after 5 days and 4 weeks decay respectively.

Samples, varying in weight up to 200 mg, are packed in vials of very high purity polyethylene. Spectrometers are equipped with both 'normal' and well-type semiconductor detectors. The latter type has the advantage of a high photopeak efficiency, so that good detection limits can be obtained at short counting times, even after irradiation in a low flux reactor.

All spectrometers are connected to a DEC PDP 11/44 computer and are equipped with computer

controlled sample changers. The measuring equipment is thus operational 24 hours a day, 7 days a week.

Quality control

The quality of results is a matter of major concern in systems for routine analysis to be used by laymen. Accuracy and precision are often used as a measure of the performance. However, these parameters are dependent not only on the analytical procedure but also on the professional skill of the analyst.

In the IRI-system for routine INAA several checks are provided including the use of international reference materials. Along with each series of 15 samples a reference material is analyzed. The results from these analyses are handled with a special administrative program providing for each element analyzed the mean of all results obtained so far, the mean of the last 10 results and the most recent observation. The reference materials are selected from materials provided by USGS, NBS, IAEA, etc., on the basis of the similarity with the samples to be analyzed. Table 1 shows as an example the average results obtained for a number of elements in 15 analyses of USGS MAG-1. The analyses were carried out by a technician, a geologist and a soil scientist in the course of one year. For control of accuracy, the experimentally determined concentrations are compared with the data reported by Steinnes (1981). It demonstrates that the quality of the results obtained by new users is about the same as that obtained by more experienced users. Fig. 1 shows for Fe and Sc the results of MAG-1 analyses, obtained over a longer period.

Practical use of INAA as a geological tool

Primary geological processes such as partial melting and fractional crystallization or magmatic differentiation, as well as secondary ones such as sub-seafloor alteration and element fractionation during transport leave a strongly affect and modify the final chemical compositions of minerals and rocks.

The finger printing of these processes is nowadays widely performed in diagrams using more mobile elements like K, Cs, Ba, Rb, P and Ti in combination with relatively immobile ones like Cr, Ni, Ta, Zr, Y, Nb, and the REE. Several of these diagrams are also used to discriminate between possible plate tectonic configurations during the processes involved (Pearce & Cann 1973, Floyd & Winchester 1975, Pearce et al. 1984).

Most of the INAA-data on samples from Bergslagen, Central Sweden, have been now collected by the research group of the former Geological Institute of the University of Amsterdam using the analysis system described here. So far normalized rare earth element patterns using the chondritic values of Evensen et al. (1978) have been published, dealing with:

- felsic intrusives like granophyres and granites belonging to a 1.9–1.86 Ga group of Swedish granites (Fig. 2, from Baker 1985) with accompanying alteration and ore-forming systems
- mafic sills, dykes and lava flows of a similar age, either altered or unaltered (Fig. 3 from Hellingwerf & Oen 1986)
- marbles, limestones and associated mineralizations (Hellingwerf 1986)
- slates and turbiditic tuffites (Kuipers 1987)
- felsic volcanics (hallelinta and leptites) (Hellingwerf 1986) and their altered varieties in relation to fossil seawater hydrothermal systems (Baker & De Groot 1983).

Extended rare earth element diagrams using mobile and immobile elements, normalized to the primordial mantle values of Wood (1979) concerning the felsic intrusives and some basic rocks have been published by Baker (1985) (Fig. 4).

The same analytical data can also be used to contour element distribution maps (Fig. 5, from Hellingwerf 1986), or construct chemical profiles. Another application is the determination of partition coefficients for REE or other trace elements between minerals and melt or whole rock (Fig. 6, from Hellingwerf 1986).

INAA can be applied to small amounts (<20 mg) of material. As such, the technique is a useful tool for exploring metal-enriched oxidation/reduction boundaries, fossil black smokers or metal- or REE-enriched chemical haloes. Other applications can be found in chemo-stratigraphic studies. For samples from the Bergslagen region INAA has been applied to determine Cl and In as indicators of composition, and pH conditions of magmatic fluids and hydrothermal brines.

Finally, the potential of INAA can be demonstrated from the observed pronounced Ce-anomaly in sediments from glacial periods; by the characteristic enrichment of Ir, Co, Ni, Cr, Sb, As, Au, and U found in the deposits of the Cretaceous-Tertiary boundary, combined with typical low REE-patterns; and last, but not least, the Pt-group elements.

Table 1. Results obtained in the analysis of USGS-standard MAG-1.

Element	Mean concentration in ppm	Reference ppm	Element	Mean concentration in ppm	Reference ppm
Na	27900 ± 200	28000	Rb	151.1 ± 1.9	170
Al	87600 ± 5500	88000	Cs	9.90 ± 0.14	8
K	28500 ± 500	30000	Ba	497 ± 16	490
Sc	17.08 ± 0.06	17	La	46.7 ± 0.3	50
Cr	102.6 ± 0.9	110	Eu	1.52 ± 0.03	1.6
Mn	775 ± 16	770	Yb	2.41 ± 0.06	3.0
Fe	47100 ± 200	47000	Hf	3.59 ± 0.03	3.7
Zn	128 ± 5	130	Ta	1.02 ± 0.07	1.0
As	11.1 ± 0.3	10	Th	11.89 ± 0.10	12.6
Br	218.3 ± 1.9	–	U	2.67 ± 0.14	2.8

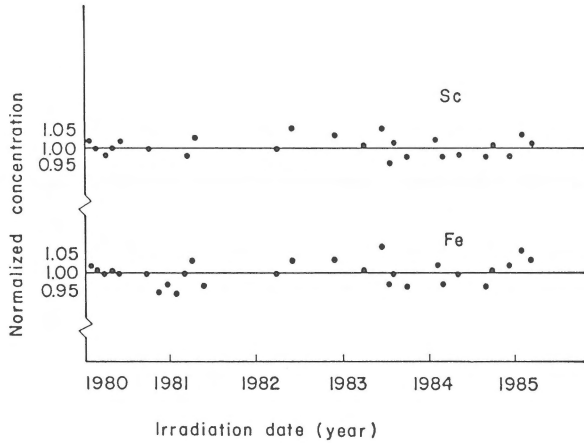


Fig. 1. Results for Sc and Fe in MAG-1, normalized to 1.00 for the recommended value.

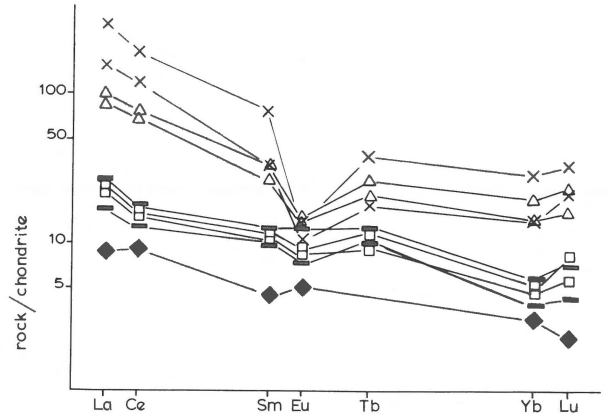


Fig. 3. Normalized REE patterns from several batches of mafic magma in W-Bergslagen, from Hellingwerf & Oen (1986) (Chondritic values Evensen et al., 1978, *1.5).

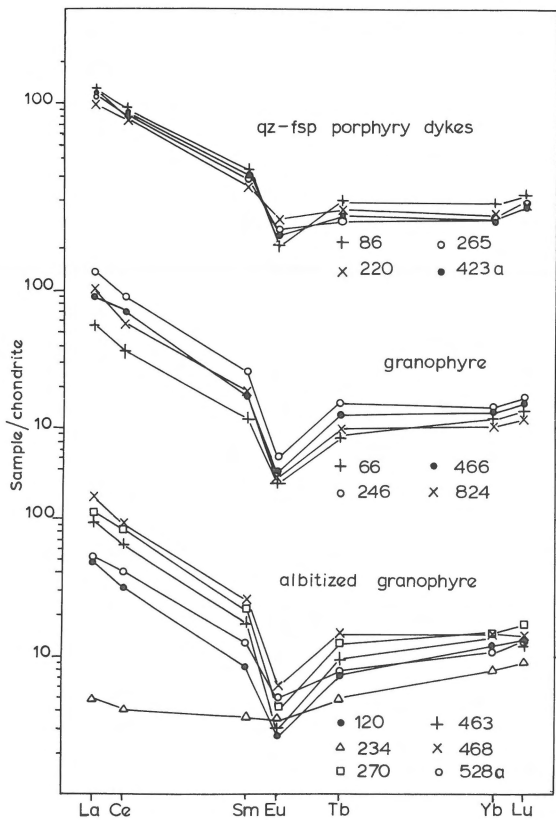


Fig. 2. Normalized REE patterns of felsic intrusive rocks from Bergslagen, from Baker (1985) (Chondritic values Evensen et al. 1978, *1.5).

Organizational aspects

All new radiological workers at IRI have to follow a two-day course on radiation, radiation-protection and health physics before starting with their research projects.

As has already been pointed out earlier, the

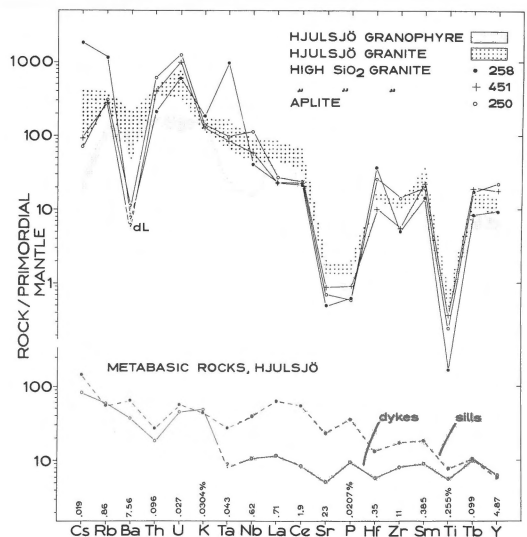


Fig. 4. Extended Rare Earth diagram of felsic and mafic intrusives in the Hjulsjö area in Bergslagen, from Baker (1985) (Primordial mantle from Wood, 1979).

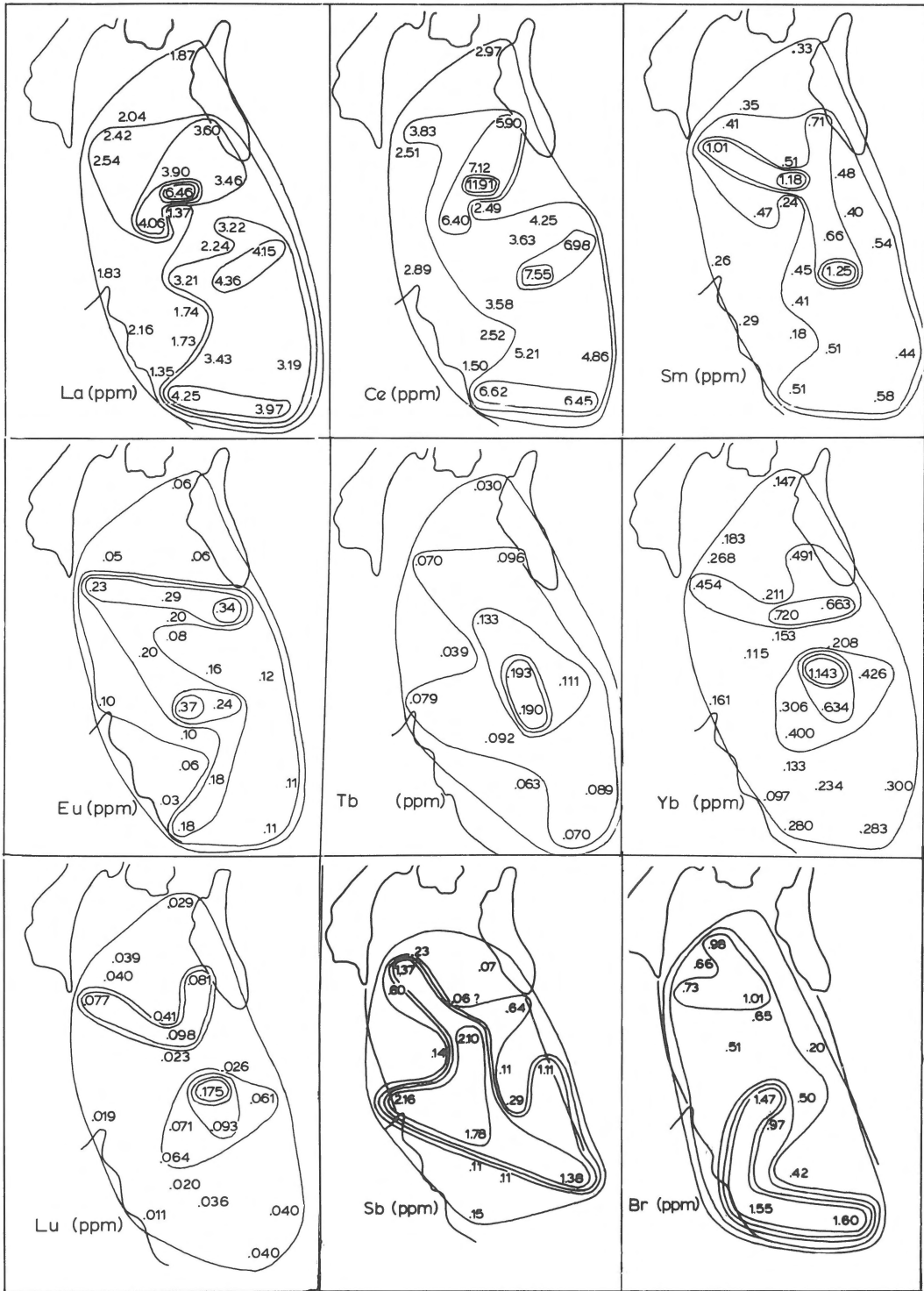


Fig. 5. Zonal concentration maps of the REE and several other trace elements in unmineralized marbles of one of the mining areas of Bergslagen (from Hellingwerf, 1986).

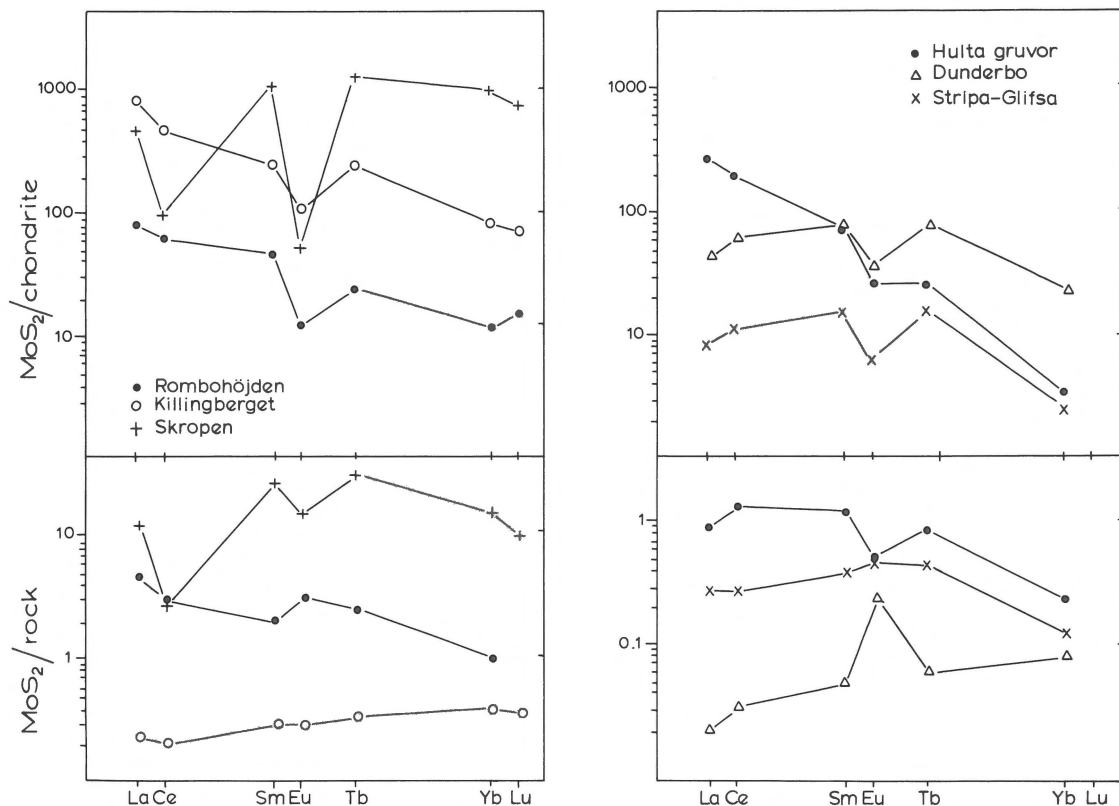


Fig. 6. Normalized Rare Earth pattern of molybdenites (Evensen et al. 1978) and the partition of the REE between mineral and whole rock (from Hellingwerf, 1986).

INAA system is intended for users not specialised in radiochemistry. This implies that a training period is necessary but this period should be short for efficiency reasons. In practice, new users of the analysis system are able to start their analyses after only a one-day instruction while they are further tutored during the course of the complete first analysis. After that they are able to analyse their samples almost independently with the help of the INAA-manual and are only incidentally assisted by an experienced radiochemist.

For the analysis of geological material, the sampling and sample preparation (including crushing, milling, etc.) is carried out by the individual geologists at the different universities. The samples are then sent to Delft, where, apart from the irradiation, all other steps in the analytical procedure (weighing-in, packing, preparation for measurement, data interpretation and reporting) is carried out by the IRI-trained geologist.

Capacity

The available instrumentation allows multi-element analyses to be performed using the routine protocol on about 8500 samples per year. In practice about 4000–5000 samples are analyzed annually, the actual limitation being, in addition to the availability of samples or the time required for sample preparation, merely the scientific interpretation of the results. As several research projects at IRI extensively make use of INAA to collect multi-element concentration data, only a part of the capacity of the system is available for the analyses of geological material. During the past 5 years, the annual number of geological samples analysed was about 1200, which covered to a large extent the existing demands for INAA at the Dutch Universities.

Analysis costs

It is the policy of the I.R.I. that for research groups at the Dutch universities no, or only partial contribution to the cost of the analyses is asked (e.g. capsules, or disposables). The total cost per sample has been estimated to be about Dfl. 280,— for a complete analysis according to the standard protocol (1988 price level; in view of the rapidly changing exchange rates, the price is given here in Dutch currency, and corresponds to about US \$ 150.00 (1988)).

Occasionally, the Institute receives requests from non-university establishments (governmental institutions or industry) to use the Institute's facilities for analyses. Such requests may be fulfilled depending on analytical feasibility, available capacity of the system whilst a fee is asked for such services, related to the analysis'cost mentioned above.

Concluding remarks

Recent evaluations of the IRI-system for INAA has shown that the approach described here has made INAA effectively available to scientists not specialized in radiochemistry. With the help of a manual, guest-scientists are able to start their analyses after a one day instruction. This implies that efficiency is maintained even for research projects involving the analysis of only a small number of samples.

For more than a decade, the IRI-system for routine INAA has been extensively used by geochemists from research groups at the universities of Amsterdam and Utrecht. In this paper, and in the references, examples are given of the creative way in which INAA is used as a tool to solve geological and geochemical problems.

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