The significance of analytical procedure in geochemical and environmental studies

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Introduction

Information on the chemical composition of geological materials is often of fundamental importance within many branches of geoscience. In the early days of the development of mineralogy and petrology, the classical wet chemical analytical methods were the only ones available, and used mainly for the determination of major elements for the characterisation and description of minerals and rocks. Since then, an intensive research in analytical inorganic chemistry has led to the development of rapid and accurate instrumental analytical methods with good element coverage and detection capabilities. This has been of great benefit for research within geology and geochemistry, where the interest for chemical data has been strongly expanding, not only with regard to elements and concentration level, but also concerning the type of geological materials, which can range from solid rocks and sediments to water and air.

The choice of analytical technique, including sample type and preparation, is in many cases of vital importance for a meaningful conclusion, and this choice must therefore be carefully based on the problem at hand. This is particularly prominent within two fields, namely: (1) Geochemical prospecting. (2) Environmental investigations.

Geochemical prospecting

The application of geochemical principles in the search for ore and mineral deposits has long traditions, and techniques based on such principles are today valuable both as independent methods and as supplements to geophysical and geological methods.

The simple principle for geochemical prospecting is to search for traces of characteristic components of potential ore or mineral deposits, and to trace these findings back to their origin. Presuppositions are that dispersion of elements from the deposit has taken place, and that the elements have been taken up or collected by some medium outside their source. Dispersion of elements from a source can take place either in the form of particles or as solutions, but also in some cases in the form of gases, and the main forms of dispersion are through transport by ice, water or air.

A variety of media have been studied and used in geochemical prospecting, e.g. stream water, stream and lake sediments, mineral soils, morainic materials, humus and different types of vegetation. Some of the most frequently used media, however, are different types of sediments.

Environmental investigations

Control and surveillance of the environment is of vital importance for all forms of life, and has become an activity with high political priority. A great deal of the damage to the environment is represented by pollution, which again is a typical result of today's complex, industrialised society. However, pollution of the environment can also, in some cases, take place in nature even without any human activity. This phenomenon is normally caused by ore or mineral deposits, or other occurrences with elevated element concentrations. No matter whether a pollution is caused by human activity or by nature itself, the consequences will be the same, and the methods for determining the degree and cause of the pollution will also be much the same.

Problems common to geochemical prospecting and environmental investigations

Both geochemical prospecting and environmental pollution studies have three basic elements in common, namely: 1. A primary source for the supply of chemical elements. 2. A mechanism for dispersion of these elements. 3. A medium for picking up or collecting the elements.

In contrast to traditional solid rock geochemistry used in modern petrology, the major goal of such investigations will be to determine quantitatively and selectively the elements or element compounds which have been supplied secondarily to the medium from external sources. This means that the ideal analytical technique would be a method where analyte elements potentially present in the medium beforehand would escape analysis. No such method exists. Therefore, compromise techniques must be chosen.

The way of attacking this problem may have great consequences for the final interpretations and conclusions and is, in fact, one of the most important parts of investigations of this kind. Good knowledge of geology, geochemistry, mineralogy and chemistry is a requisite. The ideal situation would be a neutral medium containing none of the analysed elements, and which, thus, would readily give a correct picture of the take-up of elements. This ideal situation never exists, since most geological materials contain various amounts of most chemical elements. This may complicate the situation considerably.

There are, in principle, two possible modes of analysis: (1) total analysis; (2) partial analysis based on some form of extraction. This immediately raises many important questions. In the case of total analysis, what are the absolute and relative amounts of analyte elements primarily present in the medium compared to the amounts supplied from external sources? In the case of partial analysis the same question is significant, but two additional important questions are: what are the amounts of analyte elements brought in solution by the extraction, and how selective is the extraction?

Total analysis: By all methods determining the total element content it is not possible to distinguish between analyte elements primarily present in the medium and elements supplied to the geological system from external sources.

X-ray Fluorescence (XRF) is one of the methods used for total analysis, but even though this technique uses solid samples with practically no dilution, the detection capabilities are often insufficient for many geochemical and environmental studies. Many other methods can be used for metallic elements, e.g. Atomic Absorption Spectrometry (AA), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). These methods normally apply solutions which, for total analysis, are prepared either by fusion with $LiBO_2$ followed by dissolution in dilute acid, or by dissolution in HF in combination with other mineral acids, followed by complexing of free HF with H_3BO_3. Both these techniques introduce considerable amounts of salts which generally complicate the subsequent analysis.

Partial analysis: It is evident that the use of total analyses can introduce many uncertainties and problems in geochemical and environmental studies, and there are thus many reasons for choosing an analytical technique based on partial extraction. Two factors will be especially important in relation to the extraction technique, namely: 1. The extraction attack must be strong enough to bring the secondarily supplied elements or element compounds to be studied in solution. 2. The acid attack should influence the primary sample minerals as little as possible to avoid introduction of unwanted elements.

Unwanted elements in this context are first of all potential analyte elements primarily present in the geological material, and which at the same time are completely or partly released during the extraction. Major matrix elements which go into solution during extraction are also unwanted, since a high content of dissolved solids in the analysis solution always complicates the analysis.

Partial extraction of geological materials

Most geological materials used as the medium in pollution studies or geochemical prospecting consist mainly of rock material rich in silicate minerals. The type and amount of silicate minerals can, however, vary within wide limits, and are largely dependent on the type of parent rock material. The rock-forming silicate minerals as a group have traditionally been considered as largely resistant against attacks from mineral acids, except HF. This is completely incorrect.

Systematic research at the Geological Survey of Norway (Graff & Røste 1985) has shown that a lot of silicate minerals have considerable solubility in mineral acids, such as HCl and HNO_3. Some silicate minerals even show a solubility of practically 100 %, while some are nearly insoluble. Graff & Røste have shown that a general parameter for the solubility of silicate minerals seems to be the ratio between the number of metal atoms in the mineral except Si, and the number of Si atoms. Thus, with a ratio below 1, the mineral has little solubility. With a ratio above 2.4 the solubility is high. In the range between 1 and 2.4 the solubility can vary considerably. For instance, the end member of the plagioclase series, anorthite ($CaAl_2Si_2O_8$), with a ratio equal to 1.5, has a very high solubility, while the other end member, albite ($NaAlSi_3O_8$), with a ratio equal to 0.67, has very low solubility (Fig. 1).

Muscovite, with the common formula $2H_2O.K_2O.3Al_2O_3.6SiO_2$, and a ratio equal to 1.33 has a very low solubility, while biotite, with a composition ranging mainly between $(H,K)_2(Mg,Fe)_4(Al,Fe)_2Si_4O_{16}$

and $(H,K)_2(Mg,Fe)_2Al_2Si_3O_{12}$, and a ratio normally between 1.7 and 2.0, has a high solubility. This explains why biotite is a much better soil fertilizing mineral than muscovite for the supply of K_2O, even though muscovite normally has a higher K_2O content than biotite.

The most important aspect in relation to pollution studies and geochemical prospecting will be the release of analyte elements bound in the lattice of the primary silicate minerals. The possibility of introducing such elements can, in many cases, be evaluated, but this requires: (1) knowledge of the composition of the rock material; (2) knowledge of the basic geochemical distribution laws; (3) knowledge of the general solubility of rock-forming silicate minerals.

In addition to the contribution of trace elements from silicate minerals, such elements can also be introduced from accessory minerals which usually occur in geological materials. The solubility of such minerals can differ greatly, from acid-soluble sulphides such as pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2), to more resistant sulphates, oxides and silicates, such as barite ($BaSO_4$), chromite ($FeCr_2O_4$) and beryl ($Be_3Al_2Si_6O_{18}$).

Faye (1982) has made a separate study of the solubility of some resistant accessory minerals, and a more comprehensive solubility study of silicate rocks. These studies were undertaken primarily to reveal the amount of major and trace elements which can be introduced during acid extraction procedures used in geochemical investigations. The rock material used were certified geological reference samples covering the whole range from acidic to ultramafic rocks and some sediments. Four general conclusions can be drawn from the extraction investigations, namely: 1. The extraction yield for the various elements of a rock sample varies strongly within one and the same sample. 2. The extraction yield for each single element of a rock sample varies strongly from sample to sample. 3. The extraction yields for all elements of a mineral are equal. 4. The extraction yields for the elements of a mineral in a rock sample are independent of the concentration of the mineral.

Fig. 1. Solubility of plagioclase feldspar.

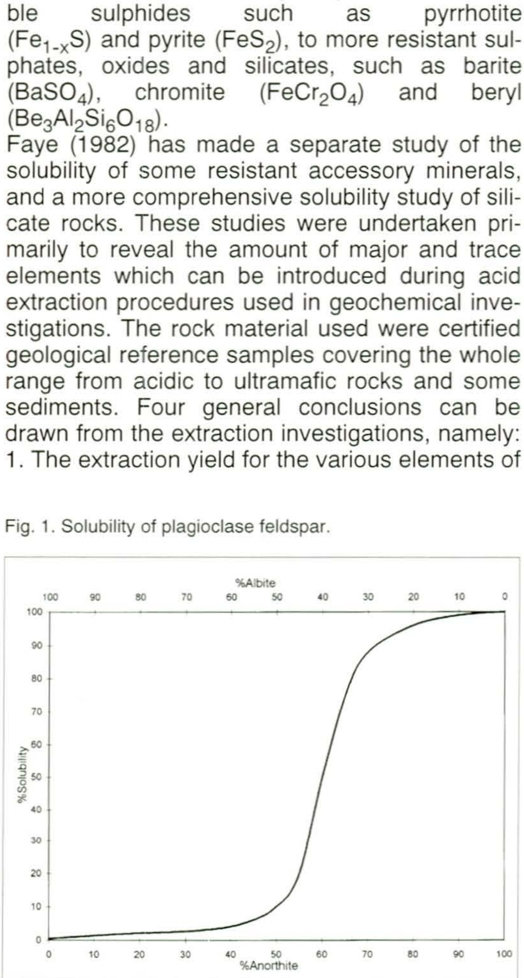

Table 1 shows some of the results obtained on the rock materials. The elements are specially selected to cover actual elements in an environmental survey of offshore oil drilling. In this activity, Ba is used in the form of barite ($BaSO_4$) as a weight agent, and this metal is therefore commonly used as a tracer in monitoring the distribution of drilling fluids in the marine environment. Sr is also a typical component of drilling fluids and is likewise used as a tracer for contamination control. The other elements are included because they are of particular toxicological interest.

The conclusions related to the extraction of pure minerals in the work of Faye (1982) are based on olivine, chromite, beryl, lepidolite and allanite. Thus, extraction tests on several standards of olivine, $(Mg,Fe)_2SiO_4$, showed a constant extraction yield of about 85% for the elements Fe, Mg and Ni, while Cr, which is found as the resistant mineral chromite ($FeCr_2O_4$), showed a constant extraction yield of 15 %. The element Ni enters the lattice of olivine. The resistant mineral beryl ($3BeO{\cdot}2Al_2O_3{\cdot}6SiO_2$) showed a constant extraction yield of 1.4%, while the Li mineral lepidolite $\{K,Li[Al(OH,F)_2]Al(SiO_3)_3\}$ correspondingly showed around 70%. Tests with standards of allanite (a complex rare earth silicate) also confirmed a constant extraction yield independent of concentration. The situation of Si during the extraction of silicate minerals is that even this element goes into solution, but will immediately precipitate as insoluble $SiO_2{\cdot}x{\cdot}H_2O$ in the prevailing acid milieu, and is therefore not found in the extract. It is important to be aware of this behaviour of Si, which falsely will give a too low solubility if the calculation is based on the weight of the residue. This may be the case for some of the work of Graff & Røste (1985), and lead to the conclusion that their solubility figures in reality systematically should be even higher than reported.

Another important discovery in the work of Faye (1982), and also with particular relevance to oil drilling activity, is that the amount of $BaSO_4$ which can go in solution during extraction is very limited, and regulated by the solubility product of $BaSO_4$. The maximum amount of Ba which could be measured by the analytical procedure used in the work of Faye (Ødegård 1981) was approxi-

Table 1. Range of extraction yield (extracted amount of element as percent of total content) for some selected elements based on extraction of 24 international reference materials with 7N HNO_3 (Faye 1982).

Element:	Extraction yield (%) :		
	Low	High	Mean
Fe	1.7	85.0	46.4
Ba	2.0	88.3	27.8
Sr	1.7	80.3	38.3
Cr	0.4	87.2	38.1
Ni	8.8	100	50.3
Zn	7.6	94.2	56.9
Cu*	Not calculated		
Pb*	Not calculated		

* The extraction yield for Cu and Pb is presented graphically, indicating that Cu, and probably also most of the Pb, mainly occurs as sulphides and largely goes quantitatively into solution.

mately 0.25%. In this procedure a sample weight of 1 g and an extrant volume of 5 ml were used. The procedure being used today applies in accordance with directions given in Norsk Standard NS 4770, a sample weight of 1 g and an extrant volume of 20 ml. This standardised procedure, which is being used in many laboratories, limits the amount of Ba (in the form of $BaSO_4$) which can be determined to around 1%. This level has recently been confirmed in separate tests by the present author. Many sample types can also be expected to contain S in the form of sulphates other than $BaSO_4$, or in the form of sulphides or other compounds which can form SO_4^{-}-ions during the extraction. In such cases the maximum amount of Ba which can be determined will be less than 1%, since the amount is regulated by a constant ion product $[Ba^{++}][SO_4^{-}]$.

With regard to the use of Sr as a tracer for the contamination of sea floor sediments by drilling fluid, it is important to take into consideration the fact that the background level of Sr is frequently relatively high, and shows great fluctuations. Sr is commonly found in silicate minerals containing K and Ca, and in a marine environment also often in carbonates. The extractable amount of Sr in e.g. K-feldspar will be very small, while the total content will be released in e.g. $CaCO_3$. From an environmental survey at the Statfjord field in 1987 (IKU-report 02.0840) it was reported that Sr is not as good as Ba in tracing drilling fluid contamination of sediments. This is probably mainly due to a much higher concentration of Ba than Sr in the drilling fluid, but may also be due to a relatively high and fluctuating background level of Sr.

Most of the extraction studies of Faye (1982) are based on boiling 7N HNO_3 and the analyses were done by the ICP-AES technique (Ødegård 1981). The solubility studies of Graff & Røste (1985) are based on both boiling 6N HNO_3 and boiling 6N HCl. Even if the experimental conditions used in these investigations are not identical, the results are unambiguous and have the same general conclusions on solubility.

Conclusions

A general conclusion is that the amount of major and trace elements which can be introduced from rock material during a standard acid extraction procedure can vary within very wide limits, depending on the type and amount of both rock-forming silicate minerals and accessory minerals. This may in extreme cases disturb, or even overshadow, effects which are to be studied; the danger being especially great when working at low concentration levels and with marginal effects. This is often the case when studying the effects of moderate or marginal environmental loads.

For the conclusions it is very important that the background contribution is stable, which means that the medium must be homogeneous. This can be a problem for sediments which often are inhomogeneous due to mineral segregations.

The use of reference materials is a central element in quality control. However, such materials are as a rule certified for total element content, and are therefore of limited value for extraction analyses. The best alternative will be to base the control on interlaboratory comparisons, and where identical and reproducible extraction procedures are being used.

The main intention of this work has been to demonstrate some of the many problems and pitfalls which can be encountered in geochemical and environmental studies based on geological materials, and the few examples outlined show that such activity requires multiprofessional knowledge at all stages from planning to the final interpretation.

Systematic research on the general solubility of rock-forming silicate minerals has been of particular significance in this field, and has contributed considerably towards providing a safer basis for drawing conclusions. A great challenge lies in utilising this knowledge in the future development of extraction routines with optimum selectivity.

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