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Denis M. Shaw
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Introduction

1.1 Defining trace elements

The intent of this book is to examine processes which lead to the accumulation of trace elements in magmatic and metamorphic minerals and rocks, so at the beginning we must consider and define the terms to be encountered.

The first task is to examine what is meant by a *trace element*. In a literal sense it is an element which is present in a rock, mineral or fluid at a low concentration. It is usual in the field of geochemistry to define *major elements* as those which give the sample whatever distinctive character it has, such as its mineralogical make-up; for example, the major elements of cherty limestone would include Ca, C, Si and O. In the case of most common rocks the major elements would include Si, Ti, Al, Fe, Mn, Mg, Ca, Na and K, with abundances in excess of perhaps 1% (in this book % will always be taken as a weight ratio, unless otherwise indicated). Note that O is not usually listed, because the other elements are bound to it.

A number of *minor elements* occur at concentrations usually below 1%; in part they correspond to the presence of accessory minerals such as, apatite (P), zircon (Zr), fluorite (F) etc.

Elements at low concentrations, but which do not give rise to characteristic minerals are classed as *trace elements*. Their manner of occurrence is to be discussed later. The terms used for concentration are %, ppm (1 ppm $= 10^{-6}$ gg^{-1} $= 0.0001\%$) and gt^{-1} (1 $\mathrm{gt}^{-1} = 1$ ppm).

So far, this is the language of the chemical analyst, and a statement of the kind ‘the trace element rubidium comprises 25 ppm of the rock’ gives no problem about its intended message: in 1 tonne of the rock there are 25 g of the metal Rb. Sometimes, however, the meaning is not so clear; e.g. to speak of ‘the partition of Ni between olivine and clinopyroxene’ raises the question of whether Ni, as a metallic element, can somehow occur in the silicate olivine or, in other words, what form Ni must take in order for it to be involved in some sort of reaction or equilibrium between

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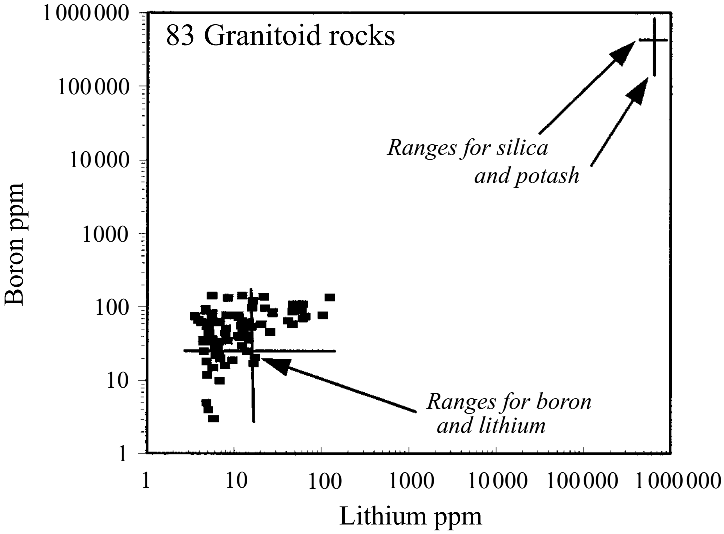

Fig. 1.1 Analyses of 83 granitoid rocks from the Peña Negra complex in central Spain (Pereira and Shaw, 1997) show how trace elements Li and B vary in concentration over two orders of magnitude, whereas the major components SiO_2 and K_2O vary much less. The trace element concentrations are more sensitive to variations in conditions of origin.

the two minerals; is it present as Ni metal, or as Ni^{2+}, or as NiO, or in some other state? Without further elaboration the statement is not very precise, although useful as a kind of shorthand.

Since the behaviour of trace elements in rocks is the major topic of this book it is desirable to indicate why they merit such attention. In many geochemical studies the approach used is exploratory and, with a particular goal in mind, elemental analyses of rock or sediment samples may serve as variables to test different alternatives and reach conclusions about an origin or a historical evolution. All the elements chosen may, of course, provide useful information, but there are at least three reasons why trace elements are often given special attention in such research:

(i) the lower the concentration of an element, the more likely it is that its behaviour will be regular (*ideal*, in the language of the solution chemist) and not subject to effects linked to its absolute abundance; it may therefore provide information regarding external variables governing the evolution of the rock;
(ii) the range of concentrations is not as restricted or interdependent as major elements (see Fig. 1.1); the latter must sum to 100% and therefore their concentrations are not independent of each other;
(iii) trace elements exhibit a wider range of chemical behaviour as exhibited by their position in the periodic table, compared with the more restricted range of major element chemistry.

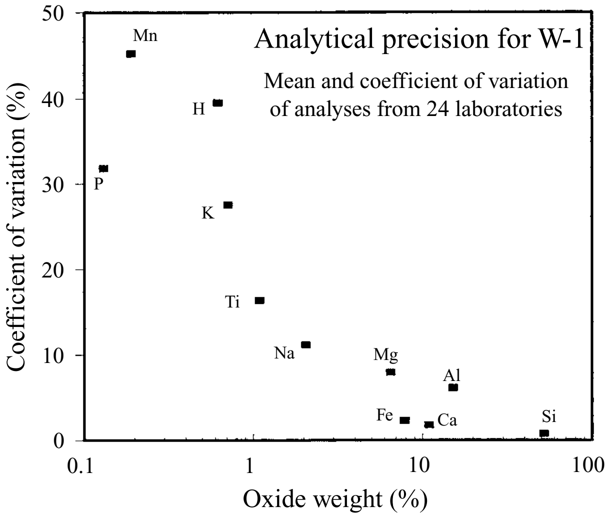

Fig. 1.2 Mean values and coefficient of variation (percentage) for some major and minor elements (expressed as oxides) in the diabase W-1, using data supplied by 24 laboratories (Fairbairn *et al.*, 1951, Table 14).

1.2 The quality of trace element data

Trace elements are inherently at low abundances and consequently they are difficult to analyse with precision and accuracy.[1] Few quantitative data were available before World War II and the quality of analyses has changed greatly since ∼1950. In the 1940s a project was initiated in the United States to calibrate two rocks (a granite G-1 and a diabase W-1) by cooperative analyses for major, minor and trace elements from a number of participating laboratories, so that the rocks could serve as standards for precision and accuracy.

The results of the project (see Fairbairn *et al.*, 1951) were disappointing, because the analyses from the participating laboratories showed many discrepancies (for major as well as trace components), leading to a confirmation of the view that rock analysis is a difficult art.

For example, five laboratories respectively reported the Sr concentration in G-1 as 900, 120, 250, 280 and 450 ppm, with similar wide ranges for other trace elements. The variation in such results may be expressed by the *coefficient of variation*, which is the ratio of the standard deviation (*sd*) of the results to their mean value, and is usually expressed as a percentage. For major and minor elements (or oxides) Fig. 1.2

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[1] It is necessary to bear in mind that *precision* (Ger: *zufälliger Fehler*, *Reproduzierbarkeit*; Fr: *réproductibilité*) refers to the ability to reproduce an analytical result by multiple measurements using a particular method, whereas *accuracy* (Ger: *Genauigkeit*; Fr: *précision*) is concerned with the ability to measure the 'true' value, without systematic bias dependent on the analytical method in use. The uncertainties introduced from these two causes are sometimes referred to, respectively, as *random error* and *systematic error.*

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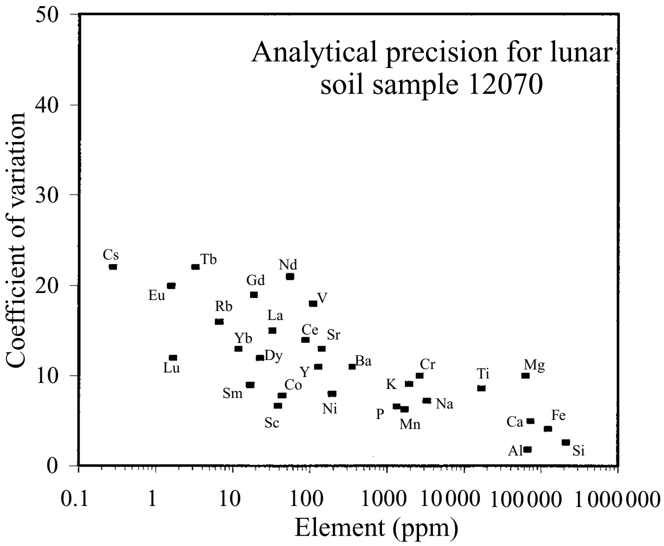

Fig. 1.3 Comparison of analytical error for many elements in the lunar soil sample 12070, as measured in 8–17 laboratories (Morrison, 1971, Table II). The errors are less for Na, Ti, K, Mn, P, than in Fig. 1.2, but remain substantial for elements at the ppm level.

shows that the degree of uncertainty in the diabase W-1 was greater for components at lower concentrations, and this was true also for G-1. Elements plotting in the upper part of Fig. 1.2 can be regarded as having little better than semi-quantitative status.

Strenuous efforts were made to improve the quality of rock analysis in ensuing years. New methods were developed and tested extensively, to verify claims of improved precision and accuracy. By the time that the Apollo missions were returning samples of lunar rocks and soils, better measures of composition could be made. For example, Fig. 1.3 shows that, for a similar group of elements to the ones previously shown, the analytical uncertainty was much less for Mn, P, K and Na, but remained considerable for the trace elements. In the case of the rare earth elements (REE), for which great efforts were invested in obtaining good analyses, Fig. 1.4 shows that the ranges in values obtained, when normalised to chondritic meteorites, were relatively consistent from La to Lu, which is not so evident in Fig. 1.3.

The preceding discussion focuses on precision or reproducibility, but of course Figs. 1.2, 1.3 and 1.4 depict analytical errors which also include systematic or interlaboratory bias; estimates of precision within a single laboratory were, in some cases, markedly superior.

In subsequent years many natural materials have been carefully analysed in many centres, certified with *recommended values* and made available for calibration purposes, as *standard reference materials* (SRM); a journal devoted to these

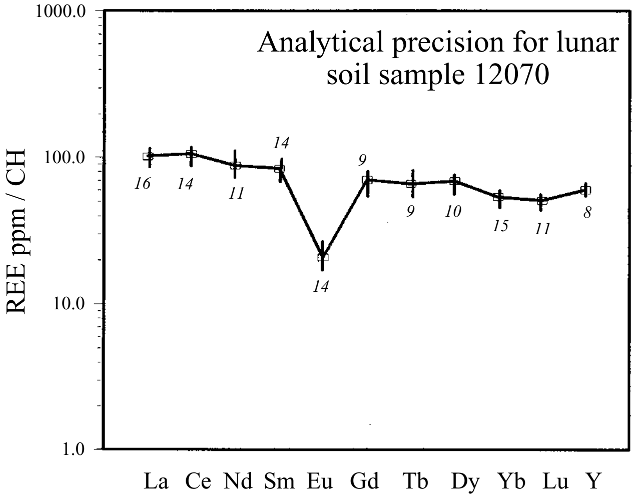

Fig. 1.4 Coefficients of variation of REE analyses (Morrison, 1971, Table II) for lunar soil 12070, from various laboratories, are quite similar in magnitude when the concentrations are normalised to chondritic meteorites (Anders and Grevesse, 1989); numbers of analyses are shown.

matters is the *Geostandards Newsletter*, founded in Nancy, France, in 1977, by K. Govindaraju and published by the Association Scientifique pour la Géologie et ses Applications. Figure 1.5 shows how about 20 such SRMs were used to calibrate the determination of Gd in silicate materials using prompt gamma neutron activation analysis. The linearity of the plot shows satisfactory precision, which by regression analysis was determined (as a coefficient of variation) to be 3–5% of the amount present at concentrations of 1 ppm and greater, and somewhat less at lower abundances.

1.3 Sample heterogeneity

The quality of analytical data depends also on the nature of the samples analysed. The previous discussion has centred on analysis of rocks, yet rocks are mixtures of minerals, and every sample taken will have different mineral proportions. Figure 1.6 sketches a hypothetical volcanic rock composed of large feldspar phenocrysts set in a fine-grained ground-mass, from which samples i, j and k are taken. The first is entirely within feldspar, the second is entirely ground-mass and the third is a mixture of the two; evidently their compositions will be very different. Averaging such compositions will confuse attempts to get a good measure of analytical precision, not to speak of rock composition. This simple example characterises all the problems of sampling inhomogeneous mixtures. The question of how large

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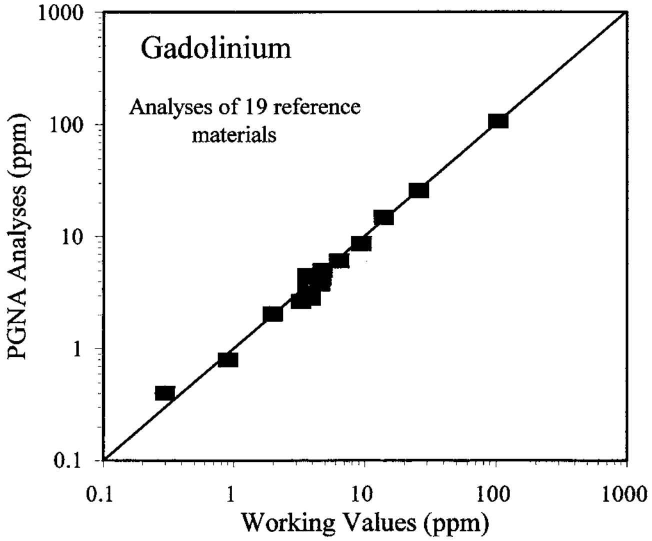

Fig. 1.5 About 20 SRMs, with recommended Gd concentration values (Govindaraju, 1989), used to calibrate a prompt gamma neutron activation analysis method to determine Gd in silicates (Shaw and Smith, 1991). Each of the points represents the average of several PGNA analyses plotted against the recommended value for that SRM. The well-defined linearity shows that precision is satisfactory, except at the lowest concentration where some curvature is apparent.

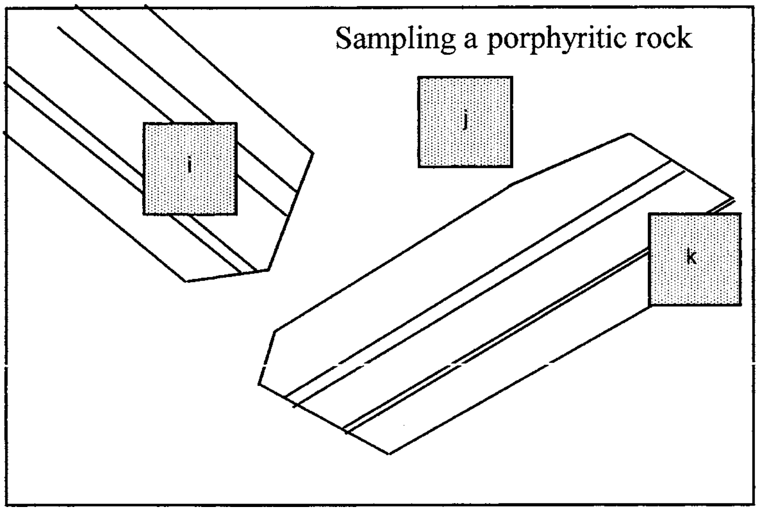

Fig. 1.6 An inhomogeneous volcanic rock composed of large feldspar phenocrysts in a fine-grained ground-mass or matrix. Sample i takes material only from the phenocryst, j is only in matrix while k takes a mixture of both. Analyses of i, j and k will differ greatly for some constituents and such data will confuse attempts to measure analytical precision, as well as attempts to get a good estimate of the rock's composition.

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a sample is needed to get a good estimate of rock composition has been treated by many authors, since this is a central problem for economic geologists in estimating ore grade (see for example Gy, 1954), but for geochemical purposes the approach of Laffitte (1957) is convenient.

Thus, a certain volume of rock having weight W consists of various minerals in proportions $p_1, p_2, \ldots, p_j$; a sample of weight w_s is taken and crushed to a fine grain size and then analysed for the element of interest. If

X is the concentration in the whole volume,
x_i is the concentration in grain i, whose weight is w_i,
N is the number of grains in the whole volume,
n is the number of grains in the sample w_s

then the variance associated with the determination of the concentration of the element in the sample is

$$s^2 = \left(\frac{W}{w} - 1\right) \sum \left(\frac{w_i}{W}\right)^2 (x_i - X)^2 \tag{1.1}$$

The summation is over the N grains in the whole volume. If it is assumed that the grains are all about the same size, then the variance reduces to

$$s^2 = \frac{\text{average value of } (x_i - X)^2}{n} \tag{1.2}$$

Since the mineral proportions in W are $p_1, p_2, \ldots, p_j$, and the element concentrations in the minerals are $x_1, x_2, \ldots, x_j$, then

$$s^2 = \frac{p_1(x_1 - X)^2 + p_2(x_2 - X)^2 + \cdots + p_j(x_j - X)^2}{n} \tag{1.3}$$

This expression is now in its most useful form, because it permits estimating how many grains should be taken to achieve a chosen precision level for the element concentration.

For example, suppose that a granodiorite contains 40% plagioclase containing 6% CaO, and 60% other minerals (quartz, mica, orthoclase) containing 0% CaO. Then the rock contains 2.4% CaO, and the sampling variance will be

$$s^2 = \frac{0.4(6.0 - 2.4)^2 + 0.6(0.0 - 2.4)^2}{n} = \frac{9.1}{n} \tag{1.4}$$

Suppose that a sample of 100 grains is chosen, where the grain size is 1 mm^3 with density 2.8 g cm^{-3}; the sample thus weighs 0.28 g. The standard deviations $\approx 0.3\%$ and there will be approximately 95% probability that an analysis of CaO in this sample will lie in the range $2.4 \pm 2 \times 0.3$, or 1.8 to 3.0%. If better precision is required then more grains must be taken, which of course increases the weight of

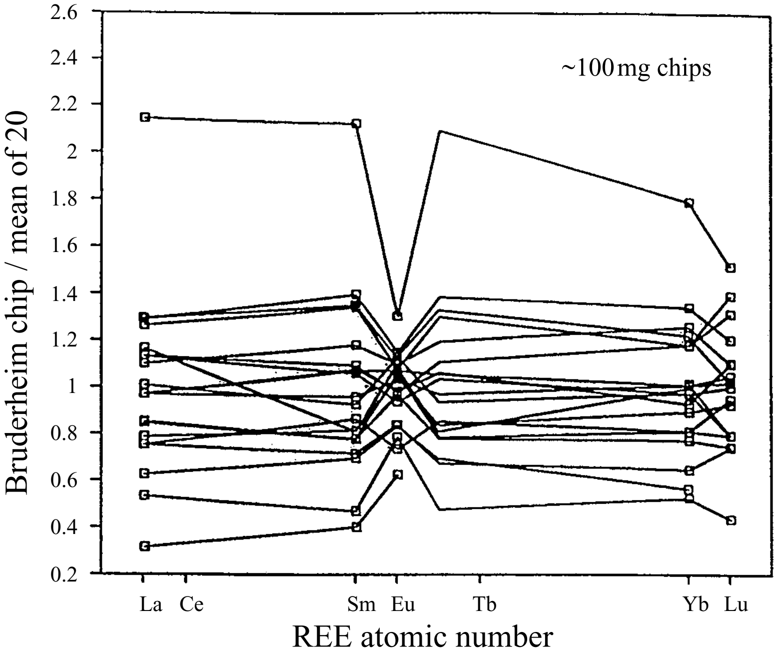

Fig. 1.7 Sampling heterogeneity shown in REE analyses of fragments of the meteorite Bruderheim (Haas and Haskin, 1991). The fragment with the highest REE concentrations is particularly rich in phosphate minerals.

the material to be analysed. For example 2500 grains will reduce the expected range to 2.4 ± 0.12%, but the weight of this sample now ≈ 7 g.

A treatment of sampling error by Kleeman (1967) covers similar topics to Laffitte but is more restricted in scope.

An experimental study of sample heterogeneity has been made by Haas and Haskin (1991). Careful analysis of 100 mg fragments of the L6 chondritic meteorite Bruderheim showed striking differences in the REE concentrations as a consequence of mineral variations from one fragment to another (Fig. 1.7). The authors comment as follows:

> Note the extensive spread in concentrations, owing mainly to different proportions of phosphate minerals among the different fragments positive and negative Eu anomalies result from different proportions of plagioclase, clinopyroxene and phosphate (Haas and Haskin, p. 16)

Because of rarity and (often) small size, meteorite analyses are often made on samples so small that grain-size heterogeneity must introduce significant error, as this study shows, but the topic is seldom discussed.

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One conclusion emerges from this discussion, which is that the geochemist must always bear in mind the heterogeneity of natural materials when sampling is conducted.

1.4 Mineral analysis for trace elements

1.4.1 Sampling

If a mineral specimen is coarse-grained, as in a pegmatite or vein deposit, a specimen for analysis may be taken as a chip sample and subsequently crushed to a fine powder. Care must be taken to avoid contamination of the powder by the trace element of interest from crushing tools or machinery, from any sieves used for sizing the powder, and from residual powder from previous samples; it may be desirable to test for contamination by processing in the same manner some sterile material, such as silica, and subsequently analysing it as a 'blank' to measure the degree of contamination introduced.

More often, the mineral of interest is a rock component and various procedures are available. The oldest approach is to crush the rock to a powder whose fragments are smaller than the mineral grain-size, and then separate the mineral of interest from other components, using heavy liquids, or magnetic separation methods, often followed by hand-picking with the aid of a binocular microscope. The resultant powder may then be analysed for the element of interest.

Such procedures can be very effective, but may also be very tedious and time-consuming. In addition, there are clearly dangers of introducing contamination of various kinds, particularly as incompletely separated grains of other minerals. Until recently, however, only this kind of approach was available, and many of the early measures of element partition coefficients (see p. 23) between the minerals of a rock relied upon analyses of two different mineral powders extracted from a rock.

The inherent assumption of these methods is that a mineral is a clean, homogeneous phase, all of whose grains will behave the same way during separation; in fact, petrographers have always known this to be only an approximation. Mineral grains are commonly zoned in chemical composition, the different zones having different magnetic and density properties and thus behaving differently during separation. Even more importantly, mineral grains usually carry smaller inclusions of different kinds, some too small to be identified by their optical properties. So the chemical composition of a mineral powder really represents the aggregate of the mineral itself plus the various natural contaminants which it has picked up and trapped.[2]

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[2] The third law of geochemistry states that 'a mineral is not only a structural sieve for elements; it is a dirty sieve' (Shaw, 1964, p. 114).

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1.4.2 Chemical analysis

The progress in geochemistry which has been seen since World War II has been very largely dependent on developments in analytical methods. The details are of great interest, but the subject is too vast to review in detail here, and lies outside the scope of this book. Some of the methods employed, however, are introduced in the following paragraphs, together with references where more detailed treatments are to be found.

Early analyses for trace elements employed a variety of methods. In North America many colorimetric methods were developed, relying on the use of a specific reagent to generate a coloured complex in a solution containing a particular element, measuring the complex concentration by its colour absorbance with a spectrophotometer.

In Europe, V. M. Goldschmidt's laboratory in Göttingen and, later, in Norway, pioneered the use of the DC arc to excite characteristic optical emission spectra of all the elements in a sample of powder, isolating the lines of interest from a particular element by prism or grating dispersion and estimating abundances by the image intensity on photographs. Optical emission spectroscopy (OES) became a major analytical tool in the mid twentieth century in many fields and industries, and geochemical applications were developed especially in L. H. Ahrens' group at the Massachusetts Institute of Technology. Optical emission spectroscopy, however, eventually yielded precedence to the more precise and more reproducible X-ray fluorescence (XRF) analysis and neutron activation analysis (NAA), but remains in use in wet laboratories as the modified technique of atomic-absorption analytical spectroscopy (AAAS).

The emergence of truly quantitative geochemical data accompanied the development of microbeam analytical tools. The electron microprobe (EMP), secondary ion mass spectrometry (SIMS) (or ion microprobe (IMP)) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) permitted analysis of a mineral or a glass matrix in a polished thin section, at low or trace concentration levels, without the necessity of a physical separation.

The development of XRF analysis by R. Castaing in France into an instrument whose electron excitation beam can be focused onto a spot of 10–100 μm diameter created the electron microprobe (EMP) and made it possible to analyse mineral grains in a thin or polished section, and even detect elements present in inclusions visible in thin sections but too small to identify otherwise. For example, the analysis of a separated pyroxene powder from a rhyolite lava (Fig. 1.8) revealed the presence of significant concentrations of the REE, but EMP analysis showed this to be attributable to minute inclusions of an REE-rich mineral. Inferences about the role