

Trace Elements in Magmas

A Theoretical Treatment

Denis M. Shaw



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DENIS M. SHAW

Formerly of McMaster University, Ontario

Edited for publication by

STUART ROSS TAYLOR



CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521822145

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First published 2006
This digitally printed version 2007

A catalogue record for this publication is available from the British Library

ISBN 978-0-521-82214-5 hardback
ISBN 978-0-521-03634-4 paperback

TRACE ELEMENTS IN MAGMAS

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Studying the distribution of certain elements, present in very low concentrations in igneous and metamorphic rocks, can yield important clues about the rocks' origin and evolution. Trace elements do not give rise to characteristic minerals, but their behaviour can be modelled to provide historical information about the source magma. This book brings together the essential theory required to understand the behaviour of trace elements in magmas, and magma-derived rocks. It presents a wide range of models and mechanisms which explain trace element distribution.

Trace Elements in Magmas provides an excellent resource for graduate students, petrologists, geochemists and mineralogists, as well as researchers in geophysics and materials science.

DENIS SHAW joined the Department of Geology at McMaster University, Ontario, in 1949, continuing his research as Professor Emeritus until 2003. Throughout his career, he taught courses in geochemistry in Canada, France and Switzerland. He worked as editor for a range of publications including *Geochimica et cosmochimica acta* and the *Handbook of Chemistry*. In 1964 he served as President of the Mineralogical Association of Canada, and received the Distinguished Service Award of the Geochemical Society in 2002. Professor Shaw passed away in October 2003 and his widow, Susan Evans Shaw, and Cambridge University Press are grateful to Professor Stuart Ross Taylor for his work in editing the final manuscript in preparation for publication.

STUART ROSS TAYLOR, a trace element geochemist, is an emeritus professor at the Australian National University and is the author of *Solar System Evolution: A New Perspective* (Cambridge University Press) and several other books.

Geochemistry is a compilation of imprecise, irreproducible and uncoordinated analyses.

(i) Keep the rocks in mind, for they cannot be reduced to analytical measurements; (ii) (from O. F. Tuttle) minerals are the archives of the rocks; (iii) keep filing [your] fingernails while waving [your] arms.

Preface

The years following World War II saw a steady improvement in the analysis of rocks for minor and trace constituents. It became clearer that trace elements were not haphazardly distributed and that chance played a minor role. To find the principles of distribution of the elements was one of the aims of geochemistry, according to V. M. Goldschmidt, and researchers began to try to understand trace element behaviour.

Two main approaches developed: one was aqueous geochemistry, where the emphasis was on the oceans and mineral genesis reactions in electrolytic solutions; the other studied the igneous and metamorphic rocks and, to some extent, metallic deposits. The second, often inappropriately called *hard-rock* or *solid-state geochemistry* was, like the former, concerned with heterogeneous phase reactions, but of different kinds. Central to it is the concept of the *partition coefficient*, and much effort has been expended in attempts to measure such parameters or variables. Many schemes were proposed and tested to show how some observed trace element or isotopic distribution pattern could be explained in petrological terms, and such accounts are scattered throughout the literature, camouflaged under various titles.

This book constitutes an attempt to gather together the wide variety of possible models or mechanisms to explain the distributions of trace elements in igneous, metamorphic and metasomatic rocks, so that they are available for application as needed. The emphasis has been quite deliberately placed on the details of the mechanisms and, as a consequence, few examples have been cited.

Another reason for the paucity here of examples from the natural world is that there are, up to the present, few trace element studies available where the analytical precision is sufficient to choose among different models, although this is not the case with many isotopic systems.

Much of the material here has formed part of graduate courses and I am grateful to successive waves of graduate students for helping to keep my thinking on track.

I have benefited from discussions with too many helpful persons to list individually. I am grateful to McMaster University for a good working environment over many years and for post-retirement services and support.

It is assumed that the reader is familiar with phase petrology and modern mineralogy.

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1

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 ($1 \text{ ppm} = 10^{-6} \text{ gg}^{-1} = 0.0001\%$) and gt^{-1} ($1 \text{ gt}^{-1} = 1 \text{ ppm}$).

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

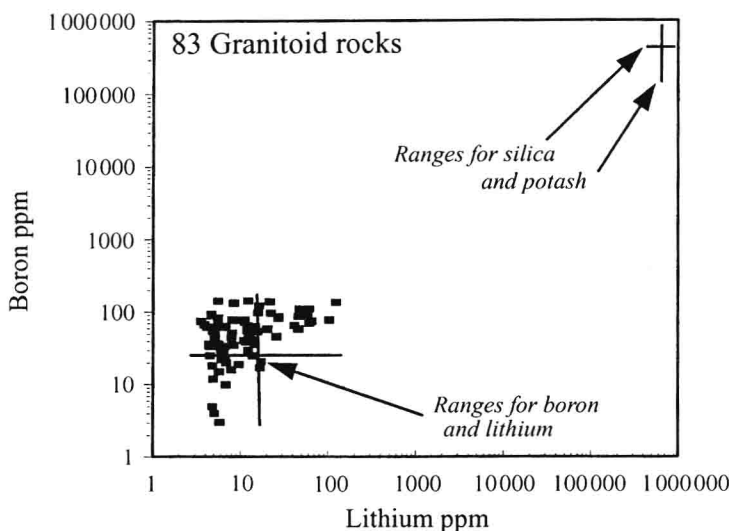


Fig. 1.1 Analyses of 83 granitoid rocks from the Peña Negra complex in central Spain (Pereira and Shaw, 1997) show how trace elements Li and B vary in concentration over two orders of magnitude, whereas the major components SiO_2 and K_2O vary much less. The trace element concentrations are more sensitive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

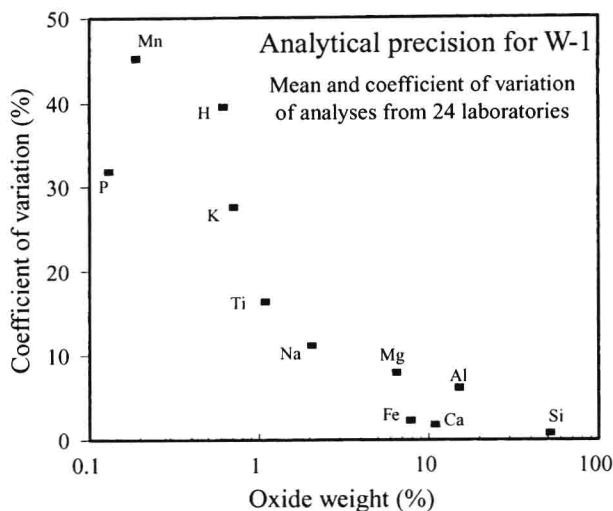


Fig. 1.2 Mean values and coefficient of variation (percentage) for some major and minor elements (expressed as oxides) in the diabase W-1, using data supplied by 24 laboratories (Fairbairn *et al.*, 1951, Table 14).

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

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*.

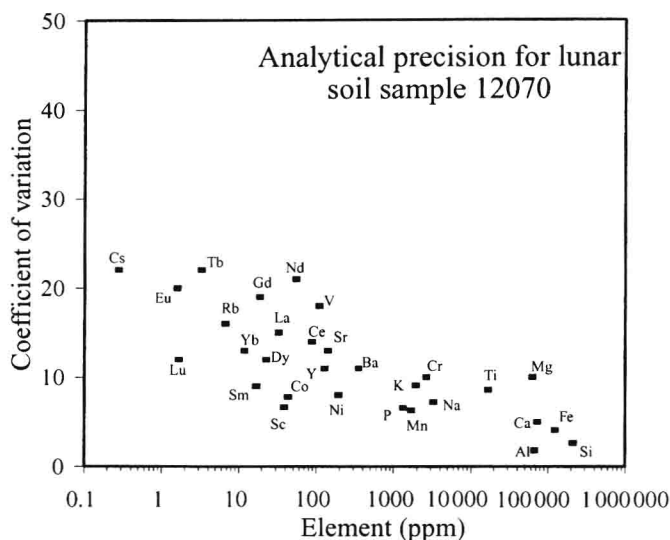


Fig. 1.3 Comparison of analytical error for many elements in the lunar soil sample 12070, as measured in 8–17 laboratories (Morrison, 1971, Table II). The errors are less for Na, Ti, K, Mn, P, than in Fig. 1.2, but remain substantial for elements at the ppm level.

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

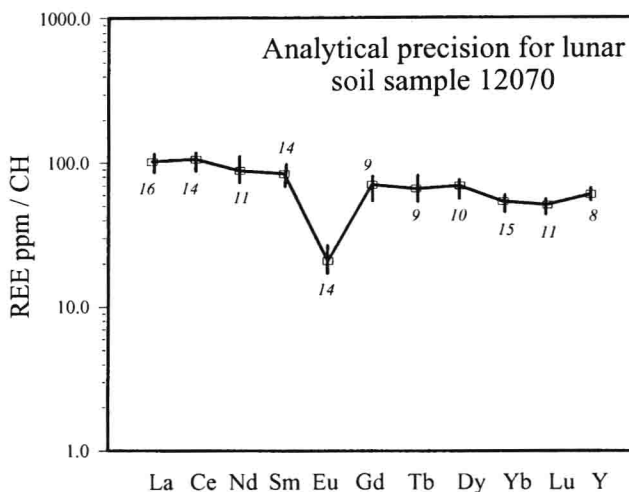


Fig. 1.4 Coefficients of variation of REE analyses (Morrison, 1971, Table II) for lunar soil 12070, from various laboratories, are quite similar in magnitude when the concentrations are normalised to chondritic meteorites (Anders and Grevesse, 1989); numbers of analyses are shown.

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

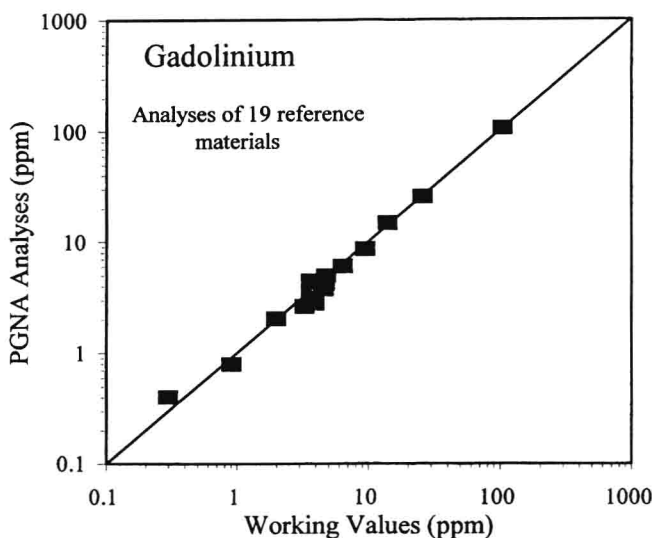


Fig. 1.5 About 20 SRMs, with recommended Gd concentration values (Govindaraju, 1989), used to calibrate a prompt gamma neutron activation analysis method to determine Gd in silicates (Shaw and Smith, 1991). Each of the points represents the average of several PGNA analyses plotted against the recommended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

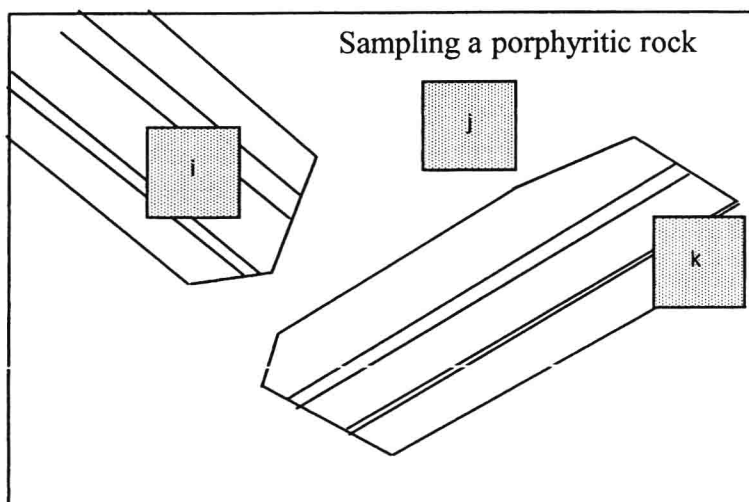


Fig. 1.6 An inhomogeneous volcanic rock composed of large feldspar phenocrysts in a fine-grained ground-mass or matrix. Sample i takes material only from the phenocryst, j is only in matrix while k takes a mixture of both. Analyses of i, j and k will differ greatly for some constituents and such data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