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978-1-107-03958-2 - Radiogenic Isotope Geochemistry: A Guide for Industry Professionals

Bruce F. Schaefer

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## RADIOGENIC ISOTOPE GEOCHEMISTRY

A Guide for Industry Professionals

What is a model age, and why do we need to know it? How can we test whether ore-forming fluids carry a mantle signature? What is the difference between a SHRIMP and a LA-ICPMS U–Pb age and is it significant?

Isotopes provide important information on many geological processes, with key relevance to the mining and petroleum industries, yet the techniques to obtain, process and interpret the data can be complex to master. This accessible book provides broad coverage of radiogenic isotopes in geochronology and geochemistry, explaining the basic principles and state-of-the-art techniques used to study them, with an emphasis on industry applications.

The major isotopic systems are fully summarised with relation to real-world applications, enabling readers to decide which technique is most relevant for the problem they want to solve, and then to rigorously evaluate existing data, or recalculate and reassess data sets to avoid duplication of effort. Written at a level appropriate for advanced undergraduate students, the book also includes detail which allows more experienced practitioners to maximise the potential value of isotopic data sets.

BRUCE F. SCHAEFER is a Senior Lecturer in isotope geochemistry at Macquarie University, Australia. His work uses isotopes to solve a broad range of geological problems, by identifying and subsequently applying, or on occasion developing, an appropriate isotopic tracer to solve the issue. His research interests include planetary differentiation, mantle plumes, Precambrian geodynamics and magmatic processes. Dr. Schaefer was awarded the Tate Memorial Medal for original research from Adelaide University, where he graduated. Subsequently he has held positions at the Open University, UK, and Monash University, Australia, before moving to Macquarie. His publications include work on magmatism, Precambrian tectonics, mineralised systems, groundwater, weathering rates, geophysics and meteorites.

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BRUCE F. SCHAEFER

*Macquarie University, Sydney, Australia*



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For Nazy  
Thank you for your unwavering love, support and belief

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## Preface

The vast majority of geoscience graduates proceed to careers in the extractive minerals industry. This includes the coal and petroleum industries, all of which require an understanding of how, why and when the commodity of interest accumulated. The ‘where’ is the focus of the exploration industry, and every year immense amounts of money are spent globally on locating the next ‘world class’ ore deposit.

In all of these endeavours, naturally occurring isotopes play a pivotal role in deciphering aspects of the resource industry. Specifically, naturally occurring radioactive isotopes can be applied as chronometers to date ‘when’ various aspects of the mineralising process took place, and the complementary stable isotopes offer mechanisms for tracking the sources of metals and reactive ligands necessary to form an economic accumulation of a resource.

Despite this, graduate geologists often have only a limited exposure to isotope geochemistry, and over time this knowledge, if not used regularly, becomes forgotten. This book is aimed to help refresh the memory of those who encounter isotopes in the course of their work – either in the minerals industry or in research fields. It is structured as a reference guide which assumes some understanding of geochemistry; however, it is hoped that it also contains enough depth for the interested reader to comprehend isotopic systems and processes they may not have previously encountered. Hence it is not designed as a conventional textbook, although it could be tackled in a sequential manner for learning, but I anticipate its utility will come for those time-poor individuals who need to ‘dip in’ to a certain section to clarify a concept, gain an understanding or recalculate a data set in order to solve a particular problem.

The world of radiogenic isotope geochemistry is one of often arcane concepts and obscure terminology, so it is also hoped that this will go some way to demystifying aspects of it while maintaining a level of rigour that allows a professional to obtain the maximum value from an (often costly) data set.

Significantly, I have resisted the urge to populate the book with specific case studies and worked examples, and focus instead on general processes. Such a broad base from first principles ultimately allows a broader range of applications and prevents a ‘one size fits all’ approach to using isotopic data. My hope is to aid the newcomer in comprehension and deepen the understanding (if possible) of the more experienced user. Time will tell if I have had any success in these measures!

## Acknowledgements

This work has been a long time in the making. The genesis for the idea came in the days of the pmc\*CRC during the mid 2000s, when I was interacting regularly with colleagues, many of whom I had gone through undergraduate study with, who were now working in the minerals industry. Consistently the message was that, while they liked using the interpretations from isotopic data, many of them didn't have the time to assess, or had forgotten how to manipulate, the very data they had paid large amounts of money to acquire. Given that such people are by definition time-poor and often have drivers other than simply understanding a piece of geology, I found myself often helping out in the course of an hour or so, (re-) interpreting the latest geochronology that had been acquired. I realised that all of these people knew enough to do this themselves if only they had some ready reference guides on hand to encourage them that they were doing the right thing and that they were on the right path. So, to all of you people, I hope this is another tool which helps you get to where you need to be, and thank you for identifying the need for it.

The numerous colleagues I have discussed aspects of isotope geochemistry with over the years I must thank, as you have all contributed in some way, knowingly or otherwise. Specifically here at Macquarie I must thank Simon Turner for being a great sounding board (about many things beyond this book!), Ron Vernon for encouraging me to stick with it and Norm Pearson for discussions about all aspects of plasma mass spectrometry and lasers. Of course, all errors or omissions are my own and cannot be laid at the feet of these people.

The team at Cambridge University Press have been fantastic – very patient with an academic trying to do too many things at once, and so a big thank-you to Zoë Preece in particular.

Finally, I must thank my wife, Nazy, for her unquestioning support and belief that I would finish it, even if I wasn't so sure! Thank you from the bottom of my heart!

## Abbreviations and symbols

AFC	assimilation–fractionation–crystallisation. A dynamic process of modification of the composition of magma through interaction with its wallrocks during ascent and crystallisation.
amu	atomic mass unit, generally defined such that $^{12}\text{C} = 12.000000$ amu
C	‘common’ mantle component determined by the convergence of the global MORB Pb isotope arrays. Almost identical to FOZO.
CDT	Canyon Diablo troilite. A standard reference material for $\delta^{34}\text{S}$ , derived from metal obtained from the meteorite responsible for Meteor Crater, Arizona.
CF	continuous flow (IMRS)
CFB	continental flood basalt
CHUR	chondritic uniform reservoir. The purported homogeneous isotopic reservoir present in the early solar system from which the earth condensed and subsequently differentiated. Based upon the composition of chondritic meteorites. Used as a comparison isotopic reservoir, particularly for Nd isotopes, to describe relative enrichment or depletion in isotopic signature in terms of $\epsilon$ notation.
cps	counts per second
DL	detection limit (level)
DMM	depleted MORB mantle. The chemically depleted upper convecting mantle. Conceptually this reservoir can be thought of as the residue after continental crust extraction, and is depleted in lithophile elements.
EMI	enriched mantle type 1. OIB mantle component interpreted to represent recycled SCLM.

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EMII	enriched mantle type 2. OIB mantle component interpreted to represent recycled continental crust, possibly in the form of terrigenous sediment.
ESA	electrostatic analyser
FOZO	focal zone. Theoretical ubiquitous mantle component defined by the intersection of MORB and OIB arrays, particularly in Pb–Nd–Sr isotope space. Differs only in detail from PHEM, PREMA and C.
GC	gas chromatographic
GS	gas source
HFSE	high field strength elements = Zr, Nb, Hf, Ta
HIMU (‘high $\mu$ ’)	OIB with high time integrated U–Pb ratios resulting in very high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Such fractionation of U from Pb and Th is thought to take place in subducted oceanic crust.
HREE	heavy REE: Er, Tm, Yb $\pm$ Lu
IC	ion counter (also sometimes used for isotope composition, which is the measured ratio of two isotopes)
ICP(-MS)	inductively coupled plasma (mass spectrometry)
ID	isotope dilution
ID-ICP-MS	isotope dilution inductively coupled plasma mass spectrometry
ID-TIMS	isotope dilution thermal ionisation mass spectrometry
INAA	instrumental neutron activation analysis
IR	infrared
IRMS	isotope ratio mass spectrometry
KDE	kernel density estimator
LA	laser ablation
LIEF	laser induced elemental fractionation
LILE	large ion lithophile elements. Elements with a large ionic radius and small ionic charge; includes K, Rb, Sr, Cs and Ba.
LOI	loss on ignition
LREE	light REE: La, Ce, Pr, Nd
max dep	maximum deposition age of a sediment, usually constrained by the age of the youngest detrital zircon population within a sample.
MC	multi-collector
MIF	mass independent fractionation. Isotopic fractionation whereby the degree of isotopic separation does not scale as a proportion of the mass difference between the isotopes.
MORB	mid ocean ridge basalt

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MREE	middle REE: Sm, Eu, Gd, Tb, Dy, Ho
MS	mass spectrometry
MSA	magnetic sector analysis
MSWD	mean square of weighted deviates; see Section 6.2.1
NAA	neutron activation analysis
N-TIMS	negative thermal ionisation mass spectrometry
OIB	Ocean island basalts. Refers to hotspot-related magmatism as opposed to island arc magmatism.
P/D	parent-on-daughter isotopic ratio
PDB	PeeDee belemnite, an early standard used in normalisation for <sup>13</sup> C isotopic work. Since supplanted by global standards such as SMOW. The formal value of PDB has been standardised by convention in Vienna, and is referred to as VPDB.
PDF	probability density function. The likelihood that an age measured falls into a given age population within a sample.
PDP	probability density plot. Used in the visualisation of zircon populations.
PGE	platinum group elements: Rh, Rh, Pd, Os, Ir, Pt
PHEM	primitive He mantle. Ubiquitous primitive mantle component containing high He isotope signatures. Differs from PREMA, FOZO and C in subtle details.
PIMS	plasma ionisation mass spectrometry (equivalent to ICP-MS)
ppb	parts per billion = ng/g
ppm	parts per million = µg/g
ppq	parts per quadrillion = fg/g
ppt	parts per trillion = pg/g. Also sometimes used for parts per thousand (mg/g).
PREMA	prevalent mantle. Ubiquitous relatively depleted mantle reservoir defined to coincide with the depleted end of continental basalt arrays, implying a common component to these magmas. Cf. FOZO and C.
PUM	primitive upper mantle. The earth's earliest mantle formed after segregation of the siderophile elements into the earth's core from a chondritic bulk composition. The (undifferentiated) primitive mantle was broadly chondritic in incompatible element abundances and ratios.
REE	rare earth elements: La, Ce, Pr, Nd, (Pm), Sm, Eu, Gd, Tb, Dy, Ho, Er, Th, Yb ± Lu
regression	statistical technique which estimates the relationship(s) between two or more variables. Such regressions follow

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	distinct forms, depending on the distribution of the data, and include linear regressions.
RSD	relative standard deviation (expressed as a percentage)
RF	radio frequency
SCLM	subcontinental lithospheric mantle
SE	standard error
SEM	secondary electron multiplier, a type of ion counter; or standard error of the mean
SHRIMP	sensitive high-resolution ion microprobe
SIMS	secondary ionisation mass spectrometry
SLAP	standard light Antarctic precipitation. An alternative standard reference for $\delta^2\text{D}$ , $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ .
SMOW	standard mean ocean water. Since redefined and redesignated by convention in Vienna to give VSMOW. VSMOW is a standard reference value for $\delta^2\text{D}$ , $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ .
$T_{\text{DM}}$	depleted mantle model age. Usually used for Nd isotopes but also for Hf.
tit	titanite
$T_{\text{MA}}$	osmium model age
$T_{\text{RD}}$	rhenum depletion model age. A model age calculated assuming no ingrowth from the parent Re isotope, and is only applicable for Os isotopes when a sample has subchondritic Os.
UV	ultraviolet
XRD	X-ray diffraction
XRF	X-ray fluorescence
$z$	in statistics, the critical value by which the standard error is multiplied to obtain the error at a given confidence interval.

**Greek symbols**

$\alpha$ particle	an alpha particle ejected by radioactive decay comprising a helium nucleus made up of two protons and two neutrons
$\alpha$	isotopic fractionation factor
$\beta$ particle	an electron or positron emitted from the nucleus during radioactive decay
$\gamma$ particle	A form of very short wavelength ionising radiation emitted during radioactive decay
$\Delta$	the difference between two isotopic ratios which have been expressed in $\delta$ notation

xvi	<i>List of abbreviations and symbols</i>
$\delta$	the parts per mil (‰) deviation of the isotopic ratio of a sample from a standard
$\varepsilon$	the parts per 10 000 deviation of the isotopic ratio of a sample from a standard
$\lambda$	decay constant, per unit time
$\mu$	$^{238}\text{U}/^{204}\text{Pb}$
$\mu$	SI prefix symbol for ‘micro-’
$\sigma$	population standard deviation