

Isotopes in Economic Geology, Metallogeny and Exploration— Future Challenges and Opportunities

David L. Huston and Jens Gutzmer

Abstract

Although the intent of this book is to provide readers with an overview on the current and past usage of isotopes in the broad disciplines of economic geology, metallogenesis and mineral exploration, some of the chapters highlight future challenges and opportunities for the use of both radiogenic and stable isotopes within these disciplines and more broadly. This concluding section identifies and then discusses how some of these challenges might be overcome and the opportunities that might be realized.

1 Challenges to Isotopic Research

As described throughout this book, isotopic research, both on radiogenic and stable isotopes, has been essential to develop models for the genesis of many types of mineral deposits, including information on age and duration of

J. Gutzmer Helmholtz-Institute Freiberg for Resource Technology, Helmholtz-Zentrum Dresden-Rossendorf, Chemnitzer Str. 40, 09599 Freiberg, Germany

mineralizing events, tectonic and metallogenic setting, fluid, metal and sulfur sources, and alteration and fluid pathways. Despite the usefulness of this information, the application and interpretation of isotopes in economic geology, metallogenesis and exploration faces a number of analytical and interpretational challenges.

1.1 Radiogenic Isotopes and the Geochronology of Mineralizing Systems

Many recent advances in ore genesis resulted from an improving capability to understand mineral systems in the 4th dimension, time, which, in turn, has enabled direct linkages between mineral systems, other geological systems such as tectonic systems, and Earth evolution. With the development of new analytical techniques and the application of existing analytical techniques to new minerals, economic geologists have much better insights into the absolute ages and durations of mineralising events. This insight enables not only a better understanding of mineralizing processes but allows temporal linkages of these processes to other geological events that can be identified and/or tested at scales from the global to the thin section. Despite major advances in capability, many challenges remain to incorporating time into ore genesis and metallogenic models, and exploration practices.

D. L. Huston (\boxtimes)

Geocience Australia, GPO Box 378, Canberra, ACT 2601, Australia e-mail: David.Huston@ga.gov.au

[©] The Author(s) 2023

One of the most significant challenges is to develop methodologies for dating some classes of mineral deposits and criteria for assessing ages of others. A small proportion of deposits can be robustly dated using ore minerals (i.e., those minerals extracted for metal recovery). Dateable ore minerals, however, are few, for example, molybdenite (using the Re–Os systems: Norman [2023\)](#page-9-0), cassiterite, tantalite and related minerals, uraninite and other uranium minerals (U–Pb: Chelle-Michou and Schaltegger [2023\)](#page-8-0), sphalerite (Rb–Sr: Christensen et al. [1995\)](#page-8-0), scheelite (Sm– Nd; Anglin et al. [1996\)](#page-8-0), and the interpretation of age data from some of these (e.g., uraninite and sphalerite) can be fraught for many reasons, including post-depositional open system behaviour (Chiaradia [2023](#page-8-0)).

A specific example of these challenges is the fact that while uraninite can produce robust unimodal U–Pb ages (e.g., Cross et al. [2011](#page-8-0)), it more commonly gives a range of ages that can span hundreds of millions of years (e.g., Polito et al. [2005](#page-9-0)). Hence, one of the main challenges to ore geochronology is determining the geochronological significance of isotopic data: do the data indicate mineralizing events, subsequent isotopic disturbance events or related processes such as fluid or source mixing? For example, Nash et al. [\(1981](#page-9-0)) argued that the formation of some unconformity-related uranium deposits involved repeated introduction of uranium over periods of up to a billion years. More recently, Ehrig et al. ([2021\)](#page-9-0) argued for two periods of uranium introduction at the giant Olympic Dam iron-oxide copper–gold deposit in South Australia based on laser ablationinductively coupled plasma-mass spectrometry (LA-ICP-MS) ages of uraninite—an early event at ca 1590 Ma, and a later event at ca 500 Ma. A challenge to ore geochronology is to determine if multiple ages from uraninite (and other minerals) represent independent metal introduction events, metal redistribution/recrystallization events, or mixing ages.

Some deposit types, for example orogenic gold (Vielreicher et al. [2015\)](#page-10-0), can be dated using non-ore minerals but an assumption must be made (or relationship demonstrated) that the dated non-ore mineral (e.g., monazite or xenotime) is coeval with the ore mineral (gold). Other deposits can be dated using minerals in the associated alteration assemblage; this requires, however, the assumption that the alteration assemblage directly relates to the mineralizing event. A third method to infer mineralization ages is assuming a relationship between a dated rock and mineralization; for example, a skarn deposit can be dated by assuming that its age is the same as the associated granite, or an (assumed) syngenetic deposit can be dated from the age of the host rocks. In many (most) cases, such assumptions are justified and the reported ages reflect the ages of mineralization, but in other cases, the assumption may be wrong. A challenge to ore geochronologists and economic geologists is producing a set of criteria to assess geological relationships and the resulting inferred ages of mineralization.

The greatest challenge to ore geochronology is dating mineralizing events for which dateable ore, ore-related or alteration minerals are not (known to be) present and that cannot be confidently related to other dateable geological events. A good example of this challenge are Mississippi Valley-type deposits, which commonly lack dateable minerals and have ambiguous or controversial relationships to local and/or regional geological events. This challenge may be partly resolved by careful petrographic studies targeted at identifying previously-unidentified but dateable minerals. Other methods of dating, such as paleomagnetic dating (Symons et al. [1998\)](#page-10-0), may offer alternative methods of determining ages.

In addition to challenges specific to mineral deposit studies, geochronology more generally faces continued challenges to produce more precise and more accurate ages, including: (1) precise determination and calibration of decay constants across all isotopic systems used in geochronology, (2) inter-laboratory and intermethod (e.g., secondary ion mass spectrometry (SIMS) versus LA-ICP-MS) calibration, (3) improvements in analytical precision, and (4) improvements in the understanding of isotopic systems. Finally, the integration of "bulk" analyses with low spatial resolution but high

analytical precision with in-situ analyses with high spatial resolution but (commonly) low analytical precision is a challenge not only for radiogenic isotopes but also for light and metallic stable isotopes.

1.2 Radiogenic Isotopes in Tracing and Mapping

One of the major challenges facing radiogenic isotopic mapping is developing consistent methodologies for mapping and interpreting the significance of variations in isotopic data. As discussed by Champion and Huston ([2023\)](#page-8-0), Huston and Champion [\(2023](#page-9-0)) and Waltenberg [\(2023](#page-10-0)), there are many options of parameters to map, and multiple models of isotopic evolution complicate these options. To be comparable, isotopic maps must be constructed using similar isotopic growth models, for similar parameters and using similar interpolation methods (e.g., Champion and Huston [2023](#page-8-0)). Although it is sometimes necessary to use locally constrained models to address local questions, the use of inconsistent methods/models between different regions can produce erroneous maps and interpretations. These issues are in addition to challenges of compiling datasets from different sources and laboratories and the challenges of constructing maps from low-density datasets.

A second challenge to isotopic mapping is to understand and account for processes that affect measured isotopic ratios and derived parameters. These processes, which most strongly affect lead, include pre-mineralizing processes that can modify the source region (e.g., high-grade metamorphism) and post-mineralizing processes that can change initial ratios (e.g., ingrowth and isotopic disturbance). Consistent criteria must be developed to allow isotopic maps to account for such processes, which can produce highly anomalous isotopic signatures. A challenge specific to the Lu–Hf system, in which several tens of zircon spot analyses are acquired per sample (e.g., Waltenberg [2023](#page-10-0)), is developing consistent methods to determine meaningful

parameters (i.e., age and ε_{Hf}) from complex data populations that can be used in isotopic mapping.

The integration of "bulk" and in situ analyses is also a challenge to the use of lead isotopes to trace metal sources and mineralizing processes. This challenge is particularly well illustrated by the work of Gigon et al. [\(2020\)](#page-9-0), who observed variations in lead isotopic ratios of high spatial resolution but low precision SIMS analyses of galena from the HYC deposit in Australia much greater than the variability observed in low resolution but high precision double-spiked thermal ionization mass spectrometry (DS-TIMS) analyses. Gigon et al. ([2020\)](#page-9-0) argued that the in situ SIMS data indicate the mixing of two lead sources, but these relationships are not seen in the DS-TIMS data. Reasons for differences in the datasets are, at this point, unclear.

Finally, like other isotopic systems, access to inexpensive analyses with rapid turnaround is also a challenge for radiogenic isotope analyses used age determinations, source tracing and isotopic mapping. Analyses of most radiogenic isotopic systems still occurs in University or government research laboratories, although commercial geochemical laboratories are starting to offer lead isotope analyses using ICP-MS analyses.

1.3 Light Stable Isotopes

The main challenges to the use and interpretation of stable isotopes are the availability of abundant, low cost and high quality analyses and reconciling differences between bulk and in situ analyses. As indicated by Barker et al. ([2013\)](#page-8-0), analyses of light stable isotopes must have a fast turn-around time, be relatively inexpensive and be produced in large number before they are routinely incorporated into mineral exploration programs. The last point is critical, as large populations are required to statistically assess anomalies produced from isotopic data. The availability of inexpensive microanalytical tools such as LA-ICP-MS may achieve rapid production of large numbers of rapid, inexpensive

analyses, but as discussed below, interpretation of the results are commonly not simple.

In reviewing stable isotopes in shale-hosted zinc deposits, Williams [\(2023](#page-10-0)) found that sulfur isotope values determined using in situ analysis were much more variable that values determined from bulk analyses. Hence, like radiogenic isotopes, the integration of bulk and in situ analyses also presents a challenge to the interpretation of stable isotope data. Even though sample aliquots might only be a few milligrams, bulk analyses homogenize variability seen in in situ analyses, based on much smaller sample volumes. Consequently, the challenge remains to integrate these two broad analytical techniques, with implications for interpretating the scale and process of mineralizing events.

1.4 Metallic Stable Isotopes

As variations in metallic stable isotopes were only discovered in the last two to three decades, research into this field is less mature, and the challenges differ to other fields of isotopic research. The main challenge for metallic stable isotopes is to acquire sufficient data to document natural variability in isotopic ratios and determine processes that cause this variation. The amount of basis data varies according to metal; for zinc, there is a small, but growing, dataset for sediment-hosted deposits, but datasets for other deposit types are very small, in some cases constituting only a handful of analyses (Wilkinson [2023](#page-10-0)). The datasets for iron and copper are larger (Lobato et al. [2023;](#page-9-0) Mathur and Zhao [2023\)](#page-9-0), but still require additional data, particularly to understand processes that control isotopic fractionation.

A second challenge is the experimental determination of temperature-dependent mineralfluid, mineral-melt and mineral–mineral fractionation curves for common Fe-, Cu- and Znbearing minerals, including biologicallymediated fractionation. Although fractionation curves for iron and copper isotopes have been determined for some minerals (cf. Lobato et al. [2023;](#page-9-0) Mathur and Zhao [2023](#page-9-0)), similar curves for zinc isotopes are limited (Wilkinson [2023\)](#page-10-0). Hence, one of the greatest challenge to interpreting metallic stable isotope data is the acquisition of well-calibrated experimental fractionation curves and understanding application of experimentally determined equilibration relationships to real world ore deposits.

A third challenge for metallic stable isotopes is developing rapid and inexpensive analytical methods, including automation. Like other isotopes, metallic stable isotopes will not be routinely used by the exploration industry until this last challenge is met, although it is important to stress that there is significant interest from industry to use metallic isotopes to resolve specific ore genesis problems.

2 Opportunities for Isotopic Research

Like most other fields of scientific research, there have been important advances in the capability to determine isotopic ratios and understanding processes that cause changes in isotopic ratios. These advances present opportunities to apply the isotopic data to geological and, more specifically, mineral system problems.

In many cases, opportunities in isotopic research have come from unorthodox research, which, in some cases, were in conflict with perceived wisdom at the time—for example, expectations that isotopic fractionation should be mass dependent or that metallic isotopes should not fractionate. Some of these unorthodox opportunities, as described in this book, have provided not only entirely new datasets that can be used to test new and existing models for geological systems, but entirely new ideas about processes involved in mineral systems and, more broadly, Earth systems.

Like in many other fields in geoscience, another important opportunity (and challenge) for isotopic research is data integration. This includes integration of different isotopic systems and/or different analytical techniques, integration of isotopic data with other geoscience data, and

.

integration of isotopic data with data beyond geoscience disciplines. Data integration can occur from thin section to global scales and commonly provides new insights into Earth processes. This opportunity also extends to the rapidly evolving fields of artificial intelligence and machine learning. These fields offer opportunities for comprehensive evaluation of the integrated data using statistical and stochastic approaches that quantify relationships between isotopic and other geoscientific datasets.

2.1 Radiogenic Isotopes and the Geochronology of Mineralizing Events

Despite the challenges described above, ore geochronology has many opportunities, from determining the timing and duration of mineral systems, to the dating of mineralizing events using new minerals and/or isotopic systems, to integrating the geochronology data into processoriented numerical models of mineralizing events, and to linking these events to other geological events at the district to global scales. As summarized by Chiaradia [\(2023](#page-8-0)) and Chelle-Michou and Schaltegger ([2023\)](#page-8-0), the duration of individual mineralizing events in porphyry copper systems typically last a few tens of thousands or years, although multiple events may overprint each other to produce to mineralizing systems that last much longer and produce much larger metal endowments. Although well constrained for porphyry mineral systems, the duration of mineralizing events for other systems is poorly known. Moreover, information on the duration and overprinting of mineralizing events can be fed into exploration questions with direct exploration implications: Do highly endowed deposits require long durations? Or multiple events?

Although dating of some deposits is a challenge to ore geochronology, opportunities exist to resolve some of these challenges. These include recognition of dateable minerals in ore assemblages and dating of ore-related minerals not commonly dated at present. Many dateable orerelated minerals are not readily recognized during routine petrography and require systematic microanalytical methods such as scanning electron microscope (SEM)-based image analysis (*aka* automated mineralogy: Sylvester [2012;](#page-9-0) Schulz [2021\)](#page-9-0) or similar microprobe-based techniques for reliable identification. These techniques not only identify dateable minerals but also place these minerals in textural and paragenetic context. Personal experience indicates that SEM-based image analysis can identify dateable minerals such as phosphates (e.g., apatite, monazite and xenotime) in mineral deposits previously not known to have dateable minerals. In addition, many deposits contain potentially dateable minerals such as fluorite (U–Pb of Sm–Nd), allanite (U–Th–Pb), rare earth element minerals (Sm–Nd), scheelite (U–Pb) and titanite (U–Pb) for which ages are not routinely determined.

Another opportunity for research in ore geochronology is the integration of age data into numerical models of mineral system evolution. For example, Chelle-Michou et al. ([2017\)](#page-8-0) used thermal models and Monte Carlo simulations to simulate the evolution of the porphyry copper mineral system during granite emplacement. They combined this modelling with data on endowment and the duration of mineralization from eight porphyry copper deposits around the world to conclude that system duration and the total magma volume are the main controls on copper endowment, and not magma enrichment in sulfur or copper. This illustrates the potential to combine geochronological data with modelling to define the most important controls on endowment for many types of mineral systems.

The growing dataset of high precision and robust ages of mineral deposits also allows linkage of mineralizing events to other geological events at the local to global scales. This allows not only the testing of genetic models, but also incorporating mineralizing systems into Earth evolution. As an example of the former, Phillips et al. ([2012\)](#page-9-0) identified two gold mineralizing events in the Victorian goldfields (southeast Australia), an early event at ca 450–440 Ma temporally associated with the Benambran Orogeny but not with magmatism, and a second event at 380–370 Ma temporally associated the

Tabberabberan Orogeny and with granitic magmatism (see also Wilson et al. [2020](#page-10-0)). Over the last few decades, there has been a debate over the role of magmatism in orogenic gold deposits and the relationship of orogenic to intrusion-related gold deposits. The combination of geochronological (e.g., Philips et al. [2012](#page-9-0)) and structural (Wilson et al. [2020\)](#page-10-0) syntheses allow for an assessment of the roles of granites in orogenic gold mineral systems (not necessary, at least for the Benambran system in western Victoria) and between orogenic and intrusion-related gold deposits.

Meyer ([1981\)](#page-9-0), Lambert and Groves ([1981\)](#page-9-0), Lambert et al. (1992) (1992) , Kerrich et al. (2005) (2005) and many others have shown that the distribution of mineral deposits through time is not uniform, with different classes of deposits having distributions that can be related global tectonic events and environmental changes. The early observations by Meyer [\(1981](#page-9-0)) and by Lambert and Groves [\(1981](#page-9-0)) have largely held up, and the greater availability of high precision geochronological data have refined deposit distributions and demonstrated that the distribution of many deposits are related to global tectonic processes such as the assembly and break-up of supercontinents and global environmental events such as the Great Oxidation Event. Continued acquisition of ore geochronology data will test current ideas on global controls on metallogenesis and generate new ideas.

2.2 Radiogenic Isotopes in Tracing and Mapping

Radiogenic isotope mapping has shown systematic spatial patterns in Sm–Nd, Pb–Pb and Lu–Hf data that appear to be related to continental to province-scale crustal boundaries identified using other datasets (Champion and Huston [2023;](#page-8-0) Huston and Champion [2023](#page-9-0); Waltenberg [2023\)](#page-10-0). In many cases, the tectonic implications of these boundaries are either poorly known or controversial. The changes in isotopic characteristics across these boundaries can provide important constraints on the tectonic processes that

produced the boundaries. For example, Cham-pion [\(2013\)](#page-8-0) interpreted decreasing T_{2DM} from north to south in the North Australian Craton as evidence for a long-lived convergent margin along the southern margin, with implications to metallogenesis of this province.

Armistead et al. [\(2021](#page-8-0)), using lead isotope data from volcanic-hosted massive sulfide (VHMS) and orogenic gold deposits, showed that at the global scale the range in μ has changed with time, with the period after 1000 Ma having a more restricted range that the period before. Moreover, S Armistead (pers comm, 2022) suggests that individual terranes have different lead isotope characteristics that may be used as a dataset to provide independent tests of paleotectonic reconstructions and tectonic models, even back into the Paleoarchean. Hence, radiogenic isotope data and derived maps can be used to place constraints on tectonic models, with implications to metallogenic models.

Opportunities also exist to merge data from different isotopic systems into one map. Vervoot et al. ([1999\)](#page-10-0) demonstrated that ε_{Hf} and ε_{Nd} strongly correlate for terrestrial rocks, indicating that the two parameters are related by a simple linear relationship. Use of this relationship raises the possibility that isotopic maps from the Sm– Nd and Lu–Hf systems can be combined into one map. Another opportunity is extending isotopic mapping to other isotopic systems, for example the Re–Os system.

Owing to their increasing importance in the energy transition, rare earth elements (REEs) have become critical to the global economy, yet mineral systems that form REE deposits are poorly understood. As the Sm–Nd and Lu–Hf isotopic systems are integral parts of REE mineral systems, these isotopic systems can provide direct constraints on the sources of and processes that enrich REEs.

Finally, Armistead et al. ([2022\)](#page-8-0) developed an R tool to automatically calculate μ and other parameters from lead isotope data. Automation of these calculations and isotope mapping methods will allow more widespread use of isotopic data in metallogenic and tectonic studies, and, ultimately, exploration.

2.3 Light Stable Isotopes

Despite being a mature discipline, light stable isotope research has seen several analytical breakthroughs this century, leading to important new insights into process in both Earth and mineral systems (Huston et al. [2023a\)](#page-9-0). These analytical breakthroughs, and breakthroughs in data integration, have and will continue to produce opportunities to apply isotope data to mineral system problems.

A feature of the four chapters on the use of stable isotopes in specific mineral systems is data integration. Huston et al. [\(2023b](#page-9-0)) integrate oxygen-hydrogen and sulfur isotope data with temporal data to infer that the fluid temperature and sulfur source in VHMS mineral systems have broadly changed with geological time. Quesnel et al. ([2023\)](#page-9-0) integrate a range of isotopic data from orogenic gold deposits with temporal data to show how fluid sources have (and have not) evolved through time, and Hagemann et al. [\(2023](#page-9-0)) integrate data from Australia, Brazil and South Africa to show the complexities and similarities of ore fluids that upgraded iron formation to form high-grade iron ore deposits. Finally, Williams [\(2023](#page-10-0)) integrates isotopic data with paragenetic observations from major shalehosted zinc deposits from the North Australian Zinc Belt and the Northern Cordillera in North America to assess differing hypotheses of ore formation and the sources of sulfur and carbon. All four studies illustrate the opportunity of the integration of isotopic data with other data at the global scale to provide insights into mineral system processes not available through the study of individual deposits.

Opportunities for data integration extend to the microscopic scale as analytical capabilities now allow collection of a wide range of isotopic (and other) data from the same thin section and even the same analytical spot. Collection of comprehensive data from the same sample enables a much clearer and more complete view of stable isotopes and the processes that cause their fractionation.

In addition to the opportunities offered by microanalysis described above, the development of effective techniques to analyze multiple isotopes, specifically sulfur isotopes, has offered new insights into the sources of sulfur in mineral deposits and processes that have affected the sulfur cycle through time (Farquhar et al. [2000;](#page-9-0) Caruso et al. [2022](#page-8-0); Huston et al. [2023a](#page-9-0),[b\)](#page-9-0). Application of multiple sulfur isotope analyses to other mineral systems will continue to provide new constraints on sulfur sources and mineralizing processes.

Unlike multiple sulfur isotopes, clumped isotopes, that is combined variations of isotopes in molecules (isotopologues), have not as yet been used extensively in mineral system studies. Clumped isotope analyses, mostly of $CO₂$ extracted from carbonate minerals, provides information about the temperature of mineral formation that is independent of the isotopic composition of the fluid (Ghosh et al. [2006\)](#page-9-0). Mering et al. ([2018\)](#page-9-0) have shown the potential of clumped isotopes for a number of geothermal systems and mineral deposits to indicate mineralization temperatures and infer $\delta^{18}O$ of the mineralizing fluids. Because the fractionation of clumped isotopes increases with decreasing temperatures, clumped isotopes will be particularly useful in low temperature mineral systems, for example many basin-hosted systems. As temperature calibrations are developed for minerals with higher temperature of closure to isotope reordering, this new tool will have more widespread application (Quesnel et al. [2022\)](#page-9-0). The potential of clumped isotopes is enhanced by the development of new, rapid analytical techniques for very small samples (Sakai et al. [2017\)](#page-9-0). Tunable mid-infrared laser absorption spectrometry (TILDAS), as developed by Sakai et al. [\(2017](#page-9-0)), differs from virtually all other methods of isotopic analysis in that it uses infrared spectroscopy rather than mass spectrometry to determine mass ratios.

Finally, recent analytical developments also allow for determination of boron isotopes from minerals in which boron is a minor constituent;

previously boron isotope analyses have largely been restricted to tourmaline. For example, Codeço et al. ([2019\)](#page-8-0) determined hydrothermal temperatures and $\delta^{11}B$ of ore fluids at the Panasquiera W-Sn deposit in Portugal using coeval tourmaline and white mica.

2.4 Metallic Stable Isotopes

Being a relatively new discipline, metallic stable isotopes offer a number of opportunities to counterbalance the challenges described above. As both copper and iron occur naturally in multiple valence states, one of the greatest opportunities for the using isotopes of both metals is to understand reactions, in particular redox reactions, involved in hypogene mineralization and supergene enrichment (Lobato et al. [2023;](#page-9-0) Mathur and Zhao [2023](#page-9-0)). The major cause of iron isotope fractionation are redox reactions that convert ferric to ferrous iron (or vice versa). These reactions occur in many geological environments and can include both biologically mediated and abiological reactions (Johnson et al. [2008;](#page-9-0) Lobato et al. [2023\)](#page-9-0). Hence, iron isotopes can be used to better understand processes involved in formation of not only iron ore deposits, but also other deposits in which iron is a major component of the ores.

As discussed by Mathur and Zhao ([2023\)](#page-9-0), much of the variability in δ^{65} Cu in deposits stems from redox and other reactions, either during hypogene ore formation or supergene overprinting. Although δ^{65} Cu variations occur in high temperature systems such as orthomagmatic mafic-hosted Ni–Cu deposits (Zhao et al. [2017\)](#page-10-0), the greatest fractionations are associated with low temperature systems. Variations in $\delta^{65}Cu$ can track redox reactions and reflect fluid pathways in sediment-hosted copper deposits (Haest et al. [2009\)](#page-9-0), whereas δ^{65} Cu data can be used to assess the degree of weathering in leached caps that have developed over porphyry copper deposits and distinguish between hypogene versus supergene origins for copper minerals such as chalcocite (Mathur and Zhao [2023](#page-9-0)).

All three metallic isotope systems discussed in this book have potential as vectors to ore. Lobato et al. [\(2023](#page-9-0)) indicate that decreases in δ^{56} Fe (and δ^{18} O) may vector toward shear zones that have acted as fluid conduits during the upgrading of iron formation to iron ore. Similarly, Mathur and Zhao ([2023\)](#page-9-0) show δ^{65} Cu zonation in a number of deposit types (porphyry copper, epithermal, skarn and layered mafic intrusion), indicating that δ^{65} Cu may be a useful tool to distinguish ore types and test linkages between deposit types in the same district (e.g., between porphyry copper and epithermal deposits), and assess gossanous exposures. Wilkinson ([2023](#page-10-0)) also notes zonation in $\delta^{66}Zn$ in several sediment-hosted zinc deposits. These variations may have the potential for use as deposit-scale vectors, but more case studies are clearly required.

Finally, based upon current data, metallic stable isotopes have limited opportunity as a tool to identify metal sources. Mathur and Zhao [\(2023](#page-9-0)) indicate that variability of δ^{65} Cu in common rock types is limited, and most variability present in mineral deposits relates to chemical reactions during hypogene mineralization or supergene upgrading. Similarly, although based on a much smaller dataset, Wilkinson [\(2023](#page-10-0)) indicates that the variability in $\delta^{66}Zn$ in common rock types is also small. With the exceptions of Precambrian shales and iron formation, δ^{56} Fe of sedimentary and igneous rocks overlap each other and bulk silicate Earth (Dauphas and Rouxel [2006\)](#page-9-0), limiting the utility of iron isotopes to determine iron sources in most ore deposits.

3 Conclusions

The syntheses of isotopic research related to mineral system science presented in this book highlight the importance of isotopes to develop knowledge of geological processes important to ore formation. Moreover, each chapter has identified important challenges and opportunities for continued contributions of isotopes to ore formation at all scales and to mineral exploration.

Many of the challenges to isotopic science in economic geology, metallogenesis and exploration relate to the availability and quality of data. For a number isotopic systems that have only recently become viable due to analytical developments, the amount of data available is relatively small and gathering sufficient data to determine natural variations in isotopic ratios is a fundamental challenge, but also a major opportunity for further research. For other, more mature isotopic systems, improving analytical quality through inter-laboratory and inter-method calibration is a major challenge. A related challenge is the integration of bulk and in situ analyses. For most isotopic systems, the development of rapid and inexpensive analyses is essential to enable the use of isotopic data in routine mineral exploration, although it must be stressed that the data are used by industry to resolve specific ore genesis questions. New analytical methods, such as TILDAS (Sakai et al. [2017](#page-9-0)) may offer the opportunity for rapid, high-precision isotopic analyses necessary for routine usage in mineral exploration.

The opportunities for isotopic research are many and varied. They range from the development of new analytical techniques for an increasing number of isotopic systems, through the application of these new developments and more conventional analyses to develop and test concepts of ore systems, and to the integration of data from multiple isotopic systems with other geological data. Perhaps the most exciting opportunity in isotopic research is this integration at scales from the global to the microscopic. Such integration at the global scale has already proved successful in documenting secular changes in the characteristics of mineral systems and the implications of these changes to mineral system processes. Isotopic research continues to be a backbone to the development of models of ore formation, but it faces a major challenge to become widely used in mineral exploration.

Acknowledgements The authors thank Georges Beaudoin, Cyrille Chelle-Michou, Geoff Fraser, Marc Norman and Kathryn Waltenberg for comments on the original draft of the contribution, which is published with permission of the Chief Executive Officer, Geoscience Australia.

References

- Anglin CD, Jonasson IR, Franklin JM (1996) Sm-Nd dating of scheelite and tourmaline: implications for the genesis of Archean gold deposits, Val d'Or, Canada. Econ Geol 91:1372–1382
- Armistead S, Eglington B, Pehrsson S, Huston D (2021) Pb isotope variability in the Archean: insights from the Superior Province, Canada. Geosci Can 48:153
- Armistead S, Eglington B, Pehrsson S (2022) Pbiso: an R package and web app for calculating and plotting Pb isotope data. [https://eartharxiv.org/repository/view/](https://eartharxiv.org/repository/view/2841/) [2841/](https://eartharxiv.org/repository/view/2841/). [https://doi.org/10.31223/X56G84](http://dx.doi.org/10.31223/X56G84)
- Barker SL, Dipple GM, Hickey KA, Lepore WA, Vaughan JR (2013) Applying stable isotopes to mineral exploration: teaching an old dog new tricks. Econ Geol 108:1–9
- Caruso S, Fiorentini ML, Champion DC, Lu Y, Ueno Y, Smithies RH (2022) Sulfur isotope systematics of granitoids from the Yilgarn Craton sheds new light on the fluid reservoirs of Neoarchean orogenic gold deposits. Geochim Cosmochim Acta 326:199–213
- Champion DC (2013) Neodymium depleted mantle model age map of Australia: explanatory notes and user guide. Geosci Austr Rec 2013/44
- Champion DC, Huston DL (2023) Applications of Nd isotopes to ore deposits and metallogenic terranes; using regional isotopic maps and the mineral systems concept. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Chelle-Michou C, Schaltegger U (2023) U–Pb dating of mineral deposits: from age constrains to ore-forming processes. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Chelle-Michou C, Rottier B, Caricchi L, Simpson G (2017) Tempo of magma degassing and the genesis of porphyry copper deposits. Sci Rep 7:40566
- Chiaradia M (2023) Radiometric dating applied to ore deposits: theory and methods. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Christensen JN, Halliday AN, Vearncombe JR, Kesler SE (1995) Testing models of large-scale crustal fluid flow using direct dating of sulfides; Rb–Sr evidence for early dewatering and formation of Mississippi Valleytype deposits, Canning Basin, Australia. Econ Geol 90:877–884
- Codeço MS, Weis P, Trumbull R, Glodny J, Wiedenbeck M, Romer RL (2019) Boron isotope muscovitetourmaline geothermometry indicates fluid cooling during magmatic-hydrothermal W-Sn ore formation. Econ Geol 114:153–163
- Cross A, Jaireth S, Rapp R, Armstrong R (2011) Reconnaissance-style EPMA chemical U–Th–Pb dating of uraninite. Aust J Earth Sci 58:675–683
- Dauphas N, Rouxel O (2006) Mass spectrometry and natural variations of iron isotopes. Mass Spectrom Rev 25:515–590
- Ehrig K, Kamenetsky V, McPhie J, Macmillan E, Thompson J, Kamenetsky M, Maas R (2021) Staged formation of the supergiant Olympic Dam uranium deposit, Australia. Geology 49:1312–1316
- Farquhar J, Bao H, Thiemens M (2000) Atmospheric influence of Earth's earliest sulphur cycle. Science 289:756–758
- Ghosh P, Adkins J, Affek H, Balta B, Guo W, Schauble EA, Schrag D, Eiler JM (2006) ¹³C-¹⁸O bonds in carbonate minerals: a new kind of paleothermometer. Geochim Cosmochim Acta 70:1439–1456
- Gigon J, Deloule E, Mercadier J, Huston DL, Richard A, Annesley IR, Wygralak AS, Skirrow RG, Mernagh TP, Masterman K (2020) Tracing metal sources for the giant McArthur River Zn–Pb deposit (Australia) using lead isotopes. Geology 48:478–802
- Haest M, Muchez P, Petit JCJ, Vanhaecke F (2009) Cu isotope ratio variations in the Dikulushi Cu–Ag deposit, DRC: of primary origin or induced by supergene reworking. Econ Geol 104:1055–1064
- Hagemann S, Hensler A-S, Figueiredo e Silva RC, Tsikos H (2023) Light stable isotope (O, H, C) signatures of BIF-hosted iron ore systems: implications for genetic models and exploration targeting. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Huston DL, Champion DC (2023) Applications of lead isotopes to ore geology, metallogenesis and exploration. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Huston DL, Trumbull RB, Beaudoin G, Ireland T (2023a) Light stable isotopes (H, B, C, O and S) in ore studies —methods, theory, applications and uncertainties. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Huston DL, LaFlamme C, Beaudoin G, Piercey S (2023b) Light stable isotopes in volcanic-hosted massive sulfide ore systems. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Johnson CM, Beard BL, Roden EE (2008) The iron isotope fingerprints of redox and biogeochemical cycling in modern and ancient Earth. Annu Rev Earth Planet Sci 36:457–493
- Kerrich R, Goldfarb RJ, Richards JP (2005) Metallogenic provinces in an evolving geodynamic framework. Econ Geol 100^{th} Anniv Vol $1097-1136$
- Lambert IB, Groves DI (1981) Early earth evolution and metallogeny. Handbook Stratabound Stratiform Ore Deposits 8:339–447
- Lambert IB, Beukes N, Klein C, Veizer J (1992) Proterozoic mineral deposits through time. In Schopf JW Klein C (eds) The proterozoic biosphere:

a multidisciplinary study. Cambridge University Press, Cambridge, pp 59–62

- Lobato LM, Figueiredo e Silva RC, Angerer T, Mendes M, Hagemann S (2023) Fe isotopes applied to BIF-hosted iron ore deposits. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Mathur R, Zhao Y (2023) Copper isotopes used in mineral exploration. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Mering JA, Barker SLL, Huntington KW, Simmons S, Dipple G, Andrew B, Schauer A (2018) Taking the temperature of hydrothermal ore deposits using clumped isotope thermometry. Econ Geol 113:1671– 1678
- Meyer C (1981) Ore-forming processes in geologic history. Econ Geol 75th Anniv Vol 63-116
- Nash JT, Granger HC, Adams SS (1981) Geology and concepts of genesis of important types of uranium deposits. Econ Geol 75th Anniv Vol 63-116
- Norman MD (2023) The 187 Re- 187 Os and 190 Pt- 186 Os radiogenic isotope systems: techniques and applications to metallogenic systems. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Phillips D, Fu B, Wilson CJL, Kendrick M, Fairmaid A, J. McL Miller JMcL, (2012) Timing of gold mineralization in the western Lachlan Orogen, SE Australia: a critical overview. Austr J Earth Sci 59:495–525
- Polito PA, Kyser TK, Rheinberger G, Southgate PN (2005) A paragenetic and isotopic study of the Proterozoic Westmoreland uranium deposits, southern McArthur Basin, Northern Territory, Australia. Econ Geol 100:1243–1260
- Quesnel B, Jautzy J, Scheffer C, Raymond G, Beaudoin G, Jørgensen TRC, Pinet N (2022) Clumped isotope geothermometry in Archean mesothermal hydrothermal systems (Augmitto-Bouzan orogenic gold deposit, Abitibi, Québec, Canada): a note of caution and a look forward. Chem Geol 610:121099. [https://doi.org/10.](http://dx.doi.org/10.1016/j.chemgeo.2022.121099) [1016/j.chemgeo.2022.121099](http://dx.doi.org/10.1016/j.chemgeo.2022.121099)
- Quesnel B, Scheffer C, Beaudoin G (2023) The light stable isotope (H, B, C, N, O, Si, S) composition of orogenic gold deposits. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Sakai S, Matsuda S, Hikida T, Shimono A, McManus JB, Zahniser M, Nelson D, Dettman DL, Yang D, Ohk-
ouchi N (2017) High-precision simultansous ${}^{18}O/{}^{16}O$, $^{13}C/^{12}C$, and $^{17}O/^{16}O$ analyses of microgram quantities of $CaCO₃$ by tunable infrared laser absorption spectrosopy. Anal Chem 89:11846–11852
- Schulz B (2021) Monazite microstructures and their interpretation in petrochronology. Front Earth Sci 9:668566
- Sylvester PJ (2012) Use of the mineral liberation analyzer (MLA) for mineralogical studies of sediments and

sedimentary rocks. Mineral Assoc Can Short Course Notes 42:1–16

- Symons DTA, Lewchuk MT, Leach DL (1998) Age and duration of the Mississippi Valley-type mineraling fluid flow event in the Viburnaum Trend, southeast Missouri, USA, determined from paleomagnetism. Geol Soc Lond Spec Pub 144:27–39
- Vervoot JD, Patchett PJ, Blichert-Toft J, Albarede F (1999) Relationships between Lu-Hf and Sm-Nd isotopic systems in the golobal sedimentary system. Earth Planet Sci Lett 168:79–99
- Vielreicher N, Groves D, McNaughton N, Fletcher I (2015) The timing of gold mineralization across the eastern Yilgarn craton using U–Pb geochronology of hydrothermal phosphate minerals. Mineral Deposita 50:391–428
- Waltenberg K (2023) Application of Lu-Hf isotopes to ore geology, metallogenesis and exploration. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Williams N (2023) Light-element stable isotope studies of the clastic-dominated lead-zinc mineral systems of northern Australia & the North American Cordillera: implications for ore genesis and exploration. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Wilkinson JJ (2023) The potential of Zn isotopes in the science and exploration of ore deposits. In: Huston DL, Gutzmer J (eds) Isotopes in economic geology, metallogensis and exploration. Springer, Berlin (this volume)
- Wilson CJL, Moore DH, Vollgger SA, Madeley HE (2020) Structural evolution of the orogenic gold deposits in central Victoria, Australia: the role of regional stress change and the tectonic regime. Ore Geol Rev 120:103390
- Zhao Y, Xue C, Liu S-A, Symons DTA, Zhao X, Yang Y, Ke J (2017) Copper isotope fractionation during sulfidemagma differentiation in the Tulaergen magmatic Ni– Cu deposit, NW China. Lithos 286–287:206–215

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License ([http://creativecommons.org/licenses/by/4.0/\)](http://creativecommons.org/licenses/by/4.0/), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

