Paper 36

Advances in the Use of Isotopes in Geochemical Exploration: Instrumentation and Applications in Understanding Geochemical Processes

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ABSTRACT

Among the emerging techniques to detect the real footprint of buried ore deposits is isotope tracing. Novel and automated preparation systems such as continuous flow isotope ratio mass spectrometry, off-axis integrated cavity output spectroscopy for isotopic compositions of selected molecules, multi-collector ICP-MS, laser ablation ICP-MS, and a multitude of in-line prep systems have facilitated the use of isotopes as tracers in mineral exploration, as costs for isotope analyses have decreased and the time required for the analyses has improved. In addition, the isotope systems being used have expanded beyond the traditional light stable and Pb isotopes used in the past to include a multitude of elements that behave differently during processes that promote the mobilization of elements during both primary and secondary dispersion. Isotopes are also being used to understand barren areas that lack a critical process and to reveal precise redox mechanisms. The goal is to be able to use isotopes to reflect a definitive process that occurs in association with the deposit and not in barren systems, and then to relate these to something that is easier to measure, namely elemental concentrations. As new generations of explorationists and environmental scientists are becoming more comfortable with the application of isotopes to effectively trace processes involved in geoscience, and new technologies for rapid and inexpensive analyses of isotopes are continually developed, novel applications of isotope tracing are becoming more mainline.

ISOTOPES AS ADDED VALUE TO EXPLORATION

Elemental concentrations are typically used to assess element migration in the near-surface environment (e.g. Cameron et al., 2005), but until recently they were rarely integrated with isotopic information to fingerprint specific sources of the elements, in large part because of the costs and time investment required for measuring isotopes. These issues with isotope measurements have been largely addressed via recent technological advances so that the potential for isotopes to add value to exploration is substantial, but to do so they must do the following: (1) be definitive indicators of mineralization, either directly as an element with a specific isotopic composition that reflects the ore, or indirectly as tracing a specific fluid or component related to the ore generating process, (2) be timely for exploration deadlines, inexpensive to measure, and easy to interpret, (3) relate to a process that makes sense to us, such as microbial action on ores or magmatic components, and (4) hopefully be related to something that is always measured as part of exploration, such as element concentrations. The real power of isotopic compositions is that they elucidate specific processes that can be related to the mineralizing system and therefore have the potential to extend the footprint of deposits and identify false positives in element concentrations more effectively.

Recent advances in technologies for the light stable isotopes of H, C, N, O, and S, the advent of clumped isotopes to trace kinetic processes for light stable isotopes such as those involved with microbial activity, along with advancements in Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for multi-

element and metal isotope analysis have allowed the use of integrated element contents and their isotopic compositions to trace elements more effectively (e.g. Kyser et al., 2015a). Isotopic compositions can be used to fingerprint an element or compound because most reservoirs in natural systems are isotopically distinct. Elements that are known to have variations in their isotopic compositions because of separation of their isotopes due to mass and bonding environment differences and have been used in exploration and environmental science include H, Li, B, C, N, O, Mg, S, Ca, Fe, Cu, Zn, Mo, Se, Tl and U, but virtually all elements with two or more isotopes can be used for isotopic tracing (Figure 1). Most of the elements that have been used to date are redox active, as oxidation-reduction reactions produce the largest fractionations of isotopes and thus the largest variations in isotopic compositions. Other elements that have been used have isotopes produced by radioactive decay (Figure 1), thereby changing abundance with time, and include Sr, Nd and Pb that have been used in petrology, exploration and environmental science. Both radioactive decay and partitioning of isotopes between different phases make isotopes unrivalled indicators of a variety of processes involving material fluxes among the hydrosphere-geosphere-biosphere-atmosphere.

Most ore deposits are composed of high concentrations of redox active elements. They represent areas of variable electron density that are havens for microbial communities that rely on oxidation-reduction reactions for their metabolisms. These microbes can mobilize elements from the deposits as aqueous or gaseous complexes having unique isotopic compositions in their waste products or from the decay products of the microbes (Leslie et al., 2014). Such complexes migrate to the surface

during secondary dispersion processes, particularly along fractures and faults and become variably attenuated by clay and Fe-Mn oxide surfaces, and make their way into the biosphere at the surface (Figure 2). These complexes will have specific elemental and isotopic signatures that reflect the deposit at depth. Even if these signatures are altered during ascent or diluted with components at the surface, such as from anthropogenic activity, their distinct isotopic compositions should be recorded in media at the surface. Innovative techniques that lead to new exploration strategies for metals and energy-related resources with less environmental impact are industry priorities. Environmental compliance of operating mines and permitting of new mines increasingly rely on understanding element mobility, speciation and bioavailability and isotope techniques are unique tools that can separate the impacts of human activities on the environment from the impact of elements being mobilized from buried ore deposits.
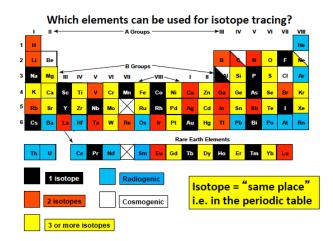

Figure 1: Periodic table showing the number of isotopes for each element. Also shown are elements with isotopes that are radiogenic or cosmogenic. Any element with 2 or more isotopes, or a radiogenic or cosmogenic isotope, can be used for isotope tracing.
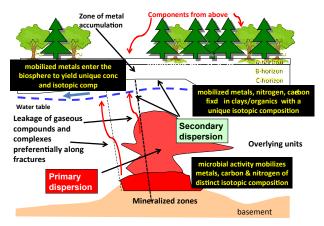

Figure 2: Processes involved in primary and secondary dispersion of elements and their isotopes.

LIGHT STABLE ISOTOPES

Stable isotopes of H, C, O, and S have been applied to mineral deposit and environmental research for the past several decades (e.g. Engel, 1959; Taylor, 1974; Clarke et al., 1983; Andrew, 1983). The isotopes of these elements have been used to trace the origin and evolution of ore-forming fluids and their effect on rocks around the deposit during primary dispersion processes, thereby extending the footprint of the mineralizing system. (e.g. Green et al., 1983; Kyser et al., 1986; Criss and Fleck, 1990; Nesbitt, 1996; Lindsay and Brasier, 1999; Large et al., 2001; Bierlein et al., 2004; Champion and Huston, 2016). These elements are the major players in most ore forming systems, and if the desire is to characterize the fluids involved, one should use what the fluid is, namely these elements.

Lack of interest in using isotopes in mineral exploration traditionally can be attributed to (1) the necessity of accessing specialist laboratories, (2) the long delays for analysis of large numbers of samples, (3) the high cost per sample, and (4) the inability of many explorationists to interpret the data correctly. Stable isotope data has potential to be of significant assistance during mineral exploration, but due to issues surrounding cost, time and uncertainty in data interpretation, it has not yet been widely applied outside of academic studies. New technologies and techniques have been developed to address many of these problems. Light stable isotope analyses were revolutionized about 30 years ago with the advent of Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) (e.g. McMillan et al., 1989), wherein the sample is prepared directly inline with the mass spectrometer using a helium carrier gas. The samples can be combusted or pyrolyzed, and the resulting gases are chemically purified and specific compounds separated by gas chromatography. The analysis time is much shorter, the amount of sample required is smaller and the cost is much less than conventional analyses. There are several commercial labs that use CF-IRMS to provide light stable isotope analyses, although most tend to provide specialized analyses for the petroleum industry. Many of the largest commercial laboratories used by the exploration, mining and environmental industries have agreements with academic labs and experts who provide high-quality analyses to the commercial labs. These special arrangements include agreements for fast turnover and preferred prices. The academic partners also provide advice and interpretation if so requested. Commercial labs will develop their own facilities as demand for isotopic analyses increases. However, certain analyses, including O isotopes in silicates and oxides and selective extraction of phases in complex mixtures, still require conventional analyses and thus tend to be expensive and labour intensive. *In Situ* analysis of light stable isotopes has only successfully been accomplished using Secondary Ion Mass Spectroscopy (SIMS) which requires standards that are isotopically homogeneous and matrix matched to the samples (Riciputi et al., 1998).

Alternative techniques have also been applied to exploration to increase output and decrease costs. These include Off-axis Integrated Cavity Output Spectroscopy (OA-ICOS) that uses infrared absorption spectroscopy to measure isotopic species (e.g. Barker et al., 2011). These instruments are somewhat smaller and less expensive than mass spectrometers and are

somewhat portable, but the sample preparation is the same as that used in conventional analyses because a purified gas is required. The successful utility so far has been in analyzing the C and O isotopic composition of carbonates in pursuit of Carlin-type Au deposits (Barker et al., 2013).

Fractionation of light stable isotopes normally occurs because the difference in mass of the isotopes results in a slight preference of the heavier isotope to bond to the phase with the stronger bond. Hence, more oxidized or condensed phases favor the heavy isotope of an element. In most physiochemical processes, disproportionation of isotopes among different phases occurs because of the difference in masses of the isotopes of an element, and hence is mass dependent (MD). However, spin-forbidden and photochemical reactions such as those that take place in the stratosphere are mass independent (MI). S isotopes record mass independent fractionations in sediments that predate the Great Oxygenation Event (GOE) because of the preponderance of photochemical reactions involving gaseous S compounds released from volcanoes into the ancient atmosphere (Farquhar et al., 2000), thereby providing a fingerprint for S in ore deposits that are derived from S that was at the surface prior to the GOE (Silva et al., 2013; Wing and Farquhar, 2003). Elements with multiple even and odd isotopes, such as S, record both MD and MI processes in their isotope ratios, which in many cases can be distinguished. Mass independent reactions also occur in oxygen and metals such as Hg, Cd, Sn, Ni, Mo, Tl and U, but only the latter three elements have been used for exploration (Voinot et al., 2015).

A relatively new technique that may find application in exploration and environmental geochemistry is clumped isotopes (e.g. Eiler, 2007), wherein the isotopes are not randomly distributed in a phase such as CO_2, N_2, phosphate or carbonate, but there is a preference for the heavy isotopes to bond (or clump) together. Clumping is a function of temperature, but also can be used to indicate microbial activity processes more precisely because microbes produce clumping independent of temperature. Thus, mobile complexes that are produced by the interaction between microbes and ores at depth (Figure 2) or areas where microbial activity is enhanced by fluxes of metals or nutrients should result in aberrant clumping of isotopes in specific compounds.

METAL ISOTOPE SYSTEMS

Measurement of the isotopic composition of many metals was traditionally done by Thermal Ionization Mass Spectroscopy (TIMS), but the advent of Multi-Collector ICP-MS (MC-ICP-MS) allowed analysis of more elements (Vanhaecke et al., 1996), much faster and somewhat cheaper. However, MC-ICP-MS requires that the element of interest be totally separated from the sample matrix and put into a simple matrix (usually 2% nitric acid solution) to minimize mass bias effects. Thus, sample preparation for both TIMS and MC-ICP-MS are similarly labour intensive, taking a similar amount of time and resources, but MC-ICP-MS requires less machine time. Both require specialized labs supported by expert personnel that are predominately resident in universities.

Many of the technological advances associated with the analysis of metal isotopes have been in more effective introduction of the sample into the ICP-MS. This is because the efficiency of ionization in the plasma and separation in the mass spectrometer results in the transmission of an element from the solution to the collector of only a few percent. These advances include more efficient nebulizers and removing much of the matrix through desolvation (Poitrasson and Dundas, 1999). Novel analytical protocols have also been developed to measure isotopic compositions, including Laser Ablation ICP-MS (LA-ICP-MS) to sample the isotopic composition of solids *in situ* (Fryer et al., 1995), Weak Acid Leach (WAL) that attempts to extract mobile or loosely held elements with 2% nitric acid from samples (Holk et al., 2003), and, Continuous Leach ICP-MS (CL-ICP-MS) that uses solutions that are increasingly aggressive to leach elements (including Pb isotopes) from the sample directly in-line with an ICP-MS, and, analyze them in real-time, thereby revealing where in the sample specific elements reside (MacFarlane et al., 2007).
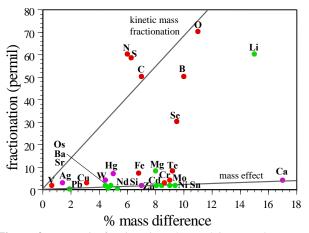

Figure 3: Range in fractionation observed in natural systems relative to difference in mass of the isotopes for various elements. Also shown for reference are the equilibrium fractionations expected purely from mass differences (mass effect) and trend expected from typical kinetic mass fractionation effects. Elements that plot above the mass effect line are involved in kinetic effects normally associated with phases of different oxidation state or they record mass independent fractionation effects. Red = multiple oxidation states, green/purple = single oxidation state of element in most natural systems.

Variations in the stable isotopic composition of metals are primarily determined by differences in the masses of their isotopes, but some elements that exceed fractionations purely on the basis of mass differences do so because of variable oxidation states, and hence different bonding environments. Some elements can undergo mass independent fractionation processes linked to nuclei effects for specific isotopes of elements such as Hg, Cd, Sn, Ni, Mo, Tl and U (Figure 3). The enhanced variations in isotopic compositions as a result of these fractionations could be used to indicate the source and processes involved in element migration from buried deposits as has been done for light stable isotopes. Despite the significant potential of

isotopes to advance our knowledge of the processes involved in dispersion of elements from buried ores, only the stable isotopes of Cu (Braxton and Mathur, 2011; Mathur et al., 2012) and U (Uvarova et al., 2014) have been exploited for exploration.

Although most radiogenic isotopic compositions are used for geochronology (Champion and Huston, 2016), Pb isotopes have been used extensively for decades in exploration geochemistry, primarily in lithogeochemistry to assess metallogeny (e.g. Bowie and Darnley, 1964; Cannon and Pierce, 1969; Doe, 1979), but also for tracing secondary migration of Pb from ores with unique isotope ratios. Rapid and inexpensive Pb isotope analysis using ICP-MS developed for uranium exploration (Holk et al., 2003) can be equally applied to sulphide ore deposits because the U/Pb ratios in the ores, and therefore the Pb isotope ratios, are dramatically different from the host rock. Given that many commercial labs now offer Pb isotopes as part of their normal ICP-MS packages, Pb isotopes should become part of geochemical analyses so that their utility in exploration can be better assessed. Recent studies have used Pb isotopes in surficial media to reflect buried ore deposits (Leybourne et al., 2009; Sitnonetti et al., 1996), but the anthropogenic contribution to the surface must be assessed for each medium to effectively use Pb isotopes as a definitive tracer of the origin of Pb in both exploration and environmental geochemistry (e.g. Kyser et al., 2015b; Stewart et al., 2016; Beyer et al., 2017).

Other radiogenic isotope systems have also been successfully applied to exploration, primarily as indicators of prospective areas, for example extension of the Thompson Nickel Belt (Boehm et al., 2007). However, analysis of metal isotopes whether radiogenic or stable, is still labour intensive, requiring separation and purification by ion chromatography of the element of interest from the matrix of the medium. Elemental Scientific has developed the prepFAST instrument that allows automated ion chromatography. Although the system does not affect the dissolution and preparation steps or significantly increase the speed of the separation process, it allows unattended chromatography and uses less reagent, making metal isotope analysis more time and cost effective. The prepFAST system has been used for a multitude of isotope systems, but few of them for exploration.

SYNOPSIS

There have been significant advances in the technologies for measuring isotopic compositions that can add value to geochemical exploration. New instruments and novel protocols have made measuring isotopes faster and less expensive, and applicable to exploration geochemistry. Although it is unlikely that isotopic compositions will be a standard geochemical tool in exploration, their utility is in tracing the origin of key elements and as effective indicators of primary and secondary dispersion processes.

REFERENCES

Andrew, A. S., 1983, Light stable isotopes in mineral exploration, in R.E. Smith ed., Geochemical exploration in deeply weathered terrains, 33-40.

Barker, S. L., G.M. Dipple, F. Dong, and D.S. Baer, 2011, Use of laser spectroscopy to measure the 13C/12C and 18O/16O compositions of carbonate minerals: Analytical Chemistry, 83, 2220-6.

Barker, S. L. L., G.M. Dipple, K.A. Hickey, W.A. Lepore, and J.R. Vaughan, 2013, Applying stable isotopes to mineral exploration; teaching an old dog new tricks: Economic Geology, 108, 1-9.

Beyer, S. R., K. Kyser, T. Kotzer, K. Ansdell, K. Wasyliuk, and D. Quirt, 2017, Expression of the McArthur River U deposit footprint in diverse surficial sampling media: GAC-MAC Annual Meeting Abstracts, 40, 26.

Bierlein, F. P., D.C. Arne, and I. Cartwright, 2004, Stable isotope (C, O, S) systematics in alteration haloes associated with orogenic gold mineralization in the Victorian gold province, SE Australia: Geochemistry: Exploration, Environment, Analysis, 4, 191-211.

Boehm, C.O., H.V. Zwanzig, and R.A. Creaser, 2007, Sm-Nd isotope technique as an exploration tool; delineating the northern extension of the Thompson nickel belt, Manitoba, Canada: Economic Geology, 102, 1217-1231.

Bowie, S.H.U., and A.G. Darnley, 1964, Uranium-thorium-lead-isotope ratios as an aid to mineral exploration: Advancement of Science, 20, 446-447.

Braxton, D., and R. Mathur, 2011, Exploration applications of copper isotopes in the supergene environment: A case study of the bayugo porphyry copper-gold deposit, Southern Philippines: Economic Geology, 106, 1447-1463.

Cameron, E.M., M.I. Leybourne, and D.L. Kelley, 2005, Exploring for deposits under deep cover using geochemistry: SEG Newsletter, 63 (5), 9-15.

Cannon, R.S., Jr., and A.P. Pierce, 1969, Lead isotope guides for Mississippi Valley lead-zinc exploration: U.S. Geological Survey Bulletin, G1-G20.

Champion, D.C., and D.L. Huston, 2016, Radiogenic isotopes, ore deposits and metallogenic terranes; novel approaches based on regional isotopic maps and the mineral systems concept: Ore Geology Reviews, 76, 229-256.

Clarke, W.B., Z. Top, and W.C. Eismont, 1983, Helium isotope and tritium content of lakes and uranium exploration in the NEA/IAEA Athabasca test area: Geological Survey of Canada, Paper 82-11, 139-146.

Criss, R.E., and R.J. Fleck, 1990, Oxygen isotope map of the giant metamorphic-hydrothermal system around the northern part of the Idaho Batholith, USA: Applied Geochemistry, 5, 641-655.

Doe, B.R., 1979, Lead isotopes applied to mineral exploration: U. S. Geological Survey Professional Paper, 12 p.

Eiler, J.M., 2007, "Clumped-isotope" geochemistry; the study of naturally-occurring, multiply-substituted isotopologues: Earth and Planetary Science Letters, 262, 309-327.

Engel, A.E.J., 1959, Review and evaluation of studies of the O (super 18) /O (super 16) ratio in mineral deposits: Economic Geology, 54, 1343.

Farquhar, J., H. Bao, and M. Thiemans, 2000, Atmospheric influence of Earth's earliest sulfur cycle: Science, 289, 756-758.

Fryer, B., S. Jackson, and H. Longerich, 1995, The design, operation and role of the laser-ablation microprobe coupled with an inductively coupled plasma-mass spectrometer (LAM-ICP-MS) in the earth sciences: Canadian Mineralogist, 33, 303-312.

Green, G.R., H. Ohmoto, J. Date, and T. Takahashi, 1983, Whole-rock oxygen isotope distribution in the Fukazawa-Kosaka area, Hokuroku District, Japan, and its potential application to mineral exploration: Economic Geology Monograph, 5, 395-411.

Holk, G.J., T.K. Kyser, D. Chipley, E.E. Hiatt, and J. Marlatt, 2003, Mobile Pb-isotopes in Proterozoic sedimentary basins as guides for exploration of uranium deposits: Journal of Geochemical Exploration, 80, 297-320.

Kyser, T.K., B.W. Janser, M.R. Wilson, and I. Hattie, 1986, Stable isotope geochemistry related to gold mineralization and exploration in the Western Shield: Canadian Institute of Mining and Metallurgy, Special Volume, 38, 470-498.

Kyser, K., J. Barr, and C. Ihlenfeld, 2015a, Applied Geochemistry in Mineral Exploration and Mining: Elements, 11, 241-246.

Kyser, K., L. Lahusen, G. Drever, C. Dunn, E. Leduc, and D. Chipley, 2015b, Using Pb isotopes in surface media to distinguish anthropogenic sources from undercover uranium sources: Comptes Rendus Geoscience, 347, 215-226.

Large, R.R., S.W. Bull, and P.R. Winefield, 2001, Carbon and oxygen isotope halo in carbonates related to the McArthur River (HYC) Zn-Pb-Ag deposit, North Australia; implications for sedimentation, ore genesis, and mineral exploration: Economic Geology, 96, 1567-1593.

Leslie, K., C.J. Oates, T.K. Kyser, and D.A. Fowle, 2014, Biogeochemical controls on metal mobility: modeling a Cu-Zn VMS deposit in column flow-through studies: Geochemistry: Exploration, Environment, Analysis, 14, 59-70.

Leybourne, M.I., B.L. Cousens, and W.D. Goodfellow, 2009, Lead isotopes in ground and surface waters; fingerprinting heavy metal sources in mineral exploration: Geochemistry: Exploration, Environment, Analysis, 9, 115-123.

Lindsay, J.F., and M.D. Brasier, 1999, Stable isotopes - signposts for mineralisation. A new regional exploration tool: AGSO Research Newsletter, 17-19.

MacFarlane, W.R., T.K. Kyser, and D. Chipley, 2007, Measurement of Pb isotope ratios by continuous leach-inductively coupled plasma-mass spectrometry: quantification of precision and accuracy: Geochemistry: Exploration, Environment, Analysis, 7, 319-327.

Mathur, R., S.R. Titley, W.J. Schlitt, and M. Wilson, 2012, Cu isotope fractionation in: Exploration geology and hydrometallurgy: Examples from porphyry copper deposits: Mining Engineering, 64, 42-46.

McMillan, D.C., T. Preston, and D.P. Taggart, 1989, Analysis of 18O enrichment in biological fluids by continuous flow-isotope ratio mass spectrometry: Biological Mass Spectrometry, 18, 543-6.

Nesbitt, B.E., 1996, Applications of oxygen and hydrogen isotopes to exploration for hydrothermal mineralization: Society of Economic Geologists Newsletter, 27, 1, 8-13.

Poitrasson, F., and S.H. Dundas, 1999, Direct isotope ratio measurement of ultra-trace lead in waters by double focusing inductively coupled plasma spectrometry with an ultrasonic nebulizer and a desolvation unit (2 copies): Journal of Analytical Atomic Spectrometry, 14, 1573-1577.

Riciputi, L., B. Paterson, and R. Ripperdam, 1998, Measurement of light stable isotope ratios by SIMS: Matrix effects for oxygen, carbon, and sulfur isotopes in minerals: International Journal of Mass Spectrometry, 178, 81-112.

Silva, R.C.F.E., L. Lobato, S. Hagemann, and J. Cliff, 2013, Mass independent and mass dependent sulfur isotopes of hydrothermally altered jaspilite and mafic wallrocks, Serra Norte iron ore deposits, Carajas mineral province, Brazil: Mineral Deposit Research for a High-Tech World, 1-4, 734-737.

Sitnonetti, A., K. Bell, and G.E.M. Hall, 1996, Pb isotopic ratios and elemental abundances for selective leachates from near-surface till: implications for mineral exploration: Applied Geochemistry, 11, 721-734.

Stewart, P., T.K. Kyser, D. Griffiths, and L. Lahusen, 2016, Dendrochemistry and soil clay geochemistry applied to exploration for deep U mineralization at the Halliday Lake Prospect, Athabasca Basin, Canada: Geochemistry: Exploration, Environment, Analysis, Pre-Issue Publication.

Taylor, H.P., 1974, Application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: Economic Geology, 69, 843-883.

Uvarova, Y.A., T.K. Kyser, M.L. Geagea, and D. Chipley, 2014, Variations in the uranium isotopic compositions of uranium ores from different types of uranium deposits: Geochimica et Cosmochimica Acta, 146, 1-17.

Vanhaecke, F., L. Moens, R. Dams, and P. Taylor, 1996, Precise measurement of isotope ratios with a double-focusing magnetic sector ICP mass spectrometer: Analytical Chemistry, 68, 567-569.

Voinot, A., D. Chipley, and T.K. Kyser, 2015, Mo, Tl and U isotopes in U-ore deposits; proxies of redox-driven formation processes: Goldschmidt Conference Abstracts, 3282.

Wing, B., and J. Farquhar, 2003, Hydrothermal transfer of the archean oceanic D33S record to VMS deposits: Goldschmidt Conference Abstracts, A534.