DOE Patent Clearance Granted

2-12-03

Date

MP Dvorscak
Mark P. Dvorscak

(630) 252-2393

E-mail: mark.dvorscak@ch.doe.gov

Office of Intellectual Property Law
DOE Chicago Operations Office

DOE/ER14412--8

APPLICATIONS OF ICP MAGNETIC SECTOR MULTICOLLECTOR MASS
SPECTROMETRY TO BASIC ENERGY RESEARCH.

Final Report

for period December 1st 1993 – May 31st 2000

A. N. Halliday

University of Michigan,
Department of Geological Sciences,
2534 C.C. Little Building,
Ann Arbor,
MI 48109-1063

and

Department of Earth Sciences
ETH Zentrum
NO, Sonneggstrasse 5
Zürich, CH 8092
Switzerland

May 2002

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AWARD NO. DE-FG02-94ER14412

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

Thanks, to DOE, NSF and internal funding, the University of Michigan acquired the world's first multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) in December 1993. DOE funding was especially critical to the pioneering development of the research program. The DOE funding of this research can only be described as stunningly successful. With this prototype instrument we explored a vast array of isotopic systems and demonstrated applicability to problems as different as the origin of the solar system and smelting methods in the Bronze Age. In terms of publications we produced more than 40 full peer reviewed articles including 9 published in *Science* and *Nature* (see below). In terms of scientific discovery we were able to make major advances in our understanding of the early evolution of the Earth, Moon, Mars and asteroids. We opened up new fields of *in situ* isotopic microanalysis of relevance to research on climate archives, diagenesis, crustal fluid flow and magma chamber development. We developed high-resolution records of ocean circulation with new isotopic proxies. Lastly, we were able to show that we could measure the ages of corals more precisely than had hitherto been possible allowing us to extend sea-level curves further back in time and test the Milankovitch theory of climate forcing.

The primary aims of this research project were three fold. (1) To develop and utilize the new technique of multiple collector inductively coupled plasma mass spectrometry and apply it to problems in the earth, ocean and environmental sciences. (2) To develop new chronometers and improve existing chronometers to allow the accurate determination of the ages of geological features and processes. (3) To study natural fluid-mediated mass transfer processes and source of components in the crust and the oceans.

So successful has this research program been that this technique has now become the preferred method for the determination of the isotopic compositions of a variety of elements in the periodic table (Halliday *et al.*, 1995, 1998a,b, 2000a). With the move of the PI from Michigan to ETH Zürich and the gradual dispersal of the Michigan research team we focussed most of our efforts on objectives (1) and (3) above.

The PI apologizes for the delays in filing this report. This had nothing to do with the University of Michigan, and the staff of this institution should not be held to blame. The delay reflects the time consuming exercise of re-establishing such a major program elsewhere. The isotope lab and research program at Michigan with DOE support was one of the biggest in the US under a single PI. The facility that has now been established at ETH is 3 times larger and is the biggest worldwide.

In the following we summarize the long list of highlights from the pioneering program at Michigan. Some of these are treated in more detail in earlier DOE reports.

TUNGSTEN ISOTOPES AND THE EARLY SOLAR SYSTEM

We measured W isotopic compositions of iron meteorites, Martian meteorites, eucrites, chondrites and lunar samples (Lee and Halliday 1995, 1996, 1997, 1998, Lee *et al.*, 1997), and used these data to provide constraints on the rates of accretion of the terrestrial planets (Halliday 1999, 2000, Halliday and Lee 1999, Halliday *et al.* 2000b). These results have allowed us to deduce that accretion and differentiation of Mars and the eucrite parent body were completed

much more quickly than that of the Earth and Moon. We have been able to conclude that the Moon probably formed 50 ± 10 Myrs after the start of the solar system. A postdoc, Dr. Der-Chuen Lee started working on these techniques but his research then became entirely supported by NSF and NASA.

TRACE SIDEROPHILE AND CHALCOPHILE ELEMENT GEOCHEMISTRY

Trace siderophile and chalcophile elements constrain models of accretion and core formation and provide evidence for core-mantle interaction. They are of great interest in studying low temperature processes. However, the basic abundances of many of the elements of interest are not well established. We developed new MC-ICPMS isotope dilution (ID) techniques for the measurement of the platinum-group elements iridium (Ir), ruthenium (Ru), platinum (Pt) and palladium (Pd) in geological samples (Rehkämper and Halliday 1997, Rehkämper *et al.* 1998) and applied these methods to the study of African ultramafic xenoliths (Rehkämper *et al.* 1997). We then extended this research to the study of basaltic systems (Rehkämper *et al.*, 1999b) and abyssal peridotites (Rehkämper *et al.*, 1999a). We also developed ID techniques to study the volatile chalcophile trace elements indium (In), cadmium (Cd), tin (Sn) and tellurium (Te) (Yi *et al.*, 1995, 1998, 1999, 2000). With a study of 80 samples of MORB, submarine and subaerial OIB and submarine arc lavas (Yi *et al.*, 2000), we discovered that Cd is particularly uniform in all submarine glasses, and displays no relation with tectonic setting. We have extended this research to the study of hydrothermally altered oceanic crust at Ocean Drilling Project Holes 504B and 896A. The work on Cd, In, Sn and Te formed the subject of a recently completed Ph.D. thesis by Wen Yi.

HAFNIUM ISOTOPES AND THE EARLY DEVELOPMENT OF THE CONTINENTS

Evidence of mantle depletion caused by melting at a time pre-dating the formation of the oldest surviving crust has been presented in Sm-Nd isotopic studies of 3.8-4.0 Gyr rocks from Greenland and Canada. However, this interpretation is now equivocal because of the possibility that late perturbations may have re-equilibrated the Nd isotopic compositions. Independent and more robust evidence for the origin of the earliest crust and depletion of the Archaean mantle is provided by Hf isotopic compositions of zircon, which can be precisely dated by U-Pb and can survive metamorphism. However, the amounts of Hf in single zircon grains are too small to be precisely analysed by conventional methods. We have made the first highly precise Hf isotopic measurements for single zircons, using 37 single grains of the oldest known terrestrial zircons, with U-Pb ages of up to 4.2 Gyr from the Narryer Gneiss Complex, Australia. We found that none had a depleted mantle signature, but many were derived from a source with a chondritic Hf isotopic composition. Furthermore, more than half the analysed grains formed by re-melting of significantly older crust, indicating that that crustal preservation and subsequent re-working was important from earliest times (Amelin *et al.*, 1999, 2000).

EVOLUTION OF LEAD ISOTOPIC COMPOSITIONS OF THE OCEANS

Following our pioneering work on *in situ* Sr isotopic measurements by MC-ICPMS (Christensen *et al.* 1995) and their applications to volcanic phenocrysts, we developed the techniques for measuring the Pb isotopic compositions of Fe-Mn crusts, *in situ* using laser ablation (Christensen *et al.*, 1997). With this remarkable high-resolution record (each crust was sampled and a high precision Pb isotopic measurement made over 100 times), we discovered an apparent link with indicators of climate and oceanographic change, such as the oxygen isotopic composition of benthic foraminifera. An assistant research scientist, Dr. John Christensen, worked in this area. We subsequently explored the methodology of Tl corrected Pb (Rehkämper and Halliday 1998) and Pb corrected Tl (Rehkämper and Halliday 1999) isotopic measurements more rigorously. We showed that Tl isotopes are strongly fractionated in marine ferromanganese crusts – making Tl the heaviest element for which a natural isotopic fractionation had been demonstrated (Rehkämper and Halliday 1999).

THE ISOTOPIC COMPOSITION AND RESIDENCE TIME OF HF IN SEAWATER

We measured the Hf isotopic compositions of a wide range of Fe-Mn crusts (Godfrey *et al.*, 1997) and then extended this work to include time resolved Hf isotopic measurements. This work cannot be performed with the laser because the Hf concentrations are too low. Nevertheless we constructed high-resolution profiles by manual sampling and chemical separation. We found that the Hf isotopic composition of central Pacific seawater stayed reasonably constant ($\epsilon_{\text{Hf}} = +4$ to $+6$) over the past 45 Myrs but with distinctly higher values ($\epsilon_{\text{Hf}} = +6$ to $+9$) between 25 and 15 Myrs (Lee *et al.* 1999). The most likely explanations would be increased hydrothermal venting between 25 and 15 Myrs or a change in central Pacific ocean circulation patterns preferentially advecting seawater with hydrothermal components at this time. The most surprising facet was the constant Hf isotopic composition of the past 15 Myrs despite huge (supposed) changes in erosional and volcanic inputs. One postdoc, Dr. Der-Chuen Lee and a graduate student Alex Piotrowski worked on the Hf measurements who successfully completed his Masters at Michigan and is now a PhD student at LDEO. This ultimately resulted in an additional paper by Piotrowski *et al.* (2000) with the first high-resolution time resolved data for the Atlantic and Indian Oceans. The work on Fe-Mn crusts involved collaborations with Dr. Jim Hein (USGS, Menlo Park) and Dr. Linda Godfrey (Cornell University).

THE ISOTOPIC COMPOSITIONS OF SR, HF, PB AND ND IN DUST

We have extended our research on the isotopic compositions of eolian inputs to the Pacific Ocean to include downcore measurements at two sites in the north central Pacific Oceans (Pettke *et al.*, 2000, 2002a,b). We find that there are striking changes in Sr and Hf isotopic composition as a function of time and that these appear to relate to climate-driven changes in the weathering of Asia. Nd and Pb isotopic data are less variable but are strongly affected by long term changes in wind pattern. In particular the influence of the Inter-Tropical Convergence Zone on Nd isotopic compositions is dramatic presumably because of the admixing of material from central America. A postdoc, Dr. Thomas Pettke developed this research.

U-TH DISEQUILIBRIUM DATING OF CARBONATES AND SOILS

Early research on U-Th isotopic measurements demonstrated an ability to produce more precise measurements than was hitherto possible (Luo *et al.*, 1997) and developed the techniques for precise U-Th dating of carbonates including corals and carbonates from soils and weathering horizons, including terrestrial gastropods (snails) and carbonate nodules. The nodules were found to be of little use because of open system behavior. However, the corals and land snails worked very well. We acquired thirty precise U-series ages for a set of reef terraces formed during MIS 9 and MIS 15 on Henderson Island, an elevated coral atoll near Pitcairn Island in the equatorial Pacific (Stirling *et al.* 2001). The data were obtained using TIMS (at the ANU) and MC-ICPMS at Michigan. Importantly, our Henderson Island results provide the first direct U-series constraint on the timing of the MIS 15 sea-level high-stand. We determined a ^{230}Th -age of 632 ± 21 ka for reefs that grew on Henderson Island during a major atoll construction phase within MIS 15. Although relatively imprecise at the present time, this initial estimate is being refined. Our results provide excellent first-order constraints on the timing and duration of the MIS 9 sea level high-stand. In the 330 ka samples, ^{230}Th -age uncertainties (excluding the systematic contribution from the decay constants) can be smaller than ± 2 ka. This allows the timing and duration of the MIS 9 interglacial, and its temporal relationship with the Milankovitch 65°N summer solar insolation curve, to be well-resolved. The research on U-Th dating at Michigan was spear-headed by a graduate student, Xiazhong Luo who successfully completed his Ph.D. at Michigan, and a postdoc, Dr. Claudine Stirling.

IN SITU U-TH DISEQUILIBRIUM DATING OF OPAL

We also started *in situ* U-Th isotopic measurements at very high spatial resolution at U-M, using laser ablation sampling combined with MC-ICPMS. The technique offers significant potential in U-series disequilibrium studies in magmatic zircon and low-temperature opal geochronology. We have started a study of U-rich samples of opal from Yucca Mountain in an attempt to date groundwater movements in the past, in collaboration with Dr. J. Paces and Dr. Z. Peterman (USGS). Our preliminary data were very encouraging and permitted us to make spatially resolved age measurements with an uncertainty of the order of ± 10 %. The research on *in situ* U-Th dating was spear-headed by Dr. Claudine Stirling (Stirling *et al.*, 2000). The precision in $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}}$ and $[\text{}^{230}\text{Th}/\text{}^{234}\text{U}]_{\text{act}}$ translates into 2σ errors in the ^{230}Th -age of $\pm 3,000$ years in 100,000 year old samples. However, the accuracy of the $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]_{\text{act}}$ measurement can be severely compromised by elemental fractionation. Following the work of Prof. Detlef Guenther (ETH), we utilized a combined helium and argon gas system to improve the transportation efficiency of particles to the plasma. This greatly reduced fractionation between Th and U, while retaining accuracy and precision in U isotope measurement. Such an approach offers great potential for measuring U-disequilibrium series nuclides in high U materials *in situ* (Stirling *et al.*, 2000).

ARTICLES (NO ABSTRACTS) THUSFAR SUBMITTED, ACCEPTED OR PUBLISHED, SUPPORTED IN PART FROM THIS DOE GRANT (ARRANGED ALPHABETICALLY)

1. Amelin, Y., Lee, D-C. and Halliday, A.N. 2000 Early-middle Archean crustal evolution deduced from Lu-Hf and U-Pb isotopic studies of single zircon grains, *Geochim. Cosmochim. Acta*, 64, 4205-4225.

Copies removed for separate processing

2. Amelin, Y., Lee, D-C., Halliday, A.N. and Pidgeon, R.T. 1999 Nature of the earth's earliest crust from hafnium isotopes in single detrital zircons *Nature* 399, 252-255.
3. Ballentine, C., Lee, D-C. and Halliday, A. N. 1997 Hafnium isotopic studies of the Cameroon line and new HIMU paradoxes. *Chem. Geol. Hofmann volume*, 139, 111-124.
4. Barfod, D., Lee, D-C., Ballentine, C.J., Halliday, A.N. and Hall, C.M. 2002 Fractionation of helium and incompatible lithophile elements during partial melting under the Cameroon line *Earth Planet. Sci. Lett.*, in press.
5. Burton, K.W., Lee, D-C., Christensen, J.N., Halliday, A.N. and Hein, J.R. 1999 Actual timing of neodymium isotopic variations recorded by Fe-Mn crusts in the western North Atlantic. *Earth Planet. Sci. Lett.* 171, 149-156.
6. Christensen, J.N., Halliday, A.N., Godfrey, L.V., Hein, J.R. and Rea, D.K. 1997a Climate and ocean dynamics and the lead isotopic records in Pacific ferro-manganese crusts, *Science*, 277, 913-918.
7. Christensen, J.N., Halliday, A.N. Lee, D-C., and Hall, C.M. 1995 *In situ* Sr isotopic analyses by laser ablation, *Earth Planet. Sci. Lett.* 136, 79-85.
8. Godfrey, L.V., Lee, D-C., Sangrey, W.F., Halliday, A.N., Salters, V.J.M., Hein, J.R. and White, W.M., 1997 The Hf isotopic composition of ferromanganese nodules and crusts and hydrothermal manganese deposits: Implications for seawater Hf. *Earth Planet. Sci. Lett.* 151, 91-105.
9. Halliday, A.N. 1999 Excited atoms, planetary collisions and differences between Earth and Mars (in German: "Angeregte Atome, planetare Zusammenstösse und Unterschiede zwischen Erde und Mars"). *Naturforschende Gesellschaft in Zürich* 144/4, 159-168.
10. Halliday, A.N. 2000 Hf-W chronometry and inner solar system accretion rates, in: W. Benz, R. Kallenbach and G. Lugmair (eds) "From Dust to Terrestrial Planets", *Space Science Reviews* 92, 355-370.
11. Halliday, A.N. and Lee, D-C. 1999 Tungsten isotopes and the early development of the Earth and Moon. *Geochim. Cosmochim. Acta*, (C.J. Allègre 60th Birthday Volume) 63, 4157-4179.
12. Halliday, A.N., Christensen, J.N., Lee, D-C., Hall, C.M., Ballentine, C.J., Rehkämper, M., Yi, W., Luo, X. and Barfod, D. 1998a ICP multiple collector mass spectrometry and *in situ* high precision isotopic analysis. In: *Applications of microanalytical techniques to understanding mineralizing processes* eds: M.A. McKibben, W.C.P. Shanks III and W.I. Ridley, Reviews in Economic Geology 7, Society of Economic Geologists, Reviews in Economic Geology, 7, 37-51.
13. Halliday, A.N., Christensen, J.N., Lee, D-C., Rehkämper, M., Hall, C.M., and Luo, X. 2000a Multiple collector inductively coupled plasma mass spectrometry. In: *Inorganic mass spectrometry, fundamentals and applications* eds: C.B. Barshick, D.C. Duckworth and D.H. Smith, Marcel Dekker Inc., New York, Chapter 8, 291-328.

14. Halliday, A.N., Lee, D.-C. and Jacobsen, S.B. 2000b Tungsten isotopes, the timing of metal-silicate fractionation and the origin of the earth and moon, in: K. Righter and R. Canup (eds) *Origin of the Earth and Moon* Univ. Arizona Press, 45-62.
15. Halliday, A.N., Lee, D.-C., Christensen, J.N., Rehkämper, M., Yi, W., Luo, X., Hall, C.M., Ballentine, C.J., Pettke, T. and Stirling, C. 1998b Applications of multiple collector ICPMS to cosmochemistry, geochemistry and paleoceanography. (The 1997 Geochemical Society Presidential Address.) *Geochim. Cosmochim. Acta* 62, 919-940.
16. Halliday, A.N., Lee, D.-C., Christensen, J.N., Walder, A.J., Freedman, P.A., Jones, C.E., Hall, C.M., Yi, W. and Teagle, D. 1995 Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spec. Ion Process.*, 146/147, 21-33.
17. Halliday, A.N., Rehkämper, M., Lee, D.-C. and Yi, W. 1996 Early evolution of the Earth and Moon: New constraints from Hf-W isotope geochemistry. *Earth Planet. Sci. Lett.* 142, 75-90.
18. Lee, D.-C. and Halliday, A.N. 1995a Hafnium-tungsten chronometry and the timing of terrestrial core formation. *Nature* 378, 771-774.
19. Lee, D.-C. and Halliday, A.N. 1995b Precise determinations of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP source magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spec. Ion Process.*, 146/147, 35-46.
20. Lee, D.-C. and Halliday, A.N. 1996 Hafnium-tungsten isotopic evidence for rapid accretion and differentiation in the early solar system. *Science*, 274, 1876-1879.
21. Lee, D.-C. and Halliday, A.N. 1997 Core formation on Mars and differentiated asteroids. *Nature*, 388, 854-857.
22. Lee, D.-C. and Halliday, A.N., Snyder, G.A. and Taylor, L.A. 1997 Age and origin of the Moon. *Science*, 278, 1098-1103.
23. Lee, D.-C., Halliday, A.N., Hein, J.R., Burton, K.W., Christensen, J.N. and Gunther, D. 1999 Hafnium isotope stratigraphy of ferromanganese crusts. *Science* 285, 1052-1054.
24. Luo, X., Halliday, A. N., Fang, X., Van der Voo, R., Rehkämper, M. and Lee, D.-C. 2002 U-Th dating of snail shells from the Chinese loess paleosol sequence. *Chem. Geol.*, in revision.
25. Luo, X., Lee, D.-C., Rehkämper, M., and Halliday, A.N. 1997 High precision $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry. *Int. J. Mass Spec. Ion Process.* 171, 105-117.
26. Pettke, T., Halliday, A.N. and Rea, D.K., 2002a Cenozoic evolution of Asian climate and sources of Pacific seawater Pb and Nd derived from eolian dust of sediment core LL44-GPC3. *Paleoceanography* in press.
27. Pettke, T., Halliday, A.N., Hall, C.M. and Rea, D.K., 2000 Dust production and deposition in Asia and the North Pacific Ocean over the past 12 Myrs. *Earth Planet. Sci. Lett.* 178, 397-413.

28. Pettke, T., Lee, D-C., Halliday, A.N. and Rea, D.K., 2002b Radiogenic Hf isotopic compositions of continental eolian dust from Asia, its variability and its implications for seawater Hf. *Earth Planet. Sci. Lett.* Accepted pending revisions.
29. Piotrowski, A. M., Lee, D-C., Christensen, J.N., Burton, K.W., Halliday, A.N., Hein, J.R., and Gunther, D. 2000 Changes in erosion and circulation recorded in the Hf isotopic compositions of North Atlantic and Indian Ocean ferromanganese crusts. *Earth Planet. Sci. Lett.* 181, 315-325.
30. Rehkämper, M. and Halliday, A. N. 1997 Development and application of new ion-exchange techniques for the separation of the platinum group and other siderophile elements from geological samples. *Talanta*, 44, 663-672.
31. Rehkämper, M. and Halliday, A. N. 1998 Accuracy and long-term reproducibility of lead isotopic measurements by MC-ICPMS using an external method for correction of mass discrimination. *Int. J. Mass Spec. Ion Proc.*, 181, 123-133.
32. Rehkämper, M. and Halliday, A. N. 1999 The precise measurement of Tl isotopic compositions by MC-ICPMS: Application to the analysis of geological materials and meteorites. *Geochim. Cosmochim. Acta* 63, 935-944.
33. Rehkämper, M., Halliday, A. N. and Wentz, R.F. 1998 Low blank digestion of geological samples for platinum group element analysis using a modified Carius Tube design. *Fresenius J. Anal. Chem.*, 361, 217-219.
34. Rehkämper, M., Halliday, A. N., Alt, J., Fitton, J.G., Zipfel, J. and Takazawa, E. 1999a Non-chondritic platinum group element ratios in abyssal peridotites: petrogenetic signature of melt percolation? *Earth Planet. Sci. Lett.* 172, 65-81.
35. Rehkämper, M., Halliday, A. N., Barfod, D., Fitton, J.G. and Dawson, J.B. 1997 Platinum group element abundance patterns in different mantle environments. *Science*, 278, 1595-1598.
36. Rehkämper, M., Halliday, A. N., Fitton, J.G., Lee, D-C, Wieneke, M. and Arndt, N.T. 1999b Ir, Ru, Pt and Pd in basalts and komatiites: new constraints for the geochemical behavior of the platinum-group elements in the mantle. *Geochim. Cosmochim. Acta* 63, 3915-3934.
37. Stirling, C.H., Esat, T.M., Lambeck, K., McCulloch, M.T., Blake, S.G., Lee, D-C. and Halliday, A.N. 2001 Orbital forcing of the Stage 9 Interglacial: Evidence from U-series dating of Henderson Island corals, *Science* 291, 290-293.
38. Stirling, C.H., Lee, D-C., Christensen, J.N. and Halliday, A. N., 2000 High precision *in situ* ^{238}U - ^{234}U - ^{230}Th isotopic analysis using laser ablation multiple collector ICPMS. *Geochim. Cosmochim. Acta*, 64, 3737-3750.
39. Yi W., Halliday A. N., Alt J., Lee D-C., Rehkämper M., Garcia M., Langmuir C. and Su, Y., 2000 Cadmium, indium, tin, tellurium and sulfur in oceanic basalts: implications for chalcophile element fractionation in the earth. *J. Geophys. Res.* 105, 18,927-18,948.
40. Yi, W., Budd, P., McGill, R.A.R., Young, S.M.M., Halliday, A.N., Haggerty, R., Scaife, B. and Pollard, A.M. 1999 Tin isotope studies of experimental and prehistoric bronzes. In

Hauptmann, A., Pernicka, E., Rehren, T. & Yalcin, U. (eds) *The Beginnings of Metallurgy*, Der Anschnitt Beiheft 9. Deutsches Bergbau-Museum: Bochum, 285-290.

41. Yi, W., Halliday, A. N., Lee, D.-C. and Rehkämper, M., 1998 Precise determination of cadmium, indium and tellurium using multiple collector ICP-MS. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 22, 173-179.
42. Yi, W., Halliday, A.N., Lee, D.-C. and Christensen, J.N. 1995 Indium and tin in basalts, sulfides and the mantle, *Geochim. Cosmochim. Acta*. 24, 5081-5090.