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Proceedings of the 4th International Workshop on Highly Siderophile Element Geochemistry

Citation for published version:

Riches, A 2016, *Proceedings of the 4th International Workshop on Highly Siderophile Element Geochemistry*. <<https://osf.io/n5tds/>>

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

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4th International Workshop on Highly Siderophile Element Geochemistry

*4th International
Highly Siderophile Element
Geochemistry Workshop*



July 11-14th 2016

Durham University, UK

Thank you to our sponsors who have made this workshop possible:



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Welcome

The event organisers are delighted to welcome, to the 4th International Workshop on Highly Siderophile Element Geochemistry, scientists of all career levels from academic institutions and government organisations from all over the globe. Durham University's Department of Earth Sciences and its Geochemistry Group are thrilled to have brought together a large and diverse set of experts in HSE sciences, and we look forward to hosting a very productive meeting.

Overview

This specialist workshop is a 4 day event timed to occur between the 2016 Annual Goldschmidt Conference and the 79th Annual Meeting of the Meteoritical Society. It builds on the legacy of three highly-successful preceding meetings, the last of which took place in Durham in 2006 (then Chair, Dr. Ambre Luguet). This event also complements the short course on highly siderophile and strongly chalcophile elements in high temperature geochemistry and cosmochemistry held 7 months prior and linked to RiMG volume #81.

The 4th International Workshop on Highly Siderophile Element Geochemistry is of cross-disciplinary appeal in covering analytical advances, as well as low-temperature and high-temperature geo- and cosmochemistry topics pertaining to HSEs and allied elements. The meeting and related activities provide opportunities for friendly exchange between scientists of all levels, thus offering the potential for all to accelerate knowledge/technology sharing and explore new observations that advance understanding of key geo- and cosmochemistry questions. Additionally, this event allows for useful new international collaborations to nucleate; these will be highly beneficial to continued progress in HSE frontier science and will support overall advances within the geochemistry community. The workshop will help to create pathways for present and future students through interaction with other delegates, and potentially permits the early-stages of discussion to commercialise scientific applications for industry. Ample discussion time following presentations supports our goal to engage all attendees in the effective exchange of new observations, emerging analytical approaches, and the development of new hypotheses.

In light of the development of new experimental petrology facilities and the proliferation of many new specialist HSE (and related) geochemistry laboratories around the globe, we are positioned at the inception of a new era of frontier study. A dedicated special issue hosted by Elsevier's *Geochimica et Cosmochimica Acta* will be produced following this workshop and is provisionally titled "Highly Siderophile Element [and closely-related] Constraints on Low- and High- Temperature Earth and Planetary Processes". We intend for this volume to include a significant set of useful new advances in multi-disciplinary HSE-sciences and isotope geochemistry. This, therefore, is a special opportunity for delegates to engage in producing an excellent thematic volume of lasting scientific impact.

More information; <http://www.hseworkshop.co.uk/special-issue-gca>

The organising committee have strived to adhere to the principles of the UK's Athena SWAN [diversity] charter in all aspects of the 4th International Workshop on Highly Siderophile Element Geochemistry.



Local Interest

The beautiful and historic city of Durham boasts a World Heritage Site with Norman Cathedral and Castle and is home to one of the UK's oldest and most prestigious Universities (a world top-65, and top-25 with respect to Earth Sciences). The 2016 Durham Brass Festival (funk/jazz) will overlap with the workshop dates;

<http://www.brassfestival.co.uk/>

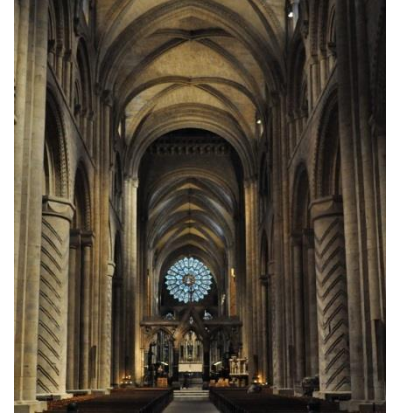
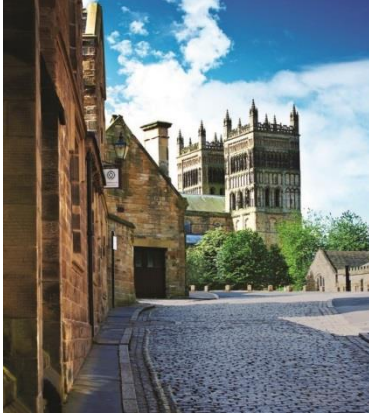


Image Credit: Durham University

Durham is well situated for access to England's northern counties including Northumberland, Yorkshire, and Cumbria and the National Parks of the Peak and Lake Districts. Further information about the local area: <http://www.thisisdurham.com> / and <http://www.durhamcityattractions.com/>. Durham, is located within a reasonable drive of the North Pennines, designated as an Area of Outstanding Natural Beauty (AONB), and also a UNESCO Global Geopark - highlighting its globally important geological heritage. - www.northpennines.org.uk



Image Credits: coolplaces.co.uk, persuasionpr.com, roughguides.com, visitalnwick.org.uk

Transport

Durham is approximately 20 minutes travel from Newcastle International Airport. This city is on the East Coast Mainline of the UK rail network - a line that runs between London and Edinburgh - and is a short distance from the A1(M) motorway.

Durham taxi services (this list is not exhaustive):

- Paddy's Taxis Ltd – 0191 386 6662
- Airport Express - <http://www.airport365.com/> - 0191 371 2352
- Polly's Taxis - <http://www.pollystaxis.co.uk/> - 07910 179 397 or 07773 227 227.

Additionally, there are taxi ranks near to the Empty Shop (see map).



Field Trip to the Isle of Rùm

Summary

All delegates attending the field trip will need to sign and return a waiver form that has been provided to them.

Thursday July 14th

- Meeting of the field party in the lecture theatre in Anthropology (Room D-110) following the closing formalities of the workshop. Attendance is compulsory for all field party attendees.

Friday July 15th

- Field party meets and loads the vehicles by Durham's Dept. of Earth Sciences, departing at 7.30 a.m. sharp.
- There will be plenty of stops during the drive.
- The field party will relax upon arrival and will stay overnight in hotels at [Arisaig](#).

Saturday July 16th

- Wake early, take breakfast and depart the hotels by 7 a.m.
- Depart from the Mallaig ferry terminal at 7.30 a.m.
- Field work!

Sunday July 17th and Monday July 18th

- Field work!

Tuesday July 19th

- The field party should be ready to depart by 9 a.m. and to board the charter boats at 9.30 a.m.
- The return drive from Mallaig will include stops and is expected to return field trip participants to Durham late in the afternoon.



Coordinator: Pierre Bouilhol, *University of Durham*



Field Leader: Brian O'Driscoll, *University of Manchester*



Organising Committee

Durham University, UK, unless stated otherwise.

Amy J. V. Riches, Workshop Chair
 Edward Inglis, Ice-breaker Coordinator
 Fienke Nanne, Banquet Coordinator
 Kathi Schweitzer, Ice-breaker Coordinator
 Paul Savage (*U of St. Andrews*), Bursary Committee
 Marc-Alban Millet (*U of Cardiff*), Bursary Committee
 Chris W. Dale, Programme Committee
 Pierre Bouilhol, Field Trip Coordinator
 Geoff M. Nowell
 Chris J. Ottley
 Kevin W. Burton
 Dave Selby
 Helen M. Williams (*U of Cambridge*)

Voluntary Assistants

Durham University, UK, unless stated otherwise.

Alex McCoy-West, Programme Committee
 Kate Horan
 Junjie Liu
 Helen Cocker (*ANU*)

Keynote Speaker

James M. D. Day, *SCRIPPS, USA*

Field Trip Leader

Brian O'Driscoll, *University of Manchester, UK*

Invited Speakers

Sarah-Jane Barnes, *Université du Québec, Canada*
 Harry Becker, *Freie Universität Berlin, Germany*
 James Brenan, *University of Toronto, Canada*
 Mario Fischer-Gödde, *Universität Münster, Germany*
 *Mouhcine Gannoun, *Clermont-Ferrand, France*
 Ambre Luguët, *Universität Bonn, Germany*
 Wolfgang Maier, *Cardiff University, UK*
 Thomas Meisel, *Montanuniversität Leoben, Austria*
 Gregory Ravizza, *SOEST, University of Hawaii, USA*
 Jessica Warren, *University of Delaware, USA*

Workshop Participants

Steve Barnes, *CSIRO, Australia*
 Diana Brown, *SCRIPPS, USA*
 Jude Coggon, *University of Southampton, UK*
 John Creech, *Inst. de Physique du Globe de Paris, France*
 Mathieu Dellinger, *University of Durham, UK*
 Arjan Dijkstra, *University of Plymouth, UK*
 Sally Gibson, *University of Cambridge, UK*
 Phillipp Gleißner, *Freie Universität Berlin, Germany*
 George Guice, *Cardiff University, UK*
 Dave Holwell, *University of Leicester, UK*
 Timo Hopp, *Universität Münster, Germany*
 *Florian Huber, *Universität Tübingen, Germany*
 Alison Hunt, *ETH Zurich, Switzerland*
 Kate Jillings, *Cardiff University, UK*
 Bartosz Karykowski, *Cardiff University, UK*
 Lotta Kemppinen, *University of Bristol, UK*
 Bianca Kennedy, *Cardiff University, UK*
 Martijn Klaver, *University of Bristol, UK*
 Stephan König, *Universität Tübingen, Germany*
 Nadine Krabbe, *Universität Münster, Germany*
 Timon Kurzawa, *Universität Tübingen, Germany*
 Jabrane Labidi, *Universität Tübingen, Germany*
 Casto Laborda-López, *Universidad de Jaén, Spain*
 Vera Laurenz, *Bayerisches Geoinstitut, Germany*
 Moritz Lissner, *Universität Bonn, Germany*
 Iain McDonald, *Cardiff University, UK*
 Arijeet Mitra, *IIT Kanpur, India - (WHOI guest, USA)*
 Jung-Woo Park, *Seoul National University, South Korea*
 Hazel Prichard, *Cardiff University, UK*
 Nichiketa Rai, *Birkbeck-UCL, University of London, UK*
 Laurie Reisberg, *CNRS-UL, France*
 Hanika Rizo, *Université du Québec à Montréal, Canada*
 Alan Rooney, *Harvard University, USA*
 *Daniel Schwander, *Universität Bonn, Germany*
 Indra Sen, *IIT Kanpur, India - (WHOI guest, USA)*
 Leanne Staddon, *University of Bristol, UK*
 Hannah Stephenson, *Cardiff University, UK*
 Robin Strack, *Universität Bonn, Germany*
 Neal Sullivan, *University of Toronto, Canada*
 Dominique Tanner, *Cardiff University, UK*
 Svetlana Tessalina, *Curtin University, Australia*
 David van Acken, *Universität Bonn, Germany*
 Quinten van der Meer, *University of Otago, New Zealand*
 Ashlea Wainwright, *Université Libre de Bruxelles, Belgium*
 Mona Weyrauch, *Leibniz Universität Hannover, Germany*
 Matthias Willbold, *University of Manchester, UK*
 Aierken Yierpan, *Universität Tübingen, Germany*
 Marina Yudovskaya, *WITS, South Africa*

*Presentation to be given by co-author.

Bursary Awards

Learned societies of the international scientific community [listed below] are thanked for their generous support of travel bursaries administered by the organising committee of this workshop. Awards were made on a competitive basis to support young researchers presenting their work. The following students are congratulated on their successful applications:

Student Travel Awards provided by the Meteoritical Society

Nadine Krabbe, *Universität Münster, Germany*

Luke Daly, *Curtin University, Australia*

Student Travel Grants funded by the Geochemical Society

Diana Brown, *SCRIPPS, USA*

Arijeet Mitra, *IIT Kanpur, India*

Student Travel Bursaries supported by the European Association of Geochemistry

Timo Hopp, *Universität Münster, Germany*

Bianca Kennedy, *Cardiff University, UK*

Mona Weyrauch, *Leibniz Universität Hannover, Germany*

Bartosz Karykowski, *Cardiff University, UK*

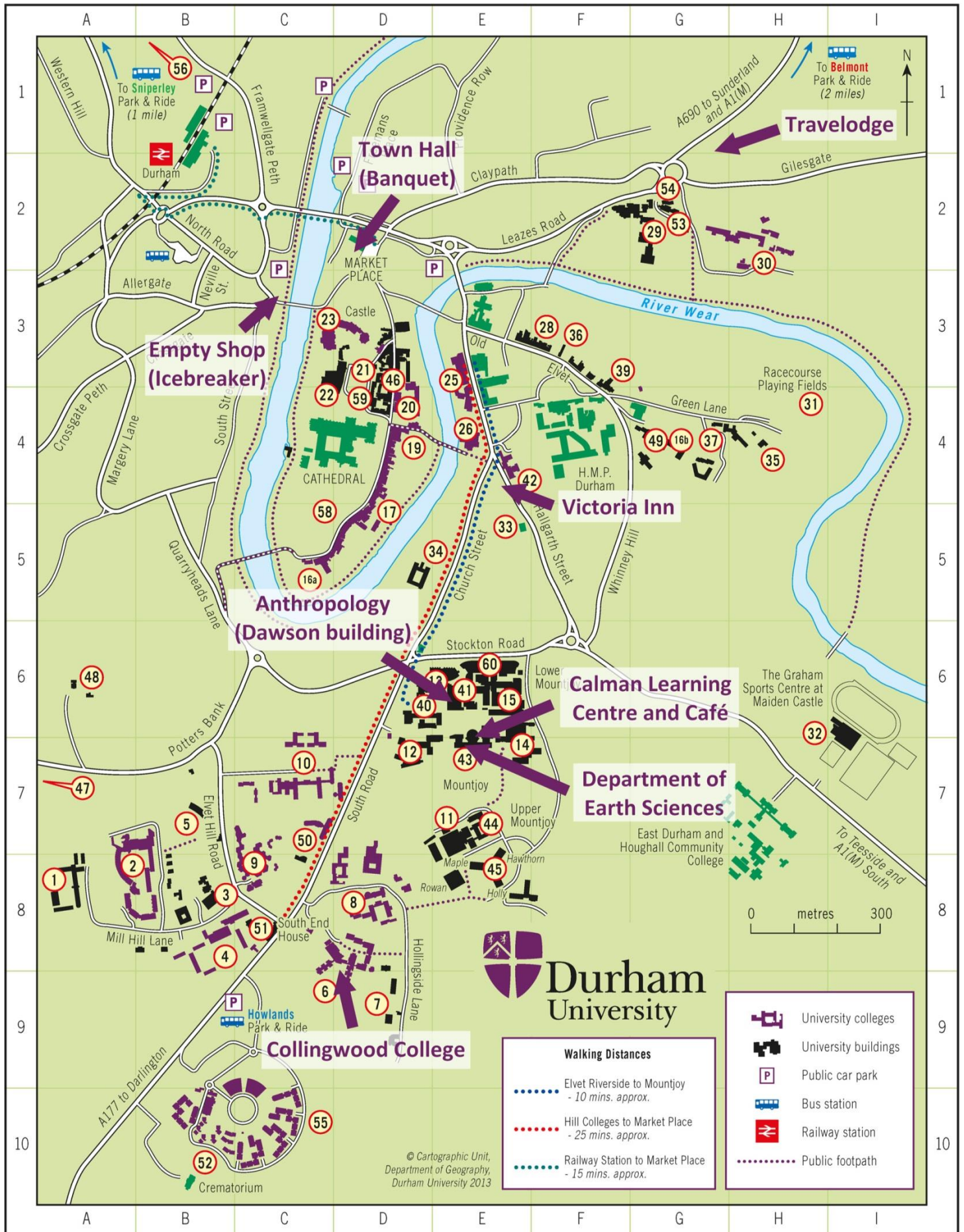
Lotta Kempinen, *Bristol University, UK*

Hannah Stephenson, *Cardiff University, UK*

Kate Jillings, *Cardiff University, UK*

Casto Laborda-López, *Universidad de Jaén, Spain*

Map Emphasising Key Locations Related to the Workshop



Number	Building	Grid reference
60	Administration (Palatine Centre)	E6
21	Advanced Study, Institute of	D3
41	Anthropology (Dawson Building)	E6
36	Applied Social Sciences: Sociology and Criminology	F3
36	Applied Social Sciences: Sport	F3
25	Applied Social Sciences: Social and Community & Youth Work	E3
41	Archaeology (Dawson Building)	E6
46	Assembly Rooms (Durham Student Theatre)	D3
11	Biological and Biomedical Sciences	E7
7	Botanic Garden	D9
43	Calman Learning Centre	E6/7
60	Careers, Employability and Enterprise Centre (Palatine Centre)	E6
15	Chemistry, Scarborough Lecture Theatre	E6
30	College of St Hild and St Bede	G2/H2
46	Classics and Ancient History	D3
6	Collingwood College	D8
25	Combined Honours in Arts and Social Sciences (Elvet Riverside II)	E3
25	Community and Youth Work Studies	E3
15	Computing and Information Services	E6
14	Computer Science	E7
60	Counselling Service (Palatine Centre)	E6
60	Disability Support	E6
56	Dryburn Court (Ustinov College)	n/a
1	Durham University Business School	A8
26	Durham Students' Union (Dunelm House)	E4
43	Earth Sciences, e-Science Research Institute	E7
1	Economics and Finance	A8
29	Education	G2
25	Elvet Riverside I and II	E3
14	Engineering	E7
26	English Language Centre	E4
33	English Studies	E5
45	Estates and Buildings	E8
25	Faculty Office (Arts and Humanities)	E3
15	Faculty Office (Science)	E6
43	Faculty Office (Social Sciences and Health)	E7
40	Geography, Applebey Lecture Theatre	D6
47	Global Learning and Executive Education, Centre for	n/a
51	Government and International Affairs: South End House (Politics)	C8
5	Government and International Affairs: Al-Qasimi Building (Middle Eastern and Islamic Studies)	B7
8	Grey College and Holgate House	D8
20	Hatfield College	D4
42	Hatfield College (Palmer's Garth)	E/F4
34	Hatfield College (James Barber House)	E5
37	Health Centre	G4
14	Health and Safety Office	E7
46	History	D3
3	House of Sport	B8
21	Institute of Advanced Study	D3
40	Institute of Hazard, Risk and Resilience	D6
60	IT Service Desk (Palatine Centre)	E6
55	Josephine Butler College	C10
3	Lafcadio Hearn Centre, Teikyo University	B8
60	Law School (Palatine Centre)	E6
29	Library (Education Section)	G2
13	Library (Bill Bryson Section)	E6
22	Library (Palace Green Section)	C3
32	Maiden Castle (The Graham Sports Centre)	I6/I7
15	Mathematical Sciences	E6
25	Modern Languages and Cultures	E3
45	Mountjoy Centre, including: - Hawthorne Wing - Holly Wing - Maple Wing - Rowan	E8
22	Museum of Archaeology (Palace Green Library)	C3
22	Music	C3
15	Natural Sciences	E6
36	Nightline	F3
53	Nursery	G2
48	Observatory	A6
3	Oriental Museum	B8
60	Palatine Centre	E6
21	Pemberton Lecture Rooms	D4
28	Philosophy	E3
12	Physics (Ogden Centre for Fundamental Physics)	D7
44	Psychology	E7
31	Racecourse playing fields	H3/4
15	Security Office	E6
50	Shoichi Hall/Etsuko Hall, Teikyo University	C7
2	St Aidan's College and Lindisfame Centre	A7/A8
19	St Chad's College	D4
16a	St Cuthbert's Society (South Bailey)	C5
49	St Cuthbert's Society, including: - Refounders House - Fonteyn Court - Parsons Field House and Court - Brooks House	G4
17	St John's College	D5
10	St Mary's College	C6/C7
59	Theology and Religion	D4
9	Trevelyan College and Sir James Knott Hall	C7/C8
21	Union Society	D4
23	University College (Durham Castle)	D3
47	Ushaw College	n/a
52	Ustinov College	B10/C10
4	Van Mildert College	B8/C8
58	5 The College, Library (Heritage Collections)	C4/5

Room Locations

Refer to map for overview.

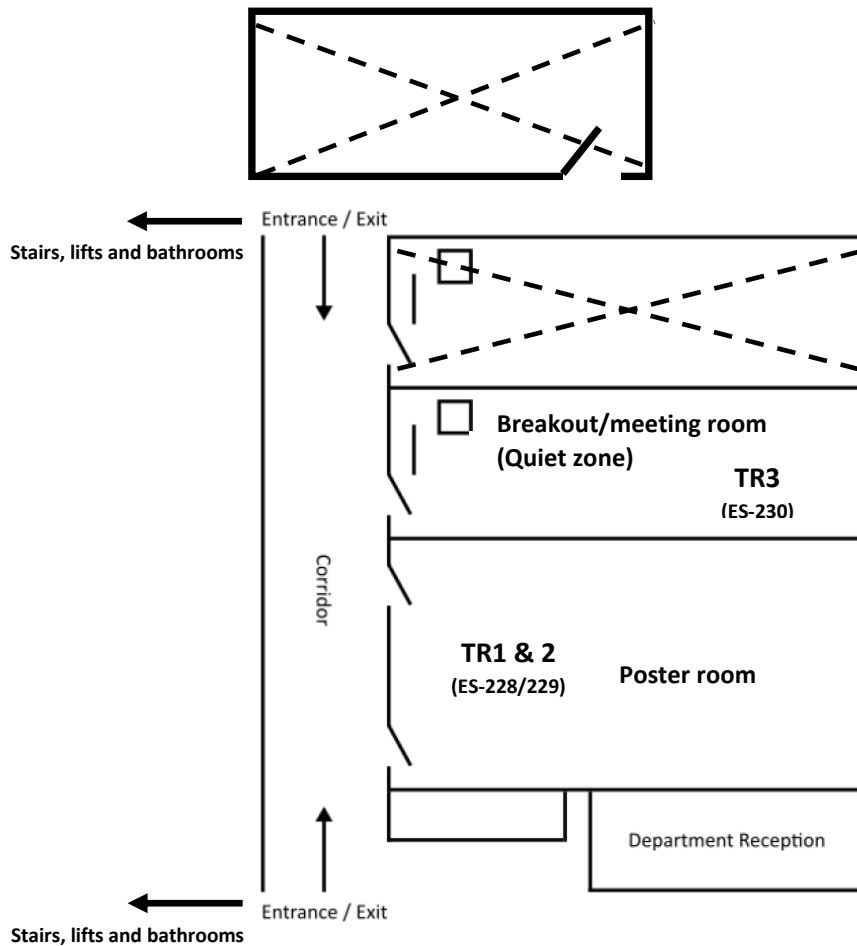
Oral Presentations and coffee

Room D-110, ground floor, Dawson Building (Dept. Anthropology), Durham University



Poster Presentations and meeting room

2nd floor, Department of Earth Sciences, Durham University – floor plan



Public Keynote Talk

Wolfendale Lecture Theatre, Calman Learning Centre

Cafés

Ground floor, Calman Learning Centre and ground floor, East Wing, Palatine Centre (#60 on the map).

Numerous cafés and restaurants are located in Durham city centre, which is a ~15-20 minute walk from the science site.

Evening Activities

Icebreaker, Sunday July 10th

7.30 p.m. - Empty Shop HQ, Durham

The Icebreaker will be hosted at Empty Shop HQ – a local art gallery and creative space in the heart of Durham City (see map). On offer will be a selection of local beers, wine, soft drinks and buffet style food. Please join us for what should be a relaxed opportunity to socialise with other workshop attendees before the scientific sessions commence on Monday morning.



Edward Inglis, Ice-breaker Coordinator



Kathi Schweitzer, Ice-breaker Coordinator

Keynote Talk, Monday July 11th

6.30 p.m. - Wolfendale Lecture Theatre

- How do meteorites tell us the story of our Solar System? *Dr. James M. D. Day*
- 6.30 p.m., Wolfendale Lecture Theatre, Calman Learning Centre, University of Durham. Public Event.

Dr. James M. D. Day is an Associated Professor at SCRIPPS, USA, and won the 2013 Houtermans Award of the European Association of Geochemistry and the 2014 Meteoritical Society Nier Prize. He is an Associate Editor of Elsevier's GCA and was Co-Editor of Reviews in Mineralogy and Geochemistry Volume #81. Dr. Day graduated the host, Durham University, twice – first as an undergraduate, subsequently earning his Ph.D under the tutelage of Prof. D. Graham Pearson. The workshop's keynote is a specialist in high-temperature HSE geochemistry as applied to terrestrial and planetary research (>70 scientific articles and review chapters, of which 9 were published by Nature/Science/Nature Geoscience, all in <15 years since PhD completion). As reflected by his record of publication and medals/awards of merit, Dr Day is a highly-esteemed and internationally prominent member of the geochemistry community and is established as an advocate for excellence with respect to HSE cosmo- and geochemistry studies. His public talk will engage a diverse audience and he will contribute much to the workshop's scientific sessions and their discussion periods.

Banquet, Tuesday July 12th

6.15 p.m. - Durham Town Hall, Market Square

The workshop's banquet will be held in Durham Town Hall - a grand Victorian building situated within Durham City's historic market place. The venue will be open and offering welcome drinks from 18:15, before taking our seats at 19.00 to enjoy a three course meal.

Table wine will be provided, with additional drinks available to buy from the bar. Tea and coffee will be served after dinner and the end of the banquet will be marked by a ceilidh until 23:00.



Fienke Nanne, Banquet Coordinator

Poster Session, Wednesday July 13th

The poster session for this workshop will include drinks and snacks and runs from the close of oral presentations on Wednesday afternoon until ~7 p.m. Presenters should stand by their posters from the beginning of this session.

Scientific programme at a glance

The opening icebreaker takes place on Sunday July 10th, at 7.30pm at the Open Shop HQ, Durham City Centre.

11 th July Monday		12 th July Tuesday	
9:00	REGISTRATION & COFFEE Dept. Anthropology <i>Page 7 & 9</i>	9:00	LAURENZ
10:10	WELCOME	9:20	DALY
10:20	BARNES Steve	9:40	WEYRAUCH
10:40	BECKER (INVITED)	10:00	LABIDI
11:10	BRENAN	10:20	COFFEE BREAK
11:30	LUGUET (INVITED)	11:00	KRABBE
12:00	COGGAN	11:20	HOPP
12:20	LUNCH (CATERED)	11:40	HUNT
13:50	BURTON	12:00	NANNE
14:10	YIERPAN	12:20	LUNCH (CATERED)
14:30	DAY	13:20	FISCHER-GÖDDE (INVITED)
14:50	GIBSON	13:50	KÖNIG
15:10	GUICE	14:10	KURZAWA
15:30	COFFEE BREAK	14:30	CREECH
16:10	VAN DER MEER	14:50	COFFEE BREAK
16:30	SCHWEITZER	15:20	RICHES
16:50	BROWN	15:40	BRENAN (INVITED)
17:10	DIJKSTRA	16:10	RAI
17:30	DALE	16:30	GLEIßNER
17:50	COFFEE BREAK <i>Calman Learning Centre, Page 7</i>	16:50	RIZO
18:30	PUBLIC KEYNOTE (JAMES DAY)	17:10	BREAK
		18:15	BANQUET




Theme 1



High temperature behaviour in Earth's mantle and magmatic systems

Theme 2

Constraints on planetary processes from meteorites, lunar and terrestrial samples

Scientific programme at a glance

13 th July Wednesday	
9:00	BARNES Sarah-Jane (INVITED)
9:30	HOLWELL
9:50	SULLIVAN 
10:10	KENNEDY
10:30	COFFEE BREAK
11:10	MAIER (INVITED)
11:40	YUDOVSKAYA 
12:00	STEPHENSON
12:20	LUNCH BREAK
13:40	COCKER 
14:00	PARK
14:20	TESSALINA
14:40	COFFEE BREAK
15:00	RAVIZZA (INVITED)
15:30	GANNOUN
15:50	ROONEY
16:10	MITRA
16:30	POSTER SESSION (Drinks and Nibbles) <i>Earth Science Dept., Page 7 & 9</i>
19:00	

14 th July Thursday	
9:00	MEISEL (INVITED)
9:30	VAN-ACKEN
9:50	WAINWRIGHT 
10:10	LISSNER
10:30	COFFEE BREAK
11:10	WARREN (INVITED)
11:40	PRICHARD 
12:00	LUGUET
12:20	STUDENT AWARDS
	CLOSING REMARKS

Theme 3

Applications for resource exploration and tracing ore genesis

Theme 4

Approaches to tracing Earth's surface geochemical cycles

Theme 5

Assessing small scale heterogeneities to better understand HSE behaviour

Presenter Instructions

- Speakers should prepare presentations in formats that are PC-compatible (power point or pdfs derived thereof).
- Dimensions of power point slides should be standard (4:3).
- Presentations should be provided on a thumb-drive and must be submitted in the presentation room prior to the start of each scientific session. For all presentations before noon, submission is required before 9 a.m. For all afternoon presentations, submission is required during the lunch break (ideally, at the start of lunch).
- Standard oral presentations should be 15 minutes in length and will be followed by 5 minutes of questions.
- Invited speakers should prepare a 25 minute presentation and anticipate 5 minutes of questions for invited talks.

- Posters should be put up in the presentation room in Durham's Dept. of Earth Sciences on Monday 11th. Rooms labelled ES-228 and ES-229 (2nd floor, connected - also known as TR1 &2) will host the poster session.
- Those giving poster presentations should stand by their work during the poster session on Wednesday July 13th.
- Posters are limited to 84 cm × 114 cm (33" × 45"). Landscape orientation is recommended.

It is not acceptable to record or photograph the presentations without the explicit permission of the authors.

Awards

The following awards are supported by the workshop:

- Best poster presentation given by a research student,
- Best oral presentation given by a research student.

Winners of these prizes will be announced during the closing remarks on Thursday 14th July and award presentations will be made by Laurie Reisberg, President of the Geochemical Society.

Venue Logistics

- In the event of a fire alarm sounding continuously please remain calm, take your valuables with you and follow the directions of the workshop organisers and/or fire marshal to leave the building by the nearest safe exit in an orderly manner.
- Bathrooms are located near to all meeting rooms and delegates should familiarise themselves with their locations, or ask one of the voluntary assistants involved in workshop organisation.
- If delegates experience any problems or accidents they should inform the event organisers immediately who will arrange for the appropriate assistance.
- Free wireless internet access is available at the science site where scientific sessions will take place. Guests will need to select the DU Guest network when connecting to the internet. Further instructions will be made available to delegates close to and/or at the time of the meeting.

If you have any queries about local provisions for child care please contact us: hse.ws@durham.ac.uk

Monday July 11th, Oral Presentations

10:00 **WELCOME ADDRESS** on behalf of Durham University's Department of Earth Sciences and Durham Geochemistry Centre given by Prof. Colin Macpherson and Prof. Kevin W. Burton.

Theme 1: High-temperature behaviour in Earth's mantle and magmatic systems

10:20 Barnes, Steve J., and Mungall J. E.

PGEs in mantle melts and mantle samples

10:40 Becker, H., Wang, Z., and Chunhui L.

INVITED: *Open-system mantle melting, recycling of oceanic crust and chalcophile element abundances in mantle rocks*

11:10 Brenan, J.M., and Fowler-Gerace, N.A.

Partitioning of Se and Te in mantle melting residues: Implications for the upper mantle Se-Te array

11:30 Luguët, A.,

INVITED: *Strongly chalcophile element systematics in terrestrial mantle-derived rocks*

12:00 Coggon, J.A., Matter, J.M., Teagle D.A.H., and Kelemen, P.

An introduction to the Oman Drilling Project

LUNCH (CATERED)

13:50 Burton, K.W., Dale C.W., Parkinson, I.J., and Gannoun, A.

Decrypting the osmium isotope signature of MORB using individual sulfide grains

14:10 Yierpan, A., König, S., Labidi, J., Huber F., Kurzawa, T., and Schoenberg, R.

The elemental S-Se-Te and Se isotopic signature of MORB

14:30 Day J.M.D., Walker, R.J., and Jackson M.G.

¹⁸⁶Os-¹⁸⁷Os systematics of ocean island basalts

14:50 Gibson S.A., Dale C.W., and Brüggmann, G.

The influence of melt flux and crustal processing on Re-Os isotope systematics of ocean island basalts: constraints from Galápagos

15:10 Guice, G.L., McDonald, I., Hughes, H.S.R., and Anhaeusser, C.R.

Using PGE to characterise ultramafic-mafic complexes in Archaean craton

COFFEE

16:10 Van der Meer, Q.H.A., Klaver, M., Reisberg, L., and Davies, G.R.

A whole rock Re-Os isochron for the Kaapvaal lithospheric mantle

16:30 Schweitzer, K.M., Luguët, A., Coggon, J.A., Fonseca, R.O.C., Nowell G.M., Ottley, C.J., and Scribano, V.

Highly siderophile elements and ¹⁸⁷Os signatures of peridotite xenoliths from the Hyblean Plateau, Sicily

16:50 Brown, D.B., and Day, J.M.D.

Effect of serpentinization on the HSE and ¹⁸⁷Os/¹⁸⁸Os in oceanic peridotites

17:10 Dijkstra, A.H., Dale, C.W., Oberthür, T., Nowell, G.M., and Pearson D.G.

Detrital Os-rich alloys from the Rhine River record a global? late Mesoproterozoic mantle depletion event

17:30 Dale, C.W., Nowell, G.M., Pearson, D.G., Oberthür, T., Malitch, K., and Eglington B.M.

Archaean crust-mantle links: Os isotopes in Witwatersrand PGM

BREAK

18:30 **PUBLIC KEYNOTE TALK:** **How do meteorites tell us the story of our Solar System?**

Dr. James M.D. Day. See Page 10.

Tuesday July 12th, Oral Presentations

Theme 2: Constraining planetary processes and building block compositions

09:00 Laurenz, V., Rubie, D.C., and Frost, D.J.

Sulfide-silicate partitioning of Re and Os at high P-T conditions

09:20 Daly, L., Bland, P.A., Forman, L.V., Reddy, S.M., Rickard, W.D.A., Saxey, D.W., La Fontaine, A., Yang, L., Trimby, P.W., Cairney, J., Ringer, S., Schaefer, B.F.

Atom probe tomography of refractory metal nuggets

09:40 Weyrauch, M., Zipfel, J., and Weyer, S.

Constraints on the formation of zoned metal grains in CB and CH chondrites from Ni and Fe isotope signatures and HSE abundances

10:00 Labidi, J., König S., Kurzawa, T., and Schoenberg, R.

The stable selenium isotopic composition of chondrites

COFFEE

11:00 Krabbe, N., Kruijer, T.S., Kleine, T.

Tungsten stable isotope variations in meteorites

11:20 Hopp, T., Fischer-Gödde, M., and Kleine, T.

Ruthenium isotope fractionation in planetesimal cores

11:40 Hunt, A.C., Ek, M., and Schönbächler, M.

Variations in the p-process Pt-190 Isotope in Iron Meteorites

12:00 Nanne, J.A.M., Millet, M.A., Dale, C.W., Burton, K.W., Harvey, J., and Williams, H.M.

Testing the late veneer hypothesis with Os stable isotopes

LUNCH (CATERED)

13:20 Fischer-Gödde, M

INVITED: Ru isotopic evidence for an inner solar system origin of the late veneer

13:50 König, S., Labidi, J., Kurzawa, T., Erkin, E., and Schoenberg, R.

Selenium isotope potential to study Earth's volatile origin and evolution

14:10 Kurzawa, T., König, S., Labidi, J., and Schoenberg, R.

Accurate stable Se isotopic determinations of ultra-low Se materials with HG-MC-ICP-MS

14:30 Creech, J.B., Baker, J.A., Bizzarro, M., Handler, M.R., and Moynier, F.

Tracing Earth's late accretion history using Pt stable isotopes

COFFEE

15:20 Riches, A.J.V., Burton, K.W., Nowell, G.M., Dale, C.W., and Ottley, C.J.

Innovative Mineral-Scale Achondrite PGE Analyses

15:40 Brenan, J.M., Mungall, J.E., Homolova, V., and Luo, D.

INVITED: A sulphide-saturated lunar mantle

16:10 Rai, N., Streenstra, E.S., Downes, H., van Westrenen, W.

Signatures of highly siderophile elements in the lunar mantle: HPHT core-mantle equilibration or late accretion addition of a chondritic component?

16:30 Gleißner, P., and Becker, H.

Highly siderophile element fractionations in lunar impact rocks: Effects of small- and large-scale processes

16:50 Rizo, H., Walker, R.J., Carlson, R.W., Horan, M.F., Mukhopadhyay, S., Manthos, V., Francis, D., and Jackson, M.G.

Preservation of Earth-forming events revealed by ¹⁸²W variations

BREAK

18:15 **BANQUET**

Wednesday July 13th, Oral Presentations



Theme 3: Applications for terrestrial resource exploration and ore genesis sponsored by

- 9:00 Barnes, Sarah-J., and Arguin, J.P.
INVITED: *The role of chromite in the fractionation and collection of PGE*
- 9:30 Holwell, D.A., McDonald, I., Barnes, Stephen J., and Keays, R.R.
Extreme concentration of PGE, Au, Se, and Te in sulphide microdroplets of the Skaegaard Intrusion
- 9:50 Sullivan, N.A., Brenan, J.M., and Canali, A.C.
Solubility of the assemblage Pt-PtAs(melt) in basalt with implications for As speciation and Pt sequestration
- 10:10 Kennedy, B., McDonald, I., Tanner, D., and Longridge, L.
PGE mineralisation in the Troctolite Marker, northern Bushveld Complex

COFFEE

- 11:10 Maier, W.D., Barnes, Sarah-J., and Karykowskyi, B.
INVITED: *A chilled komatiitic margin of the Bushveld Complex, South Africa: implications for the nature of mantle sources*
- 11:40 Yudovskaya, M., Belousova, E., Kinnaird, J., and Pearson, N.
Origin of PGM in Bushveld reefs by Re-Os LA data on the micrograins
- 12:00 Stephenson, H., McDonald, I., and Grobler, D.
Platinum-Group Element Mineralogy and Distribution in the Platreef on Turfspruit, Northern Bushveld Complex, South Africa

LUNCH

- 13:40 Cocker, H., Park, J.-W., and Campbell, I.
Sulfide saturation during the magmatic evolution of porphyry Cu ± Au systems
- 14:00 Park, J.-W., Campbell, I., Cocker, H., Malaviarachchi, S.P.K., and Kay, S.
Late sulfide saturation enhances potential to form porphyry Cu ± Au deposits
- 14:20 Tessalina, S.G.
Silver isotopes as new tracers of metal sources and ore formation processes

COFFEE

Theme 4: Tracing Earth's surface geochemical cycles

- 15:00 Ravizza, G.
INVITED: *What processes are responsible for excursions to low 187Os/188Os in the marine Os isotope record?*
- 15:30 Gannoun, A. and *Burton, K.W.
High precision elemental and isotope measurements of dissolved osmium in seawater
- 15:50 Rooney, A.D., Selby, D., Lloyd, J.M., Roberts, D.H., Lückge, A., Sageman, B.B., and Prouty, N.G.
Dating the dramatic and dynamic in the Neoproterozoic: New Re-Os age constraints and paleoweathering proxy data
- 16:10 Mitra, A., Sen, I.S., Rothenberg, S.E., Peucker-Ehrenbrink, B., and Bizimis, M.
Emerging Airborne Contaminants in Developing Countries: A case study from India
- 16:30 **POSTER SESSION:** Drinks and snacks provided.

Thursday 14th, Oral Presentations

Theme 5: Assessing small-scale heterogeneities in Earth materials sponsored by



- 9:00 Meisel, T., Bokhari, S.N.H., and Suoranta, T.
INVITED: *Recent development in PGE analysis*
- 9:30 van Acken, D., Luguët, A., Pearson, D.G., fonseca, R.O.C., Nowell, G.M., and Nagel, T.J.
Highly siderophile heterogeneity in mantle xenoliths and implications for osmium model ages
- 9:50 Wainwright, A.N., Luguët, A., Schreiber, A., Fonseca, R.O.C., Nowell, G.M., Lorand, J.-P., Wirth, R., and Janney, P.E.
¹⁸⁷Os isotopic composition and HSE variations at the nanoscale
- 10:10 Lissner, M., Landgraf, F., Nagel, T., König, S., and Luguët, A.
Mineralogical insights on the HSE-Se-Te behaviour during subduction

COFFEE

- 11:10 Warren, J.M., D'Errico, M.E., and Coble, M.
INVITED: *Constraints on mantle Pb from in situ analyses of sulphides*
- 11:40 Prichard, H.M., Dale, C.W., Barnes, S. J., Nowell, G.M., Godel, B., and Fisher, P.C.
Relating ¹⁸⁷Os to PGM located in 3D in different sites in chromitite
- 12:00 Luguët, A., Pushkarev, E., Nowell, G.M., Fonseca, R.O.C., Schreiber, A., Wirth, R., Gottman, I., and Ballhaus, C.
¹⁹⁰Pt-¹⁸⁶Os dating and FIB-TEM investigations of the Pt alloys from the Kondyor mafic-ultramafic massif (Aldan Province, Russia)
- 12:20 **STUDENT AWARD PRESENTATION** and **CLOSING ADDRESS** involving Laurie Reisberg, President of the Geochemical Society and Amy Riches, Chair of the 4th International Workshop on Highly Siderophile Element Geochemistry.

CLOSE OF THE WORKSHOP

- 13:00 Compulsory meeting for all attendees of the field trip to the Isle of Rùm.

Poster Presentations

Theme 1: High-temperature behaviour in Earth's mantle and magmatic systems

- #1 Huber, F., König, S., Babechuk, M., and Schoenberg, R.
Systematics of S-Se-Te in ocean island basalts
- #2 Inglis, E.C., Debret, B., Burton, K.W., Millet, M.-A., Nowell, G.M. Dale, C.W. and Williams, H.M.
The behaviour of Fe and Zn isotopes accompanying the subduction of oceanic crust
- #3 McCoy-West, A.J., Bennett, V.C., and Puchtel, I.S.
Pristine melt depletion signatures in Zealandian mantle xenoliths despite intense metasomatism
- #4 McCoy-West, A.J., and Williams, H.M.
Using stable isotopes to trace secular variations in Earth's mantle
- #5 Schweitzer, K.M., Luguet, A., Nowell, G.M., and Burton, K.W.
Highly siderophile element (HSE) and Hf-Os isotope signatures of carbonatites
- #6 Strack, R., Luguet, A., and Lorand, J.-P.
Why do basalt-hosted peridotite xenoliths have low Os concentrations?
- #7 Laborda-López, C., Dale, C.W., Marchesi, C., López-Sánchez-Vizcaino, V., Gómez-Pugnaire, M.T., Garrido, C.J., Jabaloy-Sánchez, A., and Padron-Navarta.
HSE & Os isotope compositions of subducted serpentinites & enclosed metaroddingites from Cerro del Almirez (Betic Cordillera, S. Spain)

Theme 2: Constraining planetary processes and building block compositions

- #8 Day, J.M.D., Strom, C.A., Dhaliwal, J.K., Liu, Y., Taylor, L.A., and the Chelybinsk Consortium
Parent-body processes revealed from siderophile elements in Chelyabinsk and other chondrite meteorites
- #9 Labidi, J., Bennett, N.R., König, S., Kurzawa, T., Schoenberg, R., and Shahaar, A.
Exploring the stable selenium isotope signature of core formation
- #10 Nunes, G.A., and Da Costa, A.R.
Mineralogical comparison between thermal treatments of Itutinga iron meteorite fragments.
- #11 Schwander, D., and Buhre, S.
On the formation mechanism of HSE-nuggets in experimental and meteoritic silicate systems
- #12 Wang, Z., and Becker, H.
Low sulfur in the Martian mantle: Insights from chalcophile elements in SNC meteorites

Theme 3: Applications for terrestrial resource exploration and ore genesis

- #13 Jillings, K.E.L., Maier, W.D., Tinkham, D.K., and Barnes, S.J.
Assimilation of Dolomite by Bushveld magmas; implications for the origin of Ni-Cu-PGE mineralization
- #14 Liu, J., and Selby, D.
RM8050: A reference material for petroleum Re-Os analysis
- #15 Karykowski, B.T., Polito, P.A., Maier, W.D., and Gutzmer, J.
Key characteristics of magnetite-hosted PGE-Au-Cu reef type mineralisation in the Jameson Range, Musgrave Province, Western Australia
- #16 McDonald, I., Jones, R.E., Holwell, D.A., Butler, I.B., and Hughes, H.S.R.
Sulphide melt-magma processes recorded in sulphide melt inclusions from the Platreef
- #17 Tanner, D., McDonald, I., Holwell, D.A., and Hughes, H.S.R.
Along-strike variation in HSE, Northern Limb of the Bushveld Complex, South Africa

Poster Presentations cont'd

Theme 4: Tracing Earth's surface geochemical cycles

- #18 Dellinger, M., Hilton, R.G., West, A.J., Torres, M., Burton, K.W., and Clark, K.E.,
Rhenium as a tracer of oxidative weathering from the Andes to the lowland Amazon Basin
- #19 Horan, K., Hilton, R.G., Burton, K.W., Selby, D., and Ottley, C.J.
Enhanced oxidative weathering in glaciated mountain catchments: A stabilising feedback on atmospheric carbon dioxide
- #20 Reisberg, L., Blamart, D., and Zimmermann, C.
Do Os isotopes track glacial-interglacial cycling? The strange case of the Benguela Upwelling System
- #21 Rooney, A.D., Selby, D., Lloyd, J.M., Roberts, D.H., Lückge, A., Sageman, B.N., and Prouty, N.G.
Tracking millennial-scale Holocene glacial advance and retreat using Osmium isotopes: Insights from the Greenland Ice Sheet
- #22 Sproson, A.D., Selby, D., Pogge von Strandman, P., Hladil, J., Jarochovska, E., Fryda, J., Slavik, L., and Loydell, D.K.
The Silurian Icehouse: Insights from Osmium and Lithium Isotopes

Theme 5: Assessing small-scale heterogeneities in Earth materials

- #23 Barnes, S. J., Godel, B., Le Vaillant, M., Fisher, L.A., Ryan, C.G., and Pearce, M.A.
Microbeam X-ray imaging of trace PGM phases in cumulate rocks
- #24 D'Errico, M.E., Warren, J.M., and Coble, M.
In situ trace element measurements of mantle sulfides by SHRIMP-RG
- #25 Kemppinen, L., Kohn, S.C., Parkinson, I.J., Bulanova, G. and Smith, C.
Understanding the timing and nature of diamond-forming events from the study of sulphide inclusions
- #26 Staddon, L.G., Parkinson, I.J., and Elliott, T.
Re-Os ages of detrital grains from Jack Hills and Mt. Narryer, Yilgarn Craton, Australia

Abstracts

Theme 1:

High temperature behaviour in Earth's mantle and magmatic systems

PGEs in mantle melts and mantle samples

STEPHEN J. BARNES¹ AND JAMES E. MUNGALL²

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The array of PGE contents in unfractionated mantle melts can be modelled with some fidelity using established partition coefficients and models involving pooling of melts generated over a range of depths¹.

The mantle composition array as a whole is characterized by variable degrees of depletion of Pt, Pd and Rh in Al-poor, melt-depleted harzburgite/dunite lithologies; lack of depletion in these elements in Al-bearing lherzolites; and a lack of systematic variation in IPGEs across this range. Melt-depleted cratonic mantle samples are notably more deficient in Pd than in Pt, but comparable Pd-enriched components are not represented in the available data from continental environments. The only group of unfractionated mantle melts that systematically record high Pd/Pt ratios are MORBs; if these are indeed the complement of the depleted cratonic mantle suite then the melt depletion recorded by the cratonic mantle suite occurred at low pressure prior to tectonic underplating of the depleted lithosphere beneath the cratons.

A filtered subset of orogenic peridotite compositions that are thought not to have been affected by significant extents of melt extraction or metasomatic refertilization have median concentrations of 3.9 ppb Os, 2.9 ppb Ir, 6.3 ppb Ru, 1.0 ppb Rh, 6.2 ppb Pt, 5.4 ppb Pd, and Cu/Pd ratio of 5500, which we consider to be representative of the modern convecting mantle. The convecting mantle has PGE proportions closely resembling those of lunar impact breccias, diverging considerably from chondritic proportions and attributable to the presence of a late veneer-derived, predominantly sulfide-hosted component². The compositions of mantle peridotites show considerable scatter attributable to the combined effects of measurement error and a strong covariance due to a heterogeneous distribution of sulfide in the small samples typically chosen for pulverization. The intensity of the covariance between all of the PGE due to sampling error gives a false impression of a genetic trend toward highly enriched PGE in some samples which could be mistaken for the effects of metasomatism; however no plausible metasomatic process would be expected to retain observed correlations.

Open-system mantle melting, recycling of oceanic crust and chalcophile element abundances in mantle rocks

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The use of fertile mantle rocks to constrain the chalcophile element composition of the mantle has been contentious because melt infiltration likely plays a major role in adding these elements and lithophile incompatible elements back to harzburgitic melting residues in the mantle ("refertilization"). However, the melt infiltration reported from peridotite tectonites, which are commonly LREE depleted, should be regarded as a logical consequence of open system melting in a polybaric melting column. Previous studies have shown that in the lherzolite stability field, precipitation of pyroxenes, Al phase and sulfides are coupled, likely because the S content of basaltic magma at sulfide saturation is low at high pressures (at low pressures, the behavior is different). Thus, magma infiltration at such conditions results in coupled variations of moderately incompatible chalcophile elements (S, Se, Te, Cu, Ag, Re) with Ca and Al. Most of the inventory of these elements in such lherzolites was derived from the infiltrating magma. The HSE composition of these ephemeral magmas can be obtained from pyroxenites in mantle tectonites, which show fractionated HSE patterns as they would be expected to form at low pressures and higher melt fractions where alloy solubilities control HSE patterns. REE data on such rocks and on cpx from associated lherzolites also often display strong LREE depletion. Thus, the ephemeral mantle magmas show the chemical fractionation signature of oceanic crust. This signature appears to be retained during subduction, mechanical stretching and melting of subducted oceanic crust and subsequent transport of the derivative magmas in the mantle. The key in constraining mantle compositions of moderately incompatible chalcophiles is the co-precipitation of sulfides with pyroxenes + Al phase, the latter yielding chondritic Ca/Al at appropriate MgO contents. Chalcophile element data on little altered Munro-type komatiites and primitive undegassed MORB support this picture.

Partitioning of Se and Te in mantle melting residues: Implications for the upper mantle Se-Te array

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Uncertainty exists as to the origin of the mantle peridotite Se-Te array in terms of the roles of metasomatism and partial melting, affecting the accuracy of estimates for the Se and Te contents of the bulk silicate earth. In order to constrain the expected partial melting trajectory for mantle peridotites, partitioning of Se and Te among olivine, orthopyroxene and silicate melt, as well as the solubility of Te and Pt in sulfide and silicate liquid, has been measured at upper mantle conditions. Experiments done at 1-1.5 GPa and 1320°C, IW + 3.5 reveal that both Se and Te are incompatible in olivine and orthopyroxene, with mineral/silicate melt partition coefficients for each element nearly the same (~ 0.04) for both phases. At 1.5 GPa and 1250°C, sulfide liquid saturated in an immiscible Pt-telluride liquid contains 5.2 wt% Te and 3.8 wt% Pt, and telluride-silicate melt partition coefficients ($D^{\text{TeLiq/SilLiq}}$) for Se, Te and Pt are ~ 400 , $\sim 4 \times 10^4$ and $\sim 7 \times 10^7$, respectively. The values of $D^{\text{TeLiq/SilLiq}}$ for Te and Pt are similar to past measurements of $D^{\text{SulLiq/SilLiq}}$, whereas Se is 10x less compatible in telluride than sulfide melt.

Combining these results with previous measurements of MSS- and sulfide liquid-silicate liquid partitioning allows the composition of peridotite melting residues to be calculated. Model results involving residual MSS predict relatively little Se/Te fractionation up to, and past, the point of sulfide exhaustion; residual sulfide liquid results in relatively constant Se/Te in residues over the initial 10% melting, then decreasing ~ 1.5 -fold as sulfide becomes depleted. Both Te and Pt remain too low in melt residues to saturate in a Pt-Te phase, either as moncheite (PtTe_2) or immiscible melt. Overall, the mantle peridotite Se-Te array is found to be consistent with the melting residue of a CI-like initial composition, although there is also clear evidence for disturbance by accumulation of residual or metasomatic sulfides in the most depleted compositions.

Effect of serpentinization on the HSE and $^{187}\text{Os}/^{188}\text{Os}$ in oceanic peridotites

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Abyssal peridotites are interpreted to represent residues after partial melting at ridges. They can therefore be used to investigate melting processes and mantle heterogeneity. A potential issue, however, is that geochemical signatures of oceanic peridotites can be modified by sea floor alteration and serpentinization (e.g., [1]). These processes may modify highly siderophile element (HSE) and Os isotopic compositions [2]. Previously, sea-floor alteration effects were reported to have minimal effect on core-rind HSE abundance variations of Gakkel Ridge peridotites [3]. To address the issue of serpentinization, we have studied some of the deepest dredged oceanic peridotites (>8000 m water depth) from the 1967 NOVA expedition to the Tonga Trench. Samples cover a range of visible and chemical alteration metrics, from very fresh (LOI of 0 wt.%), to highly altered (LOI of 16.7 wt.%). There is little correlation between serpentinization indicators (cf. LOI, Na_2O) and relative and absolute abundances of the HSE, or with $^{187}\text{Os}/^{188}\text{Os}$ (0.119-0.137) in samples. Indeed, the strongest correlation exists between Re and LOI ($R^2 = 0.3$). These findings indicate that HSE abundances and Os isotopic ratios in Tonga Trench peridotites reflect heterogeneities imparted by melt depletion and infiltration processes over 1 Ga time-scales, with minimal disturbance due to serpentinization.

- [1] Bach, W. et al. (2006) *GRL*, 33, L13306; [2] Foustoukos, D.I., et al. (2015) *GCA*, 150, 11-25; [3] Liu, C.-Z., et al. (2009) *EPSL*, 283, 122-132.

Decrypting the Osmium Isotope Signature of MORB using Individual Sulfide Grains

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Despite the potential utility of the ¹⁸⁷Re-¹⁸⁷Os isotope system for tracing the presence of enriched and depleted material in the MORB mantle source, low Os concentrations (and high Re/Os) render such basalts highly susceptible to a number of effects not seen in lithophile element isotope systems. These include analytical artefacts, radiogenic ingrowth, seawater contamination, and heterogeneity due to contamination or magmatic phases. In contrast, MORB sulfides have high Os contents relative to coexisting glass; consequently, sulfide is much less prone to the above effects, than silicate minerals or glass.

This study presents new high-precision Os isotope data for sulfide and coexisting MORB glass from the FAMOUS region (36°50'N) on the mid Atlantic ridge. Individual sulfides preserve ¹⁸⁷Os/¹⁸⁸Os compositions that range from 0.1236 to 0.1574. Sulfides are always less radiogenic than their glass host, not easily explained by radiogenic ingrowth, rather the glass appears to be substantially affected by seawater contamination. Osmium isotope and elemental data suggest that the sulfides themselves are also variably affected by contamination. In this case only those sulfides with high Os contents > 100 ppb are likely to yield robust ¹⁸⁷Os/¹⁸⁸Os values. Sulfides hosted in glass or crystalline matrix in the picritic basalt, ARP1973-010-003, have ¹⁸⁷Os/¹⁸⁸Os compositions of ~0.1305, close to PUM estimates. However, sulfides trapped in olivine crystals possess unradiogenic ¹⁸⁷Os/¹⁸⁸Os values of 0.1196-0.1212. Either all matrix sulfides in this sample are contaminated, and only included sulfides reflect the true mantle source, or else the matrix and included melts sample distinct mantle source compositions.

Overall, these data provide little evidence for recycled material in the MORB mantle source, rather they indicate that this source has experienced long-term depletion of Re, consistent with the lithophile element isotope systems.

An Introduction to the Oman Drilling Project

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AND P. KELEMEN²

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²Lamont-Doherty Earth Observatory, Columbia University, New York, USA

The oceanic lithosphere makes up two-thirds of Earth's surface; during each phase of its ~200 million year lifecycle it plays a key role in numerous global geochemical cycles. The Samail Ophiolite, in Oman and the United Arab Emirates, is the largest, best-exposed section of subaerial oceanic lithosphere in the World. The Oman Drilling Project is a comprehensive drilling program that will sample the whole ophiolite sequence, from crust through to upper mantle, in a series of diamond- and rotary-drilled boreholes. Data collection will include analysis of rock core, geophysical logging, fluid sampling, hydrological measurements and microbiological sampling. These novel datasets will be available to natural scientists from a broad spectrum of disciplines, who will use them to address a diverse range of scientific questions relating to the formation, hydrothermal alteration and biotic and abiotic weathering of oceanic lithosphere.

Archaean crust-mantle links: Os isotopes in Witwatersrand PGM

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The evolution of ¹⁸⁷Os/¹⁸⁸Os in residual mantle effectively ceases after large-degree mantle melting events, due to almost complete depletion of Re in the residue. Thus, Os isotopes in mantle rocks can be used to constrain the timing of major mantle melting events, by comparison with a chondritic evolution curve, and to investigate the scale of such events through time [1]. Platinum-group minerals (PGM) are formed in the mantle and in mantle-derived ultramafic rocks rich in platinum-group elements (PGE). The Os isotope compositions of detrital PGM have been shown to retain a record of mantle depletion events, owing to their high Os and low Re contents and their resistance to alteration [2]. Laser ablation MC-ICPMS provides a means for generating large datasets for suites of PGM.

Osmium isotope analyses of over 450 PGM from the Witwatersrand supergroup, the largest recognised Archaean sedimentary basin, indicate major mantle melting in the region at around 3.0 Ga to 3.2 Ga, with some older ages up to ~3.5 Ga. Unlike Phanerozoic ophiolite-derived suites [2], the Wits PGM do not have a pronounced skew towards older ages, suggesting that Archaean mantle was less heterogeneous than modern day mantle. The range of ages may instead represent sampling of ultramafic sources of different ages.

The range of Os isotope values in detrital PGM bears a strong similarity to the age record of Witwatersrand zircons and gold. This suggests a primary, detrital origin for the majority of the gold, rather than in situ hydrothermal deposition [3,4]. Furthermore, the complementary zircon and PGM records support coupled crustal growth and mantle depletion in the region, and corroborates a link between the mantle depletion record and crustal growth [2].

[1] Shirey & Walker (1998) *Ann. Rev. Earth. Planet.* 26: 423-500. [2] Pearson et al. (2007) *Nature* 449(7159): 202-205. [3] Kirk et al. (2002) *Science*, 297: 1856-1858. [4] Schaefer et al. (2010) *Chem. Geol.* 276: 88-94.

¹⁸⁶Os-¹⁸⁷Os systematics of ocean island basalts

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Controversy surrounds the interpretation of ¹⁸⁶Os-¹⁸⁷Os enrichments in ocean island basalts (OIB). Originally suggested as evidence for core-mantle interactions [1], alternate models have been proposed, including melting of pyroxenite-peridotite mixtures, or sulphides, with long-term (Re+Pt)/Os enrichment [2]. To test between the various hypotheses, we have targeted OIB spanning the range of compositional 'flavours' in Sr-Nd-Pb isotope space, and that are considered to be the products of variable recycling and metasomatism. New coupled ¹⁸⁶Os-¹⁸⁷Os and highly siderophile element (HSE; Os, Ir, Ru, Pt, Pd, Re) abundance data are presented for Hawaiian (Hualalai), HIMU (Mangaia, Tubuaii), HIMU-type (Canary Islands), and EM2 (Samoa) lavas. EM-2 lavas are considered to derive from a source dominated by peridotite with some sediment, and little or no mafic component. They span a limited range of ¹⁸⁷Os/¹⁸⁸Os (0.1233-0.1301). By contrast, Canary Island lavas are some of the most radiogenic OIB ever measured for ¹⁸⁷Os/¹⁸⁸Os (0.1287-0.1751). Neither island group shows evidence for derivation from an HSE-depleted source and both have ¹⁸⁶Os/¹⁸⁸Os averaging 0.1198393±18, which is indistinguishable from the upper mantle ratio defined by abyssal and ophiolite peridotites [3]. By contrast, lavas and cumulates from Hualalai have ¹⁸⁶Os/¹⁸⁸Os of 0.1198462 ±16 that is distinctly more radiogenic. Of all OIB, elevated ¹⁸⁶Os/¹⁸⁸Os ratios have only been measured in Hawaiian lavas [4]. This observation implies that most OIB have ¹⁸⁶Os/¹⁸⁸Os signatures that are dominated by mantle with chondritic Pt/Os, whereas some Hawaiian lavas are not. Hawaiian lavas must sample a distinct mantle source that may include ancient (>1 Ga) metasomatised (high Pt/Os) recycled oceanic mantle lithosphere, stored in the lower mantle and sampled by a deep mantle plume.

[1] Brandon A.D., Walker, R.J., 2005. *EPSL*, 232, 211-225; [2] Luguet A. et al. (2008) *Science*, 319, 453-456; [3] Brandon A.D. et al. (2006) *GCA*, 70, 2093-2103; [4] Ireland T.J. et al. (2011) *GCA*, 75, 4456-4475.

Detrital Os-rich alloys from the Rhine River record a global? late Mesoproterozoic mantle depletion event

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Gold and Platinum-group mineral bearing placers in the River Rhine in Southern Germany contain Ru-Os-Ir alloys derived from residual mantle rocks in the Alps. These rocks are almost certainly part of ophiolite fragments which were derived from the active margin of Gondwana and accreted to stable Europe before the Variscan Orogeny. We obtained ¹⁸⁷Os/¹⁸⁸Os isotope ratios and mantle depletion ages of 297 Ru-Os-Ir alloys from Rhine placers using laser-ablation MC-ICPMS analysis. The distribution of modeled Re-depletion ages of the alloys analysed shows two statistically significant modes: one at ~500 Ma and one at ~1.1 Ga. Os-rich alloys are recorders of depletion episodes in the Earth mantle. The 500 Ma age peak is probably associated with mantle melting during Cadomian active margin processes at the Gondwana margins. The 1.1 Ga alloy age peak cannot easily be interpreted by the known tectonic history of the host mantle rocks, and is interpreted as a record of an ancient melting event. Os-rich alloys derived from Paleozoic ophiolites in the Urals and Tasmania record the same ~1.1 Ga melting event, and the case for a Mesoproterozoic mantle depletion event of a global nature recorded in younger mantle rocks now seems strong and convincing. This ~1.1 Ga age peak also coincides with a globally recorded peak in zircon ages. We argue that the age peaks can be explained by the unusual geodynamics of the period leading to the formation of Rodinia in late Mesoproterozoic ('Grenvillian') times.

The influence of melt flux and crustal processing on Re-Os isotope systematics of ocean island basalts: constraints from Galápagos

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The Re-Os isotope system has become increasingly used as a tracer of lithological heterogeneity in the Earth's convecting mantle, with radiogenic ¹⁸⁷Os/¹⁸⁸Os in Os-rich (>40 ppt) oceanic basalts widely interpreted as evidence of melts from ancient recycled oceanic crust. New Re-Os isotope data for recent basalts erupted across 60,000 km² of the Galápagos archipelago, combined with published regional geochemical analyses and high-resolution seismic data, suggest wide ranges in ¹⁸⁷Os/¹⁸⁸Os may be influenced by variations in melt flux from the Galápagos mantle plume to the overlying crust.

High ³He/⁴He basalts erupted near the Galápagos plume stem have low ¹⁸⁷Os/¹⁸⁸Os similar to primitive mantle (0.130). Additionally, co-variations in ¹⁸⁷Os/¹⁸⁸Os and ²⁰⁶Pb/²⁰⁴Pb for some Galápagos basalts are HIMU like, consistent with melting of ancient recycled oceanic crust. Nevertheless, basalts erupted distal to the plume stem have variable ¹⁸⁷Os/¹⁸⁸Os ratios that are decoupled from lithophile isotopic systems. This is most likely due to assimilation of young Pacific lower crust during crystal fractionation. As distance from the Galápagos plume stem increases, the amount of vertical upwelling and melt flux decreases and crustal assimilation becomes proportionally greater, accounting for co-variations in Os and ¹⁸⁷Os/¹⁸⁸Os.

The Os concentration threshold below which ¹⁸⁷Os/¹⁸⁸Os ratios of Galápagos basalts are contaminated (100 ppt) is higher than the canonical value (<50 ppt) assumed for many global OIBs (e.g. Iceland, Hawaii). This may reflect the low overall melt flux from the weak Galápagos plume (T_p=1400 °C). Similar in-situ assimilation of lower oceanic crust by high-Os and MgO-rich basalts, especially those linked to low melt flux plumes, should not be overlooked in the quest for establishing melting of ancient recycled oceanic crust in hotspots and the degree of heterogeneity in the convecting mantle.

Using PGE to characterise ultramafic-mafic complexes in Archaean cratons

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Ultramafic-mafic complexes are important, but poorly understood, components of Archaean cratons that have been affected by multiple phases of high-grade metamorphism. As a consequence, their origin(s) can only be tested using highly immobile elements. This research utilises PGE alongside rare earth and high field strength elements to better constrain the characteristics of ultramafic-mafic complexes in the Johannesburg Dome (Kaapvaal Craton) and Lewisian Complex (North Atlantic Craton).

The 3.3-3.1Ga Johannesburg Dome [1] contains poorly exposed complexes comprising dunite, peridotite, pyroxenite and gabbro [2]. Layered rocks at Cresta and Zandspruit display Pd-group PGE (PPGE) enrichment ($[Pd/Ir]_N=1.1-8.4$), while a second group of ultramafics, observed only at Cresta, exhibit Ir-group PGE (IPGE) enrichment ($[Pd/Ir]_N=0.39-1.51$). In comparison to layered ultramafics, these IPGE-rich rocks demonstrate low lithophile trace element abundances (0.2-1.1 x primitive mantle) and discrete petrographic discrepancies.

In the 3.0-2.8Ga Lewisian Complex [3], layered ultramafic complexes at Ben Strome and Camas Nam Buth are PPGE-rich ($[Pd/Ir]_N=1.9-46.1$). In contrast, a non-layered ultramafic complex (of the same metamorphic grade) at Upper Badcall, located 3km SSE of Camas Nam Buth, is IPGE-rich ($[Pd/Ir]_N=0.11-4.19$).

Our findings indicate that PGE can be used to aid characterisation of ultramafic rocks within Archaean cratons previously assumed to have a common origin. Future research will further explore inter-craton similarities between 6PGE patterns and aims to 'fingerprint' the tectonic and/or geodynamic environment(s) within which ultramafic-mafic complexes formed.

[1] Anhaeusser, C.R. 1999. *S Afr J Geology*. 102, p.303-322

[2] Anhaeusser, C.R. 2006. In: Reimold & Gibson. *Processes on the Early Earth*. p.193-210. [3] Friend, C., Kinny, P. *Contrib Mineral Petrol*. 142, p.198-218.

Systematics of S-Se-Te in ocean island basalts

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The triplet S-Se-Te of group VI elements complements the highly siderophile elements (HSE) for research related to Earth accretion, mantle-core differentiation and late meteoritic replenishment (Late Veneer). In addition, S-Se-Te are volatile elements and therefore may also contribute to our understanding of how and when volatiles arrived and evolved on Earth [1]. Previous studies scrutinizing the behavior of Se and Te in the context of mantle sulfides and geodynamic origin concluded that, different terrestrial reservoirs may have different relative and absolute Se-Te abundances [2; 3; 4] which therefore require thorough individual analyses. At the workshop we aim to address the role of mantle plumes in the quest for a reliable estimate of Se-Te abundances in the Bulk Silicate Earth (BSE). Specifically the previously suggested enrichment of Te and hence lower Se/Te ratios in plume-related lavas is of interest. Submarine oceanic island basalts (OIBs) provide valuable insights into the level of degassing and/or recycling of mantle reservoir. We therefore investigate the geochemical characteristics of representative OIBs and provide additional Se-Te data. In addition to mid-ocean ridge basalts (MORBs) these new OIB data will significantly improve existing mass balance estimates for the absolute and relative Se-Te abundance in the BSE which helps to assess planetary-scale volatile origin and evolution.

[1] WANG and BECKER, 2013; [2] König et al., 2014 [3] LISSNER et al., 2014; [4] BRENNAN, 2015

The behaviour of Fe and Zn isotopes accompanying the subduction of oceanic crust

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After formation at mid-ocean ridges the oceanic lithosphere is progressively hydrated, altered and oxidised by interaction with seawater, before being recycled back into the mantle at convergent plate margins. During the subduction of oceanic lithosphere, a progressive increase in pressure and temperature (P-T) leads to the destabilisation of hydrous mineral phases and the release of structurally bound H₂O to the overlying sub-arc mantle. The release of such fluids during slab dehydration is suggested to be linked to the elevated Fe³⁺/ΣFe ratio observed in arc lavas (Kelley & Cottrell, 2009), as they may contain oxidised or oxidising agents.

In order to assess the effect of slab dehydration on the redox budget of the sub-arc mantle, we have utilised the novel stable isotopes of Fe and Zn. These systems have been applied to a suite of metagabbros and metabasalts from Western Alpine ophiolites, which have been re-equilibrated under variable metamorphic conditions, representative of a subduction gradient.

Fe isotopes are known to be fractionated according to redox state and as such have been used to track the mobility of oxidised Fe³⁺. Whilst Zn, which is mobilised in SO₄²⁻ and CO₃-bearing fluids, has been applied to trace the movement of these oxidising agents during subduction.

Our data show that there is no systematic co-variation between stable isotope composition and indicators of prograde metamorphism for these samples. Furthermore, no correlation is observed with the whole rock Fe³⁺/ΣFe ratio. Fractionation of both the Fe and Zn isotope systems is, however, observed within rocks from a blueschist facies terrane. This fractionation is driven by varying degrees of metasomatism resulting from fluid release from metasediments during subduction.

Kelley, K. & Cottrell, E., 2009. Water and the oxidation state of Subduction Zone Magmas. *Science*, 325; 605-607

HSE & Os isotope compositions of subducted serpentinites & enclosed metarodingites from Cerro del Almirez (Betic Cordillera, S. Spain)

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The Cerro del Almirez ultramafic massif (S. Spain) is the only locality where the dehydration front of antigorite breakdown in subducted serpentinites has been recognized in the field. These outcrops have been revealed as a unique setting to investigate the prograde metamorphic evolution from Atg-serpentinite to Chl-harzburgite [1,2] and its various petrological and geochemical implications. Enclosed in both types of ultramafic rocks are metarodingites and their associated blackwalls, which represent basaltic precursors that have undergone a complex metamorphic history during seafloor alteration and subsequent subduction.

This preliminary study on the highly siderophile elements (HSE: PGE + Re) and Os isotope compositions of metarodingites and their wall rocks shows differing HSE patterns and ¹⁸⁷Os/¹⁸⁸Os according to dehydration and fluid reaction processes. Atg-serpentinites present relative enrichment of Ru and Pd compared to Pt and Ir. Chl-harzburgites are depleted in Pt and Pd and enriched in Re compared to Atg-serpentinites. HSE abundances in ultramafic rocks vary as a function of the distance from metarodingites (e.g. lower Ru/Ir & Pd/Ir in Atg-serpentinites in contact with rodingite). ¹⁸⁷Os/¹⁸⁸Os ratios differ between different types of metarodingites and also between metarodingites and their blackwalls, suggesting interaction of basaltic and peridotitic HSE within the blackwalls. ¹⁸⁷Os/¹⁸⁸Os in ultramafic rocks decreases toward the metarodingites, potentially due to removal of radiogenic interstitial sulphides.

[1] Trommsdorff et al. (1998) *Contr.Min. Pet.*, 132, 292-302.

[2] Padrón-Navarta et al. (2011) *J. Petrology*, 52, 2047-2078.

Strongly chalcophile element systematics in terrestrial mantle-derived rocks

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The strongly chalcophile elements (S, Se, Te) like the HSE have the potential to unravel the accretion and metal-silicate differentiation processes of Earth and shed light on the nature of its building blocks. As the HSE, they are key tracers of petrogenetic processes that led to the chemical evolution of the terrestrial mantle by overprinting the Primitive Mantle (PM) left after the core segregation and the Late Veneer bombardment. Due to analytical improvements, the strongly chalcophile elements (re)gain popularity these last 5 years. Here, we review the state of the art knowledge on the Se and Te HT geochemistry in terrestrial mantle-derived rocks.

In these lithologies, Se and Te concentrations are 1-100s ppb and 1-10s ppb respectively. Harzburgites have low Se and Te concentrations and high Se/Te ratios (>20) while lherzolites show higher Se and Te concentrations and lower Se/Te ratios (8-10). Such systematics supports the incompatible nature of Se and Te during partial melting with Te being more incompatible. This conclusion is reinforced by the “higher than lherzolites” Se/Te ratio (18-15) of the DMM. MORB studies also reveal the compatibility of Se and Te during sulfide segregation associated with magmatic differentiation, explaining thus the unexpectedly low Se and Te contents in MORBs.

The whole-rock Se/Te vs. Te trend observed in peridotites overlap with the Se-Te composition of residual and metasomatic Se-Te host phases respectively for the harzburgitic and lherzolitic Se-Te signatures. Hence, although the Se/Te in lherzolites is trending toward the chondrite value, it results from a strong metasomatic overprinting and cannot be taken readily as face value of the PM composition. However, the combination of Se/Te with Os/Ir, Pd/Ir and ¹⁸⁷Os/¹⁸⁸Os allows distinguishing petrological processes (e.g. melt or fluid percolation) and addressing the robustness of the Re-Os isotopic system. A similar Se/Te vs. Te trend is observed between N-, T- and E- MORB, showing that Se-Te systematics also powerfully trace the involvement of recycled crustal material in the reservoir sources of terrestrial lavas.

Pristine melt depletion signatures in Zealandian mantle xenoliths despite intense metasomatism

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Here we present highly siderophile element (HSE) data from a suite of comprehensively characterised mantle xenoliths from 13 localities from throughout the micro-continent Zealandia [1-3]. Peritectic melt modelling demonstrates that these peridotites experienced a significant range of partial melting, between 3-28 % [2]. Major element compositions are consistent with refertilisation by a basaltic component in some samples. The majority of xenoliths also show effects of cryptic metasomatic overprinting, ranging from minor to strong light rare earth element (REE) enrichments in bulk rocks (La/Yb_N = 0.16-15.9). Chemical compositions are consistent with a carbonatitic component contributing to the metasomatism of the lithosphere under Zealandia [2, 4].

Prior Re-Os isotopic study has demonstrated that a substantial portion of the lithospheric mantle underlying southern New Zealand is Paleoproterozoic in age (ca. 1.9 Ga) and thus > 1 b.y. older than the oldest overlying crustal rocks [1]. The estimated amount of melting is however independent of the Re-Os model ages of the samples. The HSE patterns record simple melt depletion histories and the retention of primary base metal sulfides in the majority of xenoliths. We show that a rapid decrease in Pt/Ir_N observed at ca. 1.0 wt% Al₂O₃ is a direct result of the exhaustion of sulfide in the mantle residue at ca. 20-25% partial melting and the inability of Pt to form a stable alloy phase. Notably, despite significant refertilisation and widespread carbonatite metasomatism the majority of xenoliths possess undisturbed HSE patterns as the HSE budget of peridotites is controlled by residual sulfide.

[1] McCoy-West et al. (2013) *Geology* 41, 231-234; [2] McCoy-West et al. (2015) *JPet* 56, 563-604; [3] McCoy-West et al. (*under revision*) *GCA*; [4] Scott et al. (2014) *CMP* 167, 1-17.

Using stable isotopes to trace secular variations in Earth's mantle

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There are few unambiguous tracers of secular variations in the oxidation state of subducted surface material and its impact on mantle chemical evolution. For example redox-sensitive tracers, such as the vanadium concentrations [1] and iron stable isotope compositions of igneous rocks [2] do not record any systematic variations in mantle oxidation state with time. Molybdenum stable isotopes provide an extremely sensitive redox tracer and have been widely used to reconstruct transitions in sedimentary palaeo-redox environments from euxinic (S-dominated) to oxic conditions that typify modern oceans ([3]; $\delta^{98/95}\text{Mo} \approx 0.5\text{--}1.5\text{‰}$). Previous work focussing on Archean komatiites has shown they range from 0.02–0.19 ‰ ([4]; $\pm 0.16\text{‰}$; 2SD), although altered samples produce significantly heavier compositions up to 0.7 ‰. Due to these large analytical uncertainties, it is not possible to resolve the effects of any primary magmatic differentiation or alteration and hence properly assess temporal variability.

To eliminate the effects that long-term weathering \pm serpentinisation may have had on these mafic rocks we have focused on their modern equivalents. Two Phanerozoic examples of extremely fresh high degree partial melts the ~69 Ma Baffin Island picrites [5] and the ~90 Ma Gorgona komatiites [2] have been analysed here. Improved long-term analytical reproducibility in this study (Ramil $\delta^{98/95}\text{Mo} \pm 0.03\text{‰}$; $n = 118$) will allow resolution of high temperature magmatic fractionations. These analyses are coupled with stable Fe and Zn isotopic measurements on the same samples to better understand the process causing isotopic variability.

[1] Canil, *EPSL* **195**, 75 (2002); [2] Hibbert et al., *EPSL* **322** 98 (2011); [3] Archer et al., *Nature Geosci* **1**, 597 (2008); Duan et al., *GCA* **74**, 6655 (2010); [4] Greber et al., *EPSL* **421**, 129 [5] Dale et al., *EPSL* **278**, 267 (2009).

Highly siderophile elements and ¹⁸⁷Os signatures of peridotite xenoliths from the Hyblean Plateau, Sicily

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Peridotite xenoliths from the Hyblean Plateau (SE Sicily) are likely to represent North African Sub Continental Lithospheric Mantle (SCLM), emplaced by Miocene-Pleistocene volcanism related to the convergence of Africa and Europe. In order to investigate the petrological history of the SCLM beneath Sicily we have analysed four xenoliths from Valle Guffari for whole-rock major and trace elements, HSE, ¹⁸⁷Os/¹⁸⁸Os and base metal sulphide (BMS) petrography.

The peridotites have low Al₂O₃ contents (1.5–1.8 wt.%) but are CaO- and P₂O₅-rich (2.8–15 and 0.03–0.94 wt%, respectively) compared to global peridotites. This unusual composition reflects metasomatic overprinting further demonstrated by interstitial pockets of clinopyroxene, apatite, spinel and carbonates. The calculated composition of this metasomatic agent is carbonatitic. The most metasomatised xenolith is BMS-poor, has a melt-like CI chondrite-normalised HSE pattern and a radiogenic ¹⁸⁷Os/¹⁸⁸Os composition (0.1545). The other three xenolith samples, which are less overprinted, are BMS-rich. Their HSE patterns are relatively flat, but have total HSE concentrations up to >40 ppb. In these three least metasomatised peridotites, the HSE concentrations and Pt/Ir, Pd/Ir ratios are positively correlated with the CaO and P₂O₅ contents. Their ¹⁸⁷Os/¹⁸⁸Os are unradiogenic (0.1223–0.1265).

The North African SCLM beneath Sicily constitutes a new example of carbonatitic melt overprinting; Evolving S-saturation (from S-undersaturated to S-saturated) results in a change from BMS dissolution and melt-like HSE signatures to BMS precipitation and significant HSE enrichment.

Highly siderophile element (HSE) and Hf-Os isotope signatures of carbonatites

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Carbonatites are carbonate-rich and SiO₂-poor magmas whose low viscosity and low melting temperature (see [1]) make them amongst one of the most mobile and unusual melts produced on Earth. They occur worldwide in various tectonic settings, such as continental rift (e.g. Tanzania, Kaiserstuhl), oceanic intraplate (e.g. Cape Verde), convergent margins (e.g. Italy) and cratons (e.g. Canada), with eruption ages spanning from 3 Ga (3007 Ma Tupertalik, Greenland, [2]) to present day (Oldoinyo Lengai, Tanzania).

Nevertheless, their genesis and reservoir source are poorly understood and intensely debated. They are either products of direct low-degree partial melting of a carbonated mantle source or products of immiscible separation or fractional crystallisation from a carbonated silicate melt (see [1] and references therein).

In order to gain further insight into the genesis and mantle source of these unusual magmas, we will present the first combined HSE and Os-Hf isotope systematics on a suite of carbonatites representative of their large age span and compositional ranges (Ca, Mg, Fe and Na-rich).

[1] Jones et al., *Mineralogy & Geochemistry*, **75**, 289-322 (2013); [2] Downes et al. *Mineralogical Magazine*, **76**, 255-257 (2012).

Why do basalt-hosted peridotite xenoliths have low Os concentrations?

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Half of the alkali basalt-hosted peridotite xenoliths studied so far exhibit much lower Os concentrations than mantle peridotite tectonites and cratonic xenoliths. The origin of this Os depletion still remains enigmatic but has been attributed to volatilisation during lava entrainment, low temperature weathering of base metal sulfides (BMS) or BMS dissolution during melt-rock reaction at high melt/rock ratio [1].

In order to address this issue, we determine the HSE, Se and Te concentrations in a representative suite of alkali-basalt borne mantle xenoliths from the French Massif Central (FMC). On the basis on their detailed BMS petrographical study [2], these xenoliths belong to two groups: Group A xenoliths, unrelated to the FMC plume, experienced BMS addition via fluid percolation while Group B xenoliths, spatially related to the FMC plume, underwent BMS removal due to percolation of large volume of silicate melts. Moreover, xenoliths in each of the two groups show variable extent of the low-temperature BMS alteration (0-100% replacement by iron oxy-hydroxydes).

Such a sample selection allows us to tackle 2 of the 3 hypotheses proposed to explain the low Os concentrations of the non-cratonic peridotite xenoliths. Such comparison of the Os concentrations along with HSE-Se-Te systematics of these xenoliths will provide insights into the origin of this puzzling and peculiar feature of the alkali-borne peridotite xenoliths.

[1] Lorand, J.P. , Luguët, A., 2016 *RIMG 81*, 441-488; [2] Lorand, J.-P. et al. 2003. *GCA* 67, 4137-4153.

A whole rock Re-Os isochron for the Kaapvaal lithospheric mantle

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The Re-Os isotope system is one of the most useful tools to put age constraints on the formation of sub-continental lithospheric mantle (SCLM). Despite the general robustness of the Re-Os system, complex multi-stage metasomatic processes have often overprinted or erased primary isotopic signatures of the SCLM. The 533 Ma Venetia kimberlite cluster is one of the oldest in the Kaapvaal Craton, South Africa, and hosts peridotite xenoliths from a very complete section (55 to >170km) of the SCLM [1]. As a result of the Cambrian age, mantle xenoliths from the Venetia kimberlite have not been affected by the pervasive mantle metasomatism throughout the Phanerozoic typical of the Kaapvaal Craton.

Whole rock Re-Os isotope analyses of 30 peridotites from the Venetia xenolith suite show that the majority of the samples have low Re/Os (<0.05) and ¹⁸⁷Os/¹⁸⁸Os (<0.114). Whereas a few samples do appear to be affected by kimberlite metasomatism, a large sample subset defines a whole rock isochron (MSWD = 14), which is unique for an Archaean xenolith sample suite. The isochron passes through CHUR and ¹⁸⁷Os/¹⁸⁸Os correlates with Re/Os, Re content and olivine Mg#, suggesting that the range in ¹⁸⁷Re/¹⁸⁸Os is controlled by melt extraction and is barely affected by later-stage metasomatism. Hence, Re appears not to have been exhausted completely during melting. These results allow for a more detailed characterisation of the melt extraction history of the SCLM and provide a rigid base to assess the quality and validity of widely used Re-Os model ages.

[1] van der Meer, Q.H.A., Klaver, M., Waight, T.E., & Davies, G.R. (2013). The provenance of sub-cratonic mantle beneath the Limpopo Mobile Belt (South Africa). *Lithos*, 170, 90-104.

The elemental S-Se-Te and Se isotopic signature of MORB

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Selenium and tellurium are moderately volatile and highly siderophile elements (HSEs) that are present in the mantle at low yet considerably higher concentrations than expected after core-mantle differentiation [1]. Their excess mantle abundances, together with the near-chondritic pattern of S-Se-Te, have been used to argue for the Late Veneer hypothesis [2]. Accordingly, the S-Se-Te signature of the primitive upper mantle (PUM) would have mostly been inherited from late-accreted chondritic materials. However, peridotites used for estimation of primitive S-Se-Te contents [2] are often susceptible to multiple melt extraction and secondary metasomatic enrichment processes [3], and therefore might fail to represent the PUM [4]. An alternative approach may be to investigate these elements in depleted MORB mantle (DMM). Studies show that different MORB reservoirs have distinct elemental S-Se-Te [5] and S isotopic signatures [6] that need to be thoroughly studied before any reliable mass balance estimates can be made for PUM compositions. Although not observed for S isotopes [6], it remains to be verified if partial melting and sulfide segregation during MORB differentiation have a measurable effect on the stable Se isotope composition of MORB. Moreover, stable S isotope systematics of MORB indicate that a late-accretion may fail to explain the terrestrial S signature [6]. Hence, provided that all relevant petrogenetic processes are thoroughly examined, S-Se-Te content and Se isotope compositions, supplementing information obtained from stable S isotopes, may broaden our understanding of volatile behavior in the mantle. At the workshop we will present elemental S-Se-Te and Se isotope data for a suit of well characterized MORB samples acquired with a recently developed method [7]. These data will be used to address the implications for the volatile content of the DMM that may contribute to unraveling Earth's volatile history.

[1] Rose-Weston et al., 2009; [2] Wang and Becker, 2013; [3] König et al., 2015; [4] König et al., 2014; [5] Lissner et al., 2014; [6] Labidi et al., 2013; [7] Kurzawa et al., this volume.

Theme 2:

Constraints on planetary processes and building block compositions

A sulfide-saturated lunar mantle?

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We report on experiments to evaluate the sulfur content at sulfide saturation (SCSS) for the high FeO compositions typical of lunar magmas, at the reduced conditions of the Moon's interior. Experiments were done to measure the SCSS for a model low Ti mare basalt with 20 wt% FeO at 1400°C as a function of fO_2 and pressure. Synthetic lunar basalt was encapsulated along with stoichiometric FeS in capsules made from Fe-Ir alloy, which serves to vary the fO_2 . Experiments were done over the pressure interval of 0.1 MPa to 2 GPa. Results for experiments involving Fe₁₀₀ capsules indicate that the SCSS decreases from ~2000 ppm (0.1 MPa) to 700 ppm (2 GPa). Experiments done at 1 GPa show a marked decrease in SCSS as fO_2 decreases. Complementary to the decrease in SCSS is a drop in the sulfur content of the coexisting sulfide melt, from ~50 at% at $\Delta IW = +2.2$ to ~20 at% at $\Delta IW = -1$. Both the composition of the sulfide melt and the SCSS are essentially indistinguishable for Fe₉₆Ir₄ and Fe₁₀₀ compositions. At reduced conditions and high pressure, the SCSS for high FeO lunar compositions overlaps with Apollo 11 melt inclusion data. Importantly, such low SCSS does not require Fe metal saturation. Therefore, results suggest that some lunar source regions could be saturated in a low sulfur, sulfide melt. A sulfide-saturated melting model employing these new data reproduces the composition of lunar basalts with mantle HSE concentrations of 0.25-0.3x terrestrial values. Such results imply a much higher component of post accretion material than previous estimates derived from the HSE, consistent with a more volatile-rich Moon.

Tracing Earth's late accretion history using Pt stable isotopes

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Stable isotope measurements of HSE represent novel tools for investigating processes relating to accretion and differentiation of terrestrial planets. We have characterised the Pt stable isotope composition (expressed as the per mil difference in ¹⁹⁸Pt/¹⁹⁴Pt ratios, $\delta^{198}\text{Pt}$, relative to the IRMM-010 standard) of a comprehensive suite of inner Solar System bodies, including Earth, Mars and primitive and differentiated asteroids. The Pt stable isotopic composition of Earth's present-day mantle ($\delta^{198}\text{Pt}_{\text{mantle}} = -0.11 \pm 0.13\text{‰}$, 2sd) overlaps with chondrites from all groups ($\delta^{198}\text{Pt}_{\text{chondrites}} = -0.14 \pm 0.09\text{‰}$, 2sd). Primitive achondrite and diogenite samples show increasingly heavy isotopic compositions (up to $\delta^{198}\text{Pt} = +0.24 \pm 0.18\text{‰}$, 2sd) that correlate with the degree of PGE depletion, suggesting that Pt isotope fractionation occurs during metal-silicate differentiation with the lightest Pt isotopes preferentially partitioned into the core. The absence of an offset between present-day mantle and chondrites (representing the composition of the bulk Earth) is consistent with the signature of core formation having been overprinted in Earth's mantle by a late-veener of chondritic material added after the core had formed. Conversely, Archean samples from southern Africa and Greenland record non-chondritic, heavy $\delta^{198}\text{Pt}$, potentially indicating preservation of the metal/silicate differentiation signature suggesting that early mantle components have escaped complete mixing with the late-veener.

Atom probe tomography of refractory metal nuggets

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Highly siderophile elements are concentrated in micrometre to sub-micrometre metallic grains called refractory metal nuggets (RMNs) in the most primitive carbonaceous chondrite meteorites. Initially thought to be unique to Ca-Al-Rich inclusions, we used synchrotron XFM to show they are present in all meteoritic components [1].

RMNs are thought to form via nebula condensation [2], although new evidence suggests they can also be produced via crystallisation from silicate melts [3]. However, *in situ* analysis of 109 RMNs combined with a literature database, reveals a wide variety of compositions that no single process can adequately explain. Our interpretation is that the inherently diverse primordial population of RMNs, incorporated into the protoplanetary disk was modified, but not completely homogenised by later solar system processing. Therefore, RMNs potentially preserve pre-solar chemical and isotopic signatures [1].

To explore this idea we present the first use of atom probe tomography on RMNs. This technique provides 3D atomic resolution reconstructions of a 100 nm wide needle prepared using a focussed ion beam; capable of revealing atomic-scale variations in chemistry and isotopic composition. Preliminary results on 3 RMNs will be discussed. Initial observations reveal nanometre scale variability in chemistry, and the presence of sulphur within RMNs, potentially indicating nebular sulphidation.

[1] Daly et al. (2016). *GCA* (in review). [2] Berg et al. (2009). *The Astrophys Jour. Let*, 702, L172 [3] Schwander et al. (2015). *GCA* 186, 70–87.

Parent-body processes revealed from siderophile elements in Chelyabinsk and other chondrites

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The Chelyabinsk asteroidal airburst on February 15, 2013 has garnered significant attention, with the meteorites that fell being equilibrated LL4-5 ordinary chondrite material (e.g., [1,2]). New whole-rock ¹⁸⁷Re-¹⁸⁷Os, highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd, Re), major-, and trace-element abundances, and phase compositional data are reported for Chelyabinsk, ordinary and carbonaceous chondrites, to examine chondrite parent-body processes. Samples were analysed at the *Scripps Isotope Geochemistry Laboratory* using methods outlined in [3]. New HSE abundance and ¹⁸⁷Os/¹⁸⁸Os values for carbonaceous chondrites are generally consistent with previous results [4, 5]. Chelyabinsk has HSE abundances similar to CI-chondrite Orgueil, while HSE abundances between ordinary and carbonaceous chondrites vary by a factor of two and partially reflect aliquot heterogeneity. The measured ¹⁸⁷Os/¹⁸⁸Os compositions of Chelyabinsk samples (0.1253-0.1284) are consistent with ¹⁸⁷Os/¹⁸⁸Os measured in other ordinary chondrites (0.1257-0.1284). Chelyabinsk shares many similarities with other equilibrated low iron ordinary chondrites (e.g., Semarkona) that tend to have lower Pd and absolute HSE concentrations than less equilibrated, high iron ordinary chondrites (e.g., Richardton). Metamorphism does not appear to have affected ¹⁸⁷Re-¹⁸⁷Os systematics for Chelyabinsk, which is consistent with limited disturbance since formation. The results indicate distinct formation conditions for the major chondrite classes and a role for Fe-Ni-S separation during parent body processing.

[1] Liu, Y. et al. 2013. *MPS*, **48** (S1), A225. [2] Taylor, L.A. et al. 2014. *LPSC Abstracts*, **45**, 2346. [3] Day, J.M.D. et al. 2015 *MPS*, **50**, 1750-1766. [4] Horan, M.F. et al. 2003. *CG*, **196**, 5-20. [5] Fischer-Godde M. et al. 2010. *GCA*, **74**, 356-379.

Ru isotopic evidence for an inner solar system origin of the late veneer

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Excess abundances of highly siderophile elements (HSE) in the Earth's mantle are commonly interpreted to reflect the addition of a late veneer of primitive meteoritic material after core formation was complete. This late accreted matter either represents a left over population of objects remaining in the terrestrial planet region after Earth's accretion, or derives from more distant asteroidal or cometary sources. Distinguishing between these origins is critical because depending on its nature the late veneer may have significantly contributed to Earth's budget of volatile elements. The genetic fingerprint of the late accreted materials as constrained by relative abundances of highly siderophile elements in the mantle, is similar to some primitive meteorite groups. However, until now it has not been possible to establish firm genetical links between the late veneer, specific groups of meteorites, and Earth's main building blocks.

In this study the presence of nucleosynthetic Ru isotope anomalies in meteorites is used to assess whether the late veneer can be linked to a specific group of meteorites or, alternatively, derives from a population of bodies distinct from meteorite parent bodies. As a highly siderophile element Ru should have been quantitatively removed from the mantle during core formation. Thus, if enriched by late accretion, the terrestrial Ru isotope composition reflects the isotopic signature of the late veneer. Consequently only meteorites (or a combination thereof) having a terrestrial Ru isotope composition can be source of the late veneer.

All analyzed chondrites have Ru isotope compositions different from that of the Earth's mantle and, therefore, cannot represent the materials of the late veneer. The magnitude of nucleosynthetic Ru isotope anomalies scales with increasing heliocentric distance (terrestrial < enstatite < ordinary < carbonaceous). Highly reduced and dry inner solar system planetary materials like enstatite chondrites have Ru isotope compositions most similar to Earth, whereas oxidized and volatile-rich carbonaceous chondrites are most different from terrestrial. Therefore, the late veneer cannot be predominantly comprised of carbonaceous chondrites, implying only a minor role of the late veneer for the delivery of Earth's volatiles. Instead the late accreted materials more likely derive from rocky inner solar system objects originating from the terrestrial planet region.

Highly siderophile element fractionations in lunar impact rocks: Effects of small- and large scale processes

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The compositional record of lunar impact rocks may provide constraints on the composition of material accreted late to the terrestrial planets and might also hold the key to understand the observed slight deviations from chondritic ratios of some highly siderophile elements (HSE) in the Earth's mantle. However, the origin of small-scale fractionations observed in multiple aliquots of the same sample as well as large-scale fractionations between samples of different lithologies and landing sites are still debated [1-3].

Mineral separates from Apollo 16 impact melt rocks display large differences in absolute HSE abundances and resolvable differences of their ratios. The latter observation is consistent with small-scale fractionations due to solid metal-liquid metal partitioning, controlled by changing abundances of light elements like sulfur and phosphorous, during cooling and crystallization. Differences between bulk samples are representative of yet another larger-scaled processes before their crystallization.

Impact rocks from different landing sites display broadly linear correlations of different HSE ratios and ¹⁸⁷Os/¹⁸⁸Os ratios [1-3]. This is consistent with variable mixing of chondrite-like impactor components with a differentiated impactor component, similar but not identical to known iron meteorite composition(s) [2]. The non-chondritic impact rocks display HSE compositions typical to residual metallic melt after significant solid metal formation from metal melt initially rich in phosphorous and/or sulfur. Fractional crystallization modeling reveals that such a large-scale fractionation is only possible during core crystallization of the parent bodies of the later impactors. Differences in Se/Te and S/Se ratios reveal different primitive impactor compositions in the chondrite-like impactor component.

- [1] Puchtel I. S. et al. (2008) *GCA*, 72, 3022–3042. [2] Fischer-Gödde M. and Becker H. (2012) *GCA*, 77, 135–156. [3] Liu J. et al. (2015) *GCA*, 155, 122–153.

Ruthenium isotope fractionation in planetesimal cores

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Most iron meteorites are presumed to be remnants of planetesimal cores because their compositions are consistent with liquid metal-solid metal partitioning during fractional crystallisation of a metallic melt. [e.g., 1]. This process should in principle induce a stable isotope fractionation between early- and late-crystallised irons from a given core, but such isotope fractionations have yet not been identified. Here we use Ru stable isotopes to assess whether the solidification of planetesimal cores induced stable isotope fractionations. Ruthenium is ideally suited for this task because it is strongly fractionated within most iron meteorite groups, where early-crystallised irons have high Ru and late-crystallised samples have low Ru contents. This chemical fractionation makes Ru a promising element to search for isotope fractionation induced by core crystallisation. We developed a ⁹⁸Ru-¹⁰¹Ru double spike for the precise measurement of mass-dependent Ru isotope variations and here present Ru isotope data for a comprehensive set of iron meteorites from different chemical groups (e.g. IIAB, IIIAB, IVB). Each group is thought to represent samples from a distinct parent body. The samples were selected to cover a wide range of the crystallisation sequence within each group. We also analysed four different ordinary chondrites to assess the Ru isotopic composition of undifferentiated material. As a highly siderophile element, Ru has been quantitatively removed to the core during differentiation and so ordinary chondrites provide the most reasonable Ru isotope composition of the bulk core. Our results show large Ru stable isotope variations among the iron meteorites. For each group we find a correlation between $\delta^{102/99}\text{Ru}$ and Ru contents, indicating that core crystallisation induced Ru isotope fractionation. We observe the highest $\delta^{102/99}\text{Ru}$ for late-crystallised irons, meaning that the remaining liquid became increasingly heavier during core crystallisation. Overall, our data can be well explained by isotope fractionation during core crystallisation, providing additional evidence for solidification of planetesimal cores by Rayleigh processes.

[1] Scott (1972) *GCA* 36, 1205-1236.

Variations in the p-process Pt-190 Isotope in Iron Meteorites

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Carbonaceous chondrites show *p*-process deficits for Sm and Nd isotopes [1]. Platinum isotopes are ideal to search for correlated effects, as Pt has six naturally occurring isotopes that are a mixture of *p*- (¹⁹⁰Pt), *s*- (¹⁹²Pt) and *r*- (¹⁹⁴, ¹⁹⁵, ¹⁹⁶, ¹⁹⁸Pt) process. To date, high precision data for ¹⁹⁰Pt only exist for the IAB, IIAB and IIIAB irons, and show no ¹⁹⁰Pt variations [2]. Here we present new ¹⁹⁰Pt data for the iron meteorites, including the IVB irons.

Platinum is purified following the method described by [3]. Samples are measured using a Neptune Plus MC-ICP-MS with a Cetac Aridus II desolvating system. The instrument is fitted with two 10¹² Ω amplifiers that are used to measure ¹⁹⁰Pt and ¹⁸⁸Os. The external reproducibility for $\epsilon^{190}\text{Pt}$ in our high-precision set-up is ~ 2 ε.

New data for Pt isotopes confirm the lack of *s*- and *r*-process isotope variations in the iron meteorites, in agreement with previous studies [4, 5, 6]. Comparison to the models of [7] indicate that variations are the result of exposure to galactic cosmic rays (GCR). Our low-precision $\epsilon^{190}\text{Pt}$ data show no differences between iron meteorites at the 1.5 ‰ level. While new high-precision $\epsilon^{190}\text{Pt}$ data yield values identical to the terrestrial standard for the IIAB iron meteorites, the data for the IVB irons show ¹⁹⁰Pt excesses. Excesses in ¹⁹⁰Pt correlate with other Pt isotope excesses, and therefore with exposure to GCR. Once GCR effects are corrected for, the IVB irons hint at a small *p*-process excess on ¹⁹⁰Pt, however, this is not fully resolved within the limits of our current analytical precision. In contrast, no *p*-process variations are reported for ¹⁸⁰W and ¹⁸⁴Os in iron meteorites [8, 9, 10].

[1] Andreasen & Sharma (2006) *Science* 314, 806-809. [2] Peters et al. (2015) *Chem. Geol.* 413, 132-145. [3] Hunt et al. (2015), *LPSC* 46, #1835. [4] Kruijer et al. (2013) *EPSL* 361, 162-172. [5] Wittig et al. (2013) *EPSL* 361, 152-161. [6] Kruijer et al. (2014) *Science* 344, 1150-1154 [7] Leya & Masarik (2013) *MAPS* 48, 665-685. [8] Cook et al. (2014) *GCA* 140, 160-176. [9] Peters et al. (2014) *EPSL* 391, 69-76. [10] Walker (2012) *EPSL* 351-352, 36-44.

Selenium isotope potential to study Earth's volatile origin and evolution

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Selenium is a volatile and highly siderophile element (HSE) that was mostly stripped from the Earth's silicate mantle during metal core segregation. After core formation, continuing meteoritic impacts may have replenished the HSEs to their current concentrations in the mantle (Late Veneer). Due to its volatile and highly siderophile character, Se links the Late Veneer with the origin of other volatiles on Earth. Understanding the origin and evolution of elemental Se and its isotope composition in the Earth's mantle-crust-atmosphere system - the major goal of the ERC-funded project O₂origin - is crucial to constrain how other volatiles emerged [1;2] and evolved to make Earth a habitable planet. Although Se is only an ultra trace element in the mantle it is concentrated in micrometric host mineral "capsules" such as sulfides and platinum group minerals up to hundreds of ppm [2;3]. At the same time Se is concentrated in the same host mineral phases as Os [2;3;4] allowing for the simultaneous determination of Se and Os isotope signatures and, via the ¹⁸⁷Re-¹⁸⁷Os geochronometer, for absolute dating of the "snapshot" of these signatures. At the workshop we aim to demonstrate the potential of these combined isotope investigations together with our current applications for studying the Earth interior that may significantly push the current boundaries of our knowledge regarding terrestrial volatile origin and evolution.

[1] Wang and Becker (2013); [2] König et al. (2014); [3] König et al. (2015); [4] Brenan (2014)

Tungsten stable isotope variations in meteorites

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Tungsten isotope studies have so far almost exclusively focused on the application of the short-lived ¹⁸²Hf-¹⁸²W system to date meteorites and the differentiation of asteroids and terrestrial planets [1]. However, in addition to radiogenic ¹⁸²W anomalies, W isotope compositions may also vary as a result of mass-dependent fractionations not only among individual samples but also between distinct geochemical reservoirs (e.g., mantle and core). As such the study of W stable isotopes may help to assess the significance of Hf-W ages, especially for W model ages of core formation. To assess the magnitude and origin of mass-dependent W isotope variations in terrestrial and extraterrestrial materials, we have developed a ¹⁸⁰W-¹⁸³W double spike for the measurement of W stable isotope compositions by multi-collector ICPMS. Here we present our first results for a variety of terrestrial rock standards and meteorites. All samples were spiked prior to digestion in closed Savillex PFA vials. After complete dissolution in HF-HNO₃-HClO₄, W was separated from the sample matrix by anion exchange chromatography. The isotope measurements were performed using a Neptune Plus MC-ICPMS in Münster, and the data reduction was made with the *Double Spike Toolbox* [2]. All data are reported in $\delta^{184/183}\text{W}$ as the ‰ deviation from the NIST SRM 3163 W isotope standard. Iron meteorites and chondrites show a narrow range of $\delta^{184/183}\text{W}$ between ~0.00 to ~0.06 ‰, indicating that bulk planetary bodies in the inner solar system have uniform W stable isotope compositions. The terrestrial samples analyzed thus far reveal a similar range in $\delta^{184/183}\text{W}$ and, therefore, do not show a resolvable W isotope fractionation imparted by core formation on Earth. However, more data for terrestrial samples are needed to firmly arrive at this conclusion. Eucrites show more variable and heavy W isotope compositions, which may reflect W isotope fractionations during core formation and magmatic processes on the eucrite parent body.

References: [1] Kleine, T. et al. 2009. *GCA* 73:5150-5188. [2] Rudge J. et al. 2009. *Chem. Geol.* 265:420-431.

Accurate stable Se isotopic determinations of ultra-low Se materials with HG-MC-ICP-MS

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Selenium is a redox-sensitive element with multiple valence states and a total of six stable isotopes. Se isotopic systematics have therefore been used to track Earth's atmospheric oxygenation events in the ancient marine sedimentary record ([1] and ref. therein).

The aim of this study is to develop an analytical method that enables the use of stable Se isotopes as a tracer for planetary formation and differentiation. So far, stable Se isotopic measurements have been limited by the low Se concentrations typical for geological materials and were thus applied to samples with relatively high Se contents such as shales (>1 ppm Se). Terrestrial igneous rocks such as basalts or peridotites, however, typically display Se contents of only 10 to 200 ppb, rendering Se isotope measurements difficult. As such, the stable Se isotopic composition of terrestrial silicate reservoirs presently remain unknown. All Se isotope data were obtained on a ThermoFisher Scientific™ NeptunePlus MC-ICP-MS. Samples were doped with a ^{74/77}Se double spike, which enables correction of the instrumental mass bias and any isotopic fractionation during chemical purification of Se. The data are normalized to the NIST SRM-3149 Se reference material and is reported as $\delta^{82/76}\text{Se}$ values.

Repeated measurements of the MH-495 Se standard yield an average $\delta^{82/76}\text{Se} = -3.27 \pm 0.13\text{‰}$ (2σ , $n > 50$), which agrees within uncertainties with previously reported data (-3.44 ± 0.06 ; [2]). $\delta^{82/76}\text{Se}$ values for USGS shales SGR-1 and SCO-1 of $-0.03 \pm 0.22\text{‰}$ (2σ , $n = 3$) and $-0.08 \pm 0.20\text{‰}$ (2σ , $n = 1$), respectively are also in good agreement with previous studies ([3], [4]). In addition to accuracy tests, the first results for Se isotope composition of low abundance USGS mantle rock references will be presented at the conference.

[1] Pogge von Strandmann et al. (2015); [2] Zhu et al. (2014) [3] Mitchell et al. (2012); [4] Pogge von Strandmann et al. (2014)

Exploring the stable selenium isotope signature of core formation

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Early extraction of the Earth's core accounts for the relative depletion of siderophile (iron-loving) elements in the mantle compared to a chondritic reference. The mantle is highly depleted in selenium suggesting that, in addition to its volatile character, this element has also been partitioned into the core [1].

Here, we explore the potential of selenium isotopes to record evidence of the core formation process. We seek to address experimentally whether the incorporation of selenium into the core could have left a measurable isotopic signature on the mantle.

A preliminary experiment was conducted at 1 GPa and 1650 C for 2 hours using the piston-cylinder apparatus at Carnegie's Geophysical Laboratory. Starting materials consisted of basalt, Fe and FeSe. Metallic and silicate fractions were then separated by hand and a Se chemical extraction was done using standard procedures [2]. Stable isotopic data were obtained on a ThermoFisher Scientific™ NeptunePlus MC-ICP-MS at the University of Tübingen. We used a ^{74/77}Se double spike technique. Due to limited isotopic data obtained so far, the external 2 s.d. reproducibility on $\Delta^{82/76}\text{Se}_{\text{metal-silicate}}$ values is estimated from high Se-content standards (> 10 ppm Se) to be 0.20‰.

The Se content in the metal and silicate of our experiments is 65 ± 5 and 5130 ± 100 ppm, respectively. This yields a $D(\text{Se})_{\text{metal-silicate}}$ of 80 ± 7 at our experimental conditions, consistent with previous work [1]. No Se isotopic fractionation was resolved between metal and silicate in this experiment.

Time series and experiments performed at other conditions (e.g. S-bearing starting materials) are underway.

[1] Rose-Weston et al. (2009); [2] Kurzawa et al. (this conference)

The stable selenium isotopic composition of chondrites

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Selenium has a 50 % condensation temperature from a solar-system composition gas of 700 K [1]. Its concentration strongly varies across the different types of carbonaceous chondrites, reflecting their varying volatile element depletions [2]. For example, CI carbonaceous chondrites contain ~20 ppm Se, whereas CVs contain only ~9 ppm Se. The aim of this study is to investigate whether the variability of volatile element content, and especially that of Se, is associated with stable Se isotopic variations.

We performed Se concentration and stable isotopic determinations for 11 chondrites of CI, CM, CV, EH, EL, L and LL types. Data were obtained on a ThermoFisher Scientific™ NeptunePlus MC-ICP-MS at the University of Tübingen. We used a ^{74/77}Se double spike technique to account for the instrumental mass bias and any mass-dependent Se isotope fractionation that may occur during Se purification. $\delta^{82/76}\text{Se}$ values are given as the permil difference relative to the NIST SRM-3149 reference material. The external 2 s.d.reproducibility on $\delta^{82/76}\text{Se}$ values calculated from duplicate meteorite analyses is 0.14‰ or lower.

Se contents obtained for the different meteorite groups lie between 4.0 ± 0.4 and 19.9 ± 0.5 ppm (2σ) and are directly correlated with other proxies of volatile depletions in chondrites [2]. Preliminary data show $\delta^{82/76}\text{Se}$ values for chondrites that vary over a 1.5‰ range. However, two meteorites are identified to have experienced Se loss during hot desert weathering on Earth. When these weathered meteorites are excluded, the $\delta^{82/76}\text{Se}$ values vary over 0.4‰. Notably, enstatite chondrites have consistently lower $\delta^{82/76}\text{Se}$ values than ordinary and carbonaceous chondrites.

The large variations of Se content in carbonaceous chondrites are only weakly correlated with $\delta^{82/76}\text{Se}$ values. Absolute values for chondrites and implications for the Se isotopic volatilization-induced isotopic fractionation will be discussed at the workshop.

[1] Lodders (2003); [2] Dreibus et al. (1995)

Sulfide-silicate partitioning of Re and Os at high P-T conditions

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The origin of the highly siderophile elements (HSEs) in the Earth's mantle is generally explained by the so-called Late-Veneer hypothesis. This includes segregation of Fe-metal to form the Earth's core during which the mantle became strongly depleted in HSEs. Subsequently, HSE abundances were raised to their current values by the addition of chondritic material to the mantle. However, it has been proposed that a sulfide melt has also been sequestered to the core [1]. Recent experimental results have shown that sulfide segregation could explain suprachondritic Pd/Ir and Ru/Ir observed for the Earth's mantle, because Ru and Pd are less chalcophile than Ir and Pt under high *P-T* conditions [2].

One of the most powerful constraints for HSE mantle geochemistry is its overall enstatite chondrite-like Os-isotope composition [3]. This indicates that the Earth's mantle evolved with a long-term chondritic Re/Os ratio. To assess whether sulfide segregation is consistent with this signature requires information on the sulfide-silicate partitioning of Re and Os at high *P-T*.

Therefore, we are experimentally investigating the sulfide-silicate partitioning of Re and Os at high pressure. A molten peridotite composition is equilibrated with a FeS sulfide melt doped with Re and Os (~10 wt. % each). Experiments are performed at 2100-2400 °C and 7-21 GPa. Major element compositions of quenched silicate and sulfide melts are determined by electron microprobe, whereas Re and Os concentrations are analyzed using LA-ICPMS.

First experimental results indicate, that both Re and Os behave as chalcophile elements under high *P-T* conditions. Results will be used to model the influence of sulfide segregation on Re and Os during core formation and to test whether they become fractionated, as is the case for low *P-T* sulfide-silicate equilibration during MORB genesis.

[1] O'Neill (1991) *GCA* 55, 1159-1172. [2] Laurenz et al., submitted to *GCA*. [3] Meisel et al. (2001) *GCA* 65, 1311-1323.

Testing the late veneer hypothesis with Os stable isotopes

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During planetary differentiation, osmium is quantitatively extracted into metallic cores, leaving planetary mantles strongly depleted in Os. The abundance of Os in Earth's mantle is, however, much higher than predicted from metal-silicate equilibration experiments^[1]. One common explanation for this overabundance is the late accretion of Os-rich meteoritic materials ('late veneer') after core formation had ceased^[2]. Osmium stable isotopes can potentially test this hypothesis by comparing the composition of the silicate Earth with that of the chondritic building blocks of Earth. Therefore, our study has obtained the Os stable isotope compositions of chondrites, iron meteorites (representing planetary cores), and samples of Earth's mantle.

Osmium stable isotope analyses are carried out using the double spike method on both MC-ICP-MS and TIMS. Chondrites have a homogeneous stable isotope composition of $\delta^{190}\text{Os}/\text{Os} = 0.12 \pm 0.04\%$ (2sd). Terrestrial samples including geostandards and mantle xenoliths from Kilbourne Hole (USA), show a range in $\delta^{190}\text{Os}$ from 0.03 to 0.22‰ with an average that is similar to that of chondrites ($0.15 \pm 0.03\%$; 2sd). Finally, iron meteorites display a substantial range relative to chondrites, varying from 0.05 to 0.49‰.

The uniformity of chondritic compositions indicates that the solar nebula was homogeneous for Os stable isotopes. Consequently, that terrestrial mantle samples display chondritic stable Os isotope compositions, suggests that if any stable isotope fractionation occurred as a result of metal-silicate segregation during core formation, it was completely overprinted by a subsequent late veneer. The isotopically distinct signature observed in iron meteorites, relative to chondrites, suggests that core formation processes have the potential to substantially fractionate stable Os isotopes. The variation observed is most likely a result of fractional crystallisation processes of metal alloys. Future research will focus on Archean rocks to investigate mixing of the late accreted material into Earth's mantle.

[1] Jones & Drake (1983) Proc. Lunar. Planet. Sci. Conf. 14, 413-414. [2] Morgan (1986) Geophys. Res. 91, 37- 387.

Mineralogy comparison between thermal treatments of Itutinga Iron Meteorite fragments

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The iron meteorite Itutinga IIIAB belonging to the group and the structural classification octahedrite medium (Om)¹ has the main mass in collection of the Museum of Science and Technic of School of Mines of the Federal University of Ouro Preto, Minas Gerais state, Brazil². Fragments of the meteorite were subjected to thermal treatments in different temperatures, the usual technique in the field of Metallurgical and Materials Engineering. The first sequence of treatments used the heating temperature reached was 900°C and second 1300°C in different furnaces³. Analysis of optical microscopy for the fragments uncovered minerals how kamacita and with hatches, taenite and spheroidal, phases how plessita, α_2 structure and intergranular oxidation. Other analysis after the second sequence of thermal treatments showed the same minerals and intergranular oxidation pronounced.

[1] Buchwald, V. F. Handbook of Iron Meteorites, Their History, Distribution, Composition, and Structure. Berkeley: University of California Press, 3V., 1418p., 1975. [2] GRADY, M. M (Editor), Catalogue of Meteorites. Cambridge: Cambridge University Press, 689 p., 2000. [3] Nunes, G. A., da Costa, A. R., Comparison Between Thermal Treatments of Itutinga Meteorite Fragments. in: 78th Annual Meeting of the Meteoritical Society, 2015, Berkeley. Meteoritics & Planetary Science. Tucson: Meteoritical Society, 2015. v. 50. p. 29-29.

Signatures of highly siderophile elements in the lunar mantle: *HPHT* core-mantle equilibration or late accretion addition of a chondritic component?

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As a major consequence of core-mantle differentiation in terrestrial planetary bodies, the bulk of the siderophile elements are strongly partitioned into the iron-rich metallic core, leaving the silicate portions relatively depleted in those elements. However, the estimated concentrations of the highly siderophile elements (HSEs: Au, Re, Ru, Rh, Pd, Os, Ir, Pt) in the mantles of the Earth, Mars and Moon are found to be higher than expected [1]. Processes such as metal-silicate segregation under high-pressure and high-temperature (*HPHT*) conditions, and late addition (post-core formation) of a chondritic component have been suggested as possible mechanisms to explain the HSE abundances in planetary mantles [1,2]. Using the *HPHT* metal-silicate partitioning behaviour of the HSEs [3], we tested whether *HPHT* equilibration in a magma ocean scenario as suggested by the moderately siderophile elements [4,5] could account for their abundances in the lunar mantle. Our results suggest that the lunar mantle abundances of HSEs are too high to be accounted for by *HPHT* metal-silicate equilibration in a magma ocean, requiring a “late addition of a chondritic component” after core formation.

[1] Day et al. (2016) *Rev Mineral Geochem* 81:161–238 [2] Day & Walker (2015), *EPSL* 423, 114-124 [3] Mann et al (2012) *GCA*, 84, 593–613. [4] Rai & Westrenen (2014) *EPSL* 388, 343–352 [5] Steenstra et al (2016) *EPSL* (in press)

Innovative Mineral-Scale Achondrite PGE Analyses

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Platinum group element (PGE) abundances & Os-isotope compositions determined for magmas of Earth, the Moon, Mars, & asteroidal bodies place important constraints on planetary evolution & these data are fundamental to our understanding of the addition of material to planetary mantles following core formation. The absolute abundances & chondritic relative proportions of PGEs reported for Earth’s mantle, & the mantles of other planetary bodies, are widely considered to be inconsistent with core formation alone. PGEs, therefore, place critical constraints on protracted accretion of broadly chondritic materials to planetary mantles. New methods enabling quantitative determination of mineral-scale PGE-abundances & Os-isotope compositions in meteorite materials allow partitioning behaviour to be determined & can also trace post-crystallisation contamination by impactor material.

Our new petrographic & compositional data pertain to metals in distinct portions of coarse-grained angrites NWA 4590, NWA 4801, NWA 8535, & diogenites NWA 5480, NWA 7284, NWA 7831, NWA 7977. These observations are supported by Os-isotope data ± PGE-abundances for Fe-Ni metals (generally ≤50 µm kamacite) obtained using pioneering sampling procedures. Crucially, our new grain-scale data are compared to previous measurements for multiple powder fractions of many of the studied angrites & diogenites, thereby providing a means of quantitatively assessing this new mineral-scale approach. These innovative protocols enable, for the first time, texturally-controlled mineral-scale Os-isotope studies of differentiated achondrites; a vital investigation to constrain magmatic PGE partitioning leading us to re-evaluate existing theories concerning parent body origins & evolution.

Preservation of Earth-forming events revealed by ^{182}W variations

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Four and a half billion years of geologic activity has overprinted much of the evidence for processes involved in Earth's formation and initial differentiation. High-precision isotopic measurements, however, now allow the use of a variety of short-lived radionuclides that were present when our planet formed to provide a clearer view of events occurring during the first tens to hundreds of Ma of Earth's history. Of these short-lived systems, the ^{182}Hf - ^{182}W , with a half-life of 8.9 Ma, is a powerful tool to investigate the first 50 Ma of Solar System formation. Since Hf is lithophile and W is siderophile, the ^{182}Hf - ^{182}W system is the perfect chronometer to trace metal-silicate separation due to core formation, arguably the most important geological event to occur on a rocky planet. In the last five years, variations in ^{182}W have been detected in ancient Eoarchean rocks [1-5]. We have recently discovered ^{182}W variations in relatively young (< 120 Ma) flood basalts [6]. Since these variations can only be produced prior to 4.5 billion years ago, they imply preservation throughout most of Earth history, of regions within Earth's interior whose compositions were established by events occurring within the first 50 Ma of Solar System formation. Coupled with highly siderophile abundances, the ^{182}W discoveries provide new insights into the processes at work during planet formation, the chemical structure of the Earth's interior, and the mantle dynamics that allowed preservation of these heterogeneities for 4.5 billion years.

[1] Touboul et al., 2012 Science; [2] Touboul et al., 2014, Chem. Geol.; [3] Willbold et al., 2011, Nature; [4] Willbold et al., 2014, EPSL; [5] Rizo et al., 2016, GCA; [6] Rizo et al., 2016, Science

On the formation mechanism of HSE-nuggets in experimental and meteoritic silicate systems.

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Highly siderophile element (HSE) nuggets are observed in different natural and experimental materials. They were found in Ca-Al-rich inclusions (CAIs) and chondrules from chondritic meteorites [e.g. 1, 2] as well as in micrometeorites [3]. These cosmic nuggets are known as refractory metal nuggets (RMNs). Similar metal nuggets (called HSE micro nuggets) occur in quenched run products (relating to metal-silicate segregation [e.g. 4, 5]).

First expected to be condensates from the solar nebula, the cosmic nuggets now are interpreted as having formed by precipitation from a silicate- or CAI-liquid [1, 6]. Thus, these nugget bearing materials represent a reservoir of naturally formed nuggets and help us to understand our run products and the evolution of the earliest solar materials. As the characteristics of cosmic and synthetic HSE nuggets are very similar (6), it appears possible to synthesize cosmic nuggets. First experiments show that nugget characteristics (e.g. compositions, size, shape and abundance) can be reproduced allowing to experimentally reconstruct the evolution and formation of cosmic nuggets by varying experimental parameters. In this way, the experimental simulation in combination with meteoritic silicates enables the study of the heating duration or cooling rate and the formation mechanisms of cosmic nugget bearing materials (and synthetic HSE nuggets) and perhaps also the precursor metal phases.

A series of experiments with variations in the quench rate and a fixed duration and vice versa demonstrate a dependence of nugget size and abundance on quench rate. At the conference we will present the results from systematic experiments designed to synthesize HSE nugget bearing silicates in free space to simulate cosmic conditions and to exclude a reaction with a capsule.

[1] Schwander et al. (2015). GCA 186, 70–87. [2] Daly et al (2015) 78th Metsoc, #5061 [3] Rudraswami et al. (2014) GCA 131:247-266. [4] Cottrell and Walker (2006) EPSL 281:275-287. [5] Bennett et al. (2014) GCA 133:422-442. [6] Schwander et al. (2015) MPS 49, 1888–1901

Low sulfur in the Martian mantle: Insights from chalcophile elements in SNC meteorites

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Because of the relatively high S contents of some SNC meteorites and the abundance of sulfate on the Martian surface, it has long been assumed that Mars is rich in sulfur. High S contents in mantle and core of Mars were also assumed based on previous accretion and core-mantle differentiation models. However, recent estimates of the sulfur content at sulfide saturation for parent magmas of SNC meteorites hint that the maximum sulfur content of the Martian mantle may be only 700–1000 µg/g. Because these are maximum estimates, sulfur contents in Martian mantle sources remain poorly constrained. Moreover, contamination of Martian basaltic magma with crust, hydrothermal alteration on Mars and probably terrestrial alteration have led to variable changes of S contents in some SNC meteorites, further leading to difficulties to estimate S contents in the mantle.

Here we combine new and published data on chalcophile elements of shergottites, nakhlites and ALH84001 to show that the parent magmas of most of these SNC meteorites were sulfide undersaturated. This conclusion is consistent with the petrographic observation that most sulfides in SNC meteorites tend to occur as tiny grains, located near rims of pyroxenes or in interstitial mesostasis and intimately intergrown with Fe-Ti oxides (i.e., sulfide precipitation occurred only at a very late stage during the cooling of interstitial melt). Correlations of S and other incompatible chalcophile elements with MgO contents suggest that the sulfur content in the Martian mantle may be only a few hundreds of ppm, a level that is far lower than any previous estimate. Such a low concentration of sulfur may be completely exhausted by a few percent melting, which, in particular for shergottites, resulted in chemical variations of chalcophile elements similar to sulfide-undersaturated terrestrial magmas (e.g., komatiites).

Constraints on the formation of zoned metal grains in CB and CH chondrites from Ni and Fe isotope signatures and HSE abundances

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Chemically and isotopically zoned Fe,Ni-metal grains occur in metal-rich CB_b and CH chondrites [1]. Nickel and highly refractory elements have higher concentrations in the cores than at rims [1,2]. Iron isotope composition is lighter in the cores than at the rims [3]. Thus, an origin by condensation is being considered for zoned metal grains. Condensation in the solar nebula [1] versus condensation from an impact-induced vapor plume [4] are discussed scenarios.

We analysed Fe and Ni isotope concentration with fs-LA-MC-ICP-MS in zoned metal grains from Hammadah al Hamra 237 (CB_b), Acfer 214 (CH), and Isheyevo (CB_b/CH breccia). Highly refractory and siderophile trace element abundances were analysed with fs-LA-SF-ICP-MS.

Most refractory HSE are enriched by about 10–19xCI. However, W and Mo are depleted relative to other highly refractory siderophile elements. Nickel and Fe isotopes are overall light and show parallel zoning with the lightest compositions in the cores (e.g.; $\delta^{62/60}\text{Ni}$: $-7.6\pm 0.2\text{‰}$ core vs $-4.9\pm 0.2\text{‰}$ rim and $\delta^{56}\text{Fe}$: $-5.2\pm 0.1\text{‰}$ core vs $-2.8\pm 0.1\text{‰}$ rim).

This positive correlation of both isotope systems excludes chemical exchange diffusion as a cause of the zoning and supports a model of a condensation origin. The depletion of Mo and W relative to other refractory elements reflects oxidising conditions during condensation of the metal grains. The partial pressure of oxygen must have been higher than typically assumed for the solar nebula [5]. This might be caused by a high dust/gas ratio and may indicate condensation in an impact-induced vapor plume.

[1] Meibom et al. (1999) *JGR* **104**, 22053–22059. [2] Campbell & Humayun (2004) *GCA* **68**, 3409–3422. [3] Zipfel & Weyer (2007) *LPSC* #1927. [4] Wasson & Kallemeyn (1990) *EPSL* **101**, 148–161. [5] Fegley & Palme (1985) *EPSL* **72**, 311–326.

Theme 3:
**Applications for terrestrial
resource exploration
and ore genesis**

The Role of Chromite in the Fractionation and Collection of PGE

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There is evidence that chromite has an important role in collecting and fractionating the platinum-group elements (PGE). The largest PGE deposit in the world (the UG-2 reef of the Bushveld Complex) is found within a massive chromite layer. The narrow chromite layers within the Merensky reef of the Bushveld are enriched in PGE relative to rest of the reef. Thus in these two cases chromite appears to play a role in concentrating PGE. However, chromite does not appear to concentrate all PGE equally. Podiform chromitites are strongly enriched in Os, Ir, Ru and Rh (IPGE) relative to Pd and Pt (PPGE). Whole rock concentrations of IPGE and Cr from komatiites and basalts show positive correlations whereas PPGE do not correlate with Cr. In addition experimental work has found that IPGE are compatible with chromite, whereas PPGE are not. Thus the role of chromite in concentrating Pd and Pt in the UG-2 and Merensky reefs is not obvious. Furthermore many workers doubt that the IPGE can enter the chromite crystal lattice citing the presence of platinum-group minerals (PGM) rich in IPGE in plutonic chromite rocks. Nonetheless the recent LA-ICP-MS work on volcanic rocks (from a variety of settings) has found that IPGE are present in chromite phenocrysts. Using the empirical partition coefficients from the volcanic chromites it is possible to model the whole rock geochemistry of picrites and basalts from southern China showing that the negative Ru anomalies observed in the basalts could be produced by chromite crystallization. To explain the contrast in IPGE content of chromites from volcanic and plutonic settings we argue that chromite initially collected the IPGE prior to the magma becoming saturated in a sulphide liquid. After the chromite layer formed the PPGE-bearing sulphide liquid percolated from the over the overlying magma into the cumulate pile and collected at the level of the chromite layer because it was impermeable. During cooling there was an exchange of Fe and IPGE between the sulphides and chromite resulting in the IPGE diffusing from the chromite into the sulphides and forming various IPGM.

Sulfide saturation during the magmatic evolution of porphyry Cu ± Au systems

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Why some porphyry deposits are Cu-only whilst others are Cu-Au or even Cu-Au-Pd remains unresolved but sulfide saturation during the magmatic evolution of porphyry systems is emerging as an important control of magma fertility with respect to chalcophile elements. Platinum group elements (PGE) have extreme sulfide melt-silicate melt partition coefficients that make them sensitive indicators of the timing of sulfide saturation in an evolving magmatic system. Here we compare PGE and Re concentrations of intrusions from the El Abra porphyry Cu deposit, Chile, and the Grasberg-Ertsberg porphyry-skarn Cu-Au district, Papua, Indonesia. The El Abra results show a rapid drop in Pt and Pd abundances, which is indicative of sulfide saturation [1]. However, at El Abra, a porphyry Cu deposit was still able to form because the amount of sulfide melt that formed was very small, stripping the magma of Au and PGE but not significant Cu [1]. In contrast the Grasberg PGE results suggest that sulfide saturation did not occur during magmatic evolution of the intrusions, and so Cu, Au, and PGE could partition into the mineralizing fluid. Sulfide saturation therefore has a governing control over the availability of different chalcophile elements to partition into the hydrothermal ore-fluid phase and the type of porphyry mineralization that forms, i.e. Cu, Cu-Au, or Cu-Au-(Pd).

[1] Cocker et al. (2015) *JPet* 56, 2491-2514.

Extreme concentration of PGE, Au, Se and Te in sulfide microdroplets of the Skaergaard Intrusion

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Offset-type PGE reefs are stratiform magmatic deposits characterised by low volumes of sulfide, and offsets in the stratigraphic position of peak metal concentrations. They represent the onset of sulfide saturation in their host intrusions, usually as the result of prolonged fractional crystallisation.

The Platinova Reef is such a deposit, located in the Skaergaard Intrusion, east Greenland. As with many of these deposits, PGE concentrations peak first, with the appearance of the very first sulfides. Above this, a marked increase in sulfide volume (and Cu content) is marked by a Au peak. LA-ICP-MS data of the tiny (10-100µm) sulfides of the Platinova Reef show that above the PGE peak, the transition to higher volumes of sulfides is marked by enrichment in Au, then Te, then Se then Cu over a few metres. The data also show extreme HSE tenors in the respective peak zones: Pd ~10,000 ppm; Au ~15,000 ppm; Te ~200 ppm and Se up to 1200 ppm. As such, these are the highest tenor sulfides recorded in any magmatic ore deposit. The S/Se ratios of 120-500 are the lowest of any known deposit.

The extreme enrichment is due to a combination of diffusive and equilibrium partitioning. The offset peaks in the order PGE>Au>Te>Se>Cu is completely consistent with known $D_{\text{sul/sil}}$ values. The extreme enrichment can be linked with the minute size of the sulfide droplets, preserved almost immediately after nucleation; at which point, diffusive partitioning can produce extremely high effective R factors, producing extreme tenors of HSE in sulfide microdroplets.

Assimilation of Dolomite by Bushveld magmas; implications for the origin of Ni-Cu-PGE mineralization

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The Bushveld Complex is the world's largest Layered Mafic Intrusion (LMI) producing significant amounts of PGE, V, Ni, Cr, Cu, Fe, F & Au [1]. Prior studies have focused on characterising trigger mechanisms for mineralisation in a crystallising magma chamber. More recently, isotope studies have found that most Bushveld magmas are variably contaminated, likely by dolomites, further adding to the complexity of the system [2]. The Bushveld Complex is located within Transvaal sedimentary rocks, comprising a thick package of carbonates (including the Malmani Dolomite), quartzites & shales. Many studies have noted the abundance of dolomite or calc-silicate xenoliths in Bushveld magmas, particularly the northern limb. Here, Malmani Dolomite is found at the base of the intrusion & frequently form long rafts & xenoliths within the intrusion [3]. Dolomite assimilation is apparent from isotope studies & is believed by many to be a potential factor in the formation of the Platreef PGE deposit [2,4]. The Uitkomst deposit is a satellite intrusion, emplaced syn-magmatically with the Bushveld into the Malmani Dolomite. Numerous rafts & xenoliths of dolomites & calc-silicates have been observed. Some workers attribute the central sagging of the intrusion to thermal decomposition & devolatilization of these dolomites forming a void into which overlying magmatic units slumped [5]. Massive sulphide lenses & disseminated sulphides are found in the dolomite host-rock suggesting there may be a petrogenetic link between the 2 lithologies.

Globally, studies of the effects of dolomite contamination are ongoing. Experimental work demonstrates that carbonate devolatilization can significantly alter the oxidation state of the magma & thus the stability of phases such as clinopyroxene & the trace element composition of minerals such as olivine [6]. Voisey's bay & Noril'sk studies suggest dolomite assimilation may be a factor controlling mineralisation [7]. In the Colli Albani Volcanic District, Italy, many workers have identified endoskarns & exoskarns formed from the partial melting, metamorphism & devolatilization of the host carbonates showing clear decomposition of the country rock [8].

Addition of CO₂ not only alters magma chemistry but could have wider implications for global atmospheric change. Several studies have linked mass extinction events in the Phanerozoic to large scale magmatic events & volcanic eruptions such as the Siberian flood basalts & the end-Permian mass extinction [9]. The emplacement of the Bushveld Complex coincides with the end of a significant positive δ¹³C excursion known as the Lomagundi-Jatuli event. This excursion terminated with the Shunga event representing the deposition of supergiant petroleum deposits & the first phosphorites deposited in Karelia [10]. Detailed mineralogical & geochemical studies are aimed to constrain the amount of CO₂ liberated by reaction of the Bushveld magmas with the dolomitic floor rocks.

[1] Maier, W.D. et al (2013) *Min Deposita* [2] Harris, C. and Chaumba, J.B. (2001) *J Petrol*, [3] Kinnaird, J.A. et al. (2005) *App Earth Sci*, [4] Maier, W.D. et al. (2008) *Min Deposita* [5] Maier, W.D. et al. (2004) *Econ Geol* [6] Iacono-Marziano, G. et al. (2007) *J Volcanol Geotherm Res*, [7] Gauert, C. et al. (2001) *J Afr Earth Sci*, [8] Di Rocco, T. et al. (2012) *J Petrol*, [9] Wignall, P.B. (2001) *Earth-Sci Rev* ,

Key characteristics of magnetite-hosted PGE-Au-Cu reef-type mineralisation in the Jameson Range, Musgrave Province, Western Australia

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The Mesoproterozoic Jameson Range intrusion forms part of the Giles Complex located in the Musgrave Province of Western Australia. It is predominantly mafic in composition consisting of olivine-bearing gabbroic lithologies with abundant magnetite and ilmenite. The intrusion hosts several laterally extensive layers of massive to semi-massive magnetite which can be traced for at least 19 km along strike. Notably, only the basal magnetite shows an enrichment in platinum group element (PGE) together with Au and minor Cu + Ni. The mineralised interval has a thickness of ca. 2.7 m and reaches 68.8 wt % Fe₂O₃(t), 24.2 wt % TiO₂, 1.1 wt % V₂O₅, 0.3 wt % Cu and 2 ppm Pt + Pd. The mineralisation is hosted by sulphides mainly comprising bornite, chalcopyrite and minor pentlandite. Two different types of platinum-group minerals (PGM) were identified in surface samples: (1) Pt-Fe alloys and (2) Pd-rich PGM with varying proportions of Pt, Pb, Cu and Sn. Lath-shaped PGM may attain up to 30 µm in length, but most grains are smaller than 5 µm and are associated with fractures in Fe-Ti oxides. The PGEs are interpreted to have collected in a sulphide melt after S saturation as reached in response to extensive fractionation of the magma. Generally, the magnetites contain limited amounts of sulphide, reaching 1 to 2 vol % at most. Therefore, this type of mineralisation is difficult to identify macroscopically. However, distinct variations in Cu/Pd ratios above and below the reef can be used in vectoring towards this PGE enrichment as previously shown for other layered intrusions (e. g. Stella intrusion in South Africa).

PGE mineralisation in the Troctolite Marker, northern Bushveld Complex

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The Troctolite Marker (TM) comprises >200m of peridotite-olivine gabbro-norite-anorthosite that occur in the middle of the Main Zone and appear to be unique to the northern Bushveld Complex. The TM carries PGE mineralization and this study aims to describe, for the first time, the nature of the PGE mineralisation within the TM.

Samples of the TM were obtained from surface and from borehole VSF2 drilled by Bushveld Minerals Ltd. Samples were analysed at Cardiff University using SEM (phase identification and mapping PGM) and ICP-OES/MS for major, and trace elements and PGE.

Multiple zones of PGE mineralization occur in the TM, including one associated with a sharp rise in Cr near the top of the unit; similar to a potential reef horizon predicted by Tanner et al. (2014). PGM are typically <5 µm in size. Large PGM (>10 µm and up to 50 µm) were sporadic and comprised <5 % (by number) of the observed PGM which were limited to Pt-Pd ± Ru phases and PGE in solid solution within BMS. In order of abundance PGM phases were: antimonides > PGE-Pb alloys > arsenides > telurides > other PGE alloys > bismuthides > electrum.

Size and morphology of the PGM was not limited to any specific lithology but reflected alteration intensity. Textural evidence suggests initially orthomagmatic base metal sulphides and PGM were variably affected by later hydrothermal fluids passing through the TM.

RM8050: A reference material for petroleum Re-Os analysis

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During the past decade, rhenium-osmium (Re-Os) analysis of petroleum has been shown to be a valid dating tool to constrain the time of hydrocarbon generation, and provide insight into the source of oil. Although, there are reference materials for other material types of Re-Os analysis (e.g., for molybdenite and basalt), the increase in laboratories conducting petroleum Re-Os analysis proposes the need for a petroleum reference material for inter- and intra-laboratory calibration and quality assurance.

Here we utilise the Venezuelan oil V reference material, RM8505. Re and Os analyses were conducted on the whole oil, and the asphaltene and maltene fractions isolated by *n*-heptane by Isotope Dilution – Negative Thermal Ionization Mass Spectrometry (ID-NTIMS). Samples are digested by inverse *aqua-regia* in Carius tubes at 220°C for 24 hrs.

Approximately 90 g of asphaltene was isolated from RM8505 for the purpose of making an homogeneous reference material. The asphaltene was isolated with *n*-heptane, dried and ground to 70 mesh, mixed and dispensed into 10 bottles.

Multiple analysis of each sample type (whole oil, asphaltene and maltene) show excellent reproducibility of both Re-Os abundances, and isotopic ratios. Greater than 90% Re and 75% Os are housed in the asphaltene fraction of whole oil.

Compared with the Re-Os results determined via high pressure asher (HPA-S) digestion (spike-sample equilibration), and multicollector inductively coupled plasma mass spectrometer (ICP-MS) on the same material RM8505, results via ID-NTIMS of this study show better reproducibility of Re and Os abundances and ¹⁸⁷Os/¹⁸⁸Os. The HPA-S-ICP-MS study did not report ¹⁸⁷Re/¹⁸⁸Os data.

For the asphaltene fraction, the 95 % confidence Tukey's Biweight mean of Re and Os abundance, and 187Re/188Os and 187Os/188Os compositions are 16.49 ± 0.14 ppb, 165.6 ± 1.3 ppt, 575.2 ± 4.2 and 1.638 ± 0.007, respectively. The RM8505 oil and the isolated 90 g of asphaltene fraction can serve as a reference material for petroleum Re-Os analysis.

A chilled komatiitic margin of the Bushveld Complex, South Africa: implications for the nature of mantle sources

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A chill sequence at the base of the Lower Zone of the western Bushveld Complex at Union Section, South Africa, contains aphanitic Mg-rich basaltic andesite and spinifex textured komatiite. The basaltic andesite has an average composition of 15.2% MgO, 52.8% SiO₂, 1205 ppm Cr, 361 ppm Ni, whereas the komatiite has 18.7% MgO, 1515 ppm Cr, and 410 ppm Ni. Both rock types have very low concentrations of immobile incompatible elements (0.14–0.72 ppm Nb, 7–31 ppm Zr, 0.34–0.69 ppm Th, 0.23–0.27 wt% TiO₂), but high PGE contents (19–23 ppb Pt, 15–16 ppb Pd) and Pt/Pd ratios (Pt/Pd 1.4). Strontium and S isotopes show enriched signatures relative to most other Lower Zone rocks. The rocks could represent a ~20 % partial melt of sub-continental lithospheric mantle. This would match the PGE content of the rocks. However, this model is inconsistent with the high SiO₂, Fe, and Na₂O contents and, in particular, the low K₂O, Zr, Hf, Nb, Ta, Th, LREE, Rb and Ba contents of the rocks. Alternatively, the chills could represent a komatiitic magma derived from the asthenosphere that underwent assimilation of the quartzitic floor accompanied by crystallization of olivine and chromite. This model is consistent with the lithophile elements and the elevated Sr and S isotopic signatures of the rocks. However it does not account for the high Pt and Pd contents of the magma. A number of possible scenarios are considered to explain the high PGE contents of the rocks. a) The mantle was twice as rich in PGE as the current estimate for PUM, possibly due to a component of incompletely equilibrated late veneer; b) The komatiitic magma assimilated some Pt+Pd from the sub-continental lithospheric mantle (SCLM) by zone refine melting of sulfides as the magma passed through the SCLM.; c) The komatiitic magma became sulfide saturated in a holding chamber and some of the Pt+Pd rich sulfides were entrained during emplacement.

Sulphide melt-magma processes recorded in sulphide melt inclusions from the Platreef

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The Platreef is a 10- to 400-m-thick unit of pyroxenitic lithologies with platinum-group element (PGE) and base metal sulphide (BMS) mineralization located in the northern limb of the Bushveld Complex. Evidence for the role of a highly PGE-enriched sulphide liquid during the earliest stages of Platreef formation comes from rare sulphide melt inclusions with negative crystal shapes enclosed in chromite [1]. Some inclusions contain exsolved PGM (laurite (RuS₂) and cooperite (PtS)). Sulphide inclusions have been recorded from multiple localities (Overysel to Turfspruit) along strike of the Platreef and multiple inclusions may be enclosed in a single chromite host.

Inclusions were homogenised and analysed by SEM and LA-ICPMS for major elements [1], PGE and semi-metals. S/Se ratios vary from crustal values (>4000) to values significantly lower than mantle (400-1000). The majority of Cu and Se concentrations are greater than can be achieved by assimilation modelling of the Bushveld B1 magma even at extreme R factors (>10⁵) although the observed Pt and Pd tenors can be generated via this mechanism at R factors >10⁴. Total PGE concentrations are correlated with (Re/Os)_N and modelling indicates that high (Re/Os)_N (>1) inclusions with low PGE tenors and high S/Se ratios require assimilation of crustal sulphides with Re/Os >500. In contrast, PGE-rich, low (Re/Os)_N, and low S/Se inclusions cannot be produced by assimilation alone and require dissolution upgrading [2] of sulphide PGE and Se contents (probably in a pre-Platreef staging chamber). During this process S, Fe and Re were removed by magma passing through the plumbing system due to their lower D_{sulphide/silicate} values.

[1] Holwell et al. (2011) *Contrib. Mineral. Petrol.*, v.161, 1011-1026. [2] Kerr and Leitch (2005) *Econ. Geol.* v. 100, 311-332.

Late sulfide saturation enhances potential to form porphyry Cu±Au deposits

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Porphyry deposits are significant sources of Cu and Au mineralization, which form by precipitation of the metals extracted by magmatic volatile phases exsolved from the magmas associated with the deposit. Therefore, the availability of Cu and Au to the ore-forming fluid is strongly influenced by their concentration in the melt that crystallized to form the associated porphyry. The fertility of a magma can be estimated from Platinum Group Element (PGE) geochemistry because PGE behave similarly to Cu and Au, yet differ in being less mobile during secondary hydrothermal alteration.

We have carried out a series of studies of PGE geochemistry of volcanic and sub-volcanic rocks associated with porphyry Cu and Cu-Au deposits. In this study, we report the PGE geochemistry of three barren volcanic and granitic suites from Argentina and Japan, and compare these results with those from ore-bearing magmatic systems. The barren suites are significantly depleted in PGE abundances by the time of volatile exsolution due to early sulfide saturation in the underlying magma chamber, which may have been caused by assimilation of S- and/or C-rich crustal materials. In contrast, the ore-bearing suites contain at least an order of magnitude higher PGE contents. The fertility of the suites increases in the order: barren < porphyry Cu < porphyry Cu-Au bearing suites. The ore-bearing suites are characterized by late sulfide saturation at shallow depth, which allows the chalcophile elements to accumulate in the evolving magma from which they are scavenged by magmatic volatile phases. These results indicate the fertility of a magma is one of the critical factors in the formation of porphyry Cu±Au deposits.

Platinum-Group Element Mineralogy and Distribution in the Platreef on Turfspruit, Northern Bushveld Complex, South Africa

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The Platreef, located on the northern limb of the Bushveld Complex, is described as a broad (10-400m thick) zone of Ni-Cu-PGE mineralisation in pyroxenite rocks with an apparent lack of stratigraphic markers. However, the recent discovery of a deep section of high grade Platreef on farm Turfspruit, shows a layered sequence of pyroxenites, peridotites, norites, gabbronorites and anorthosites, that are unique to this locality on the northern limb. Samples were collected from drillhole UMT 345 in order to investigate: the origin of this layering, its relationship to PGE occurrences and identify any correlation to the stratiform PGE mineralisation on the eastern and western limbs of the Bushveld.

Whole-rock PGE data reveal three main PGE-mineralised horizons: a feldspathic orthopyroxenite, a pegmatoidal orthopyroxenite and a ≈1m thick chromitite. Ivanplats equate these to the Bastard Reef, Merensky Reef and the UG-2 chromitite, respectively. Detailed mineralogical studies to date show that, unlike the Merensky Reef and UG-2, the PGM assemblages have a strong semi-metal signature including (in order of abundance) (Pt,Pd,Ir) arsenides-antimonides, (Pt,Pd) bismuthotellurides, Pd-Sn alloys, electrum and Ag-bearing pentlandite. PGE sulphides (laurite, cooperite and braggite) have been identified associated with base metal sulphides but are restricted to chromite-rich and the least altered samples.

The size of the PGM reflects the degree and style of alteration, for example in a mafic pegmatoid a 100 µm PtPdBiTe mineral was found whereas a typical base metal sulphide altered by migrating felsic fluids typically releases PGMs of <1 µm in size.

Solubility of the assemblage Pt-PtAs(melt) in basalt with implications for As speciation and Pt sequestration

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Given the evidence in nature for a strong Pt-As association in magmas, we have done experiments to determine the solubility of the assemblage Pt+Pt-arsenide (melt or sperrylite) in basalt to elucidate As speciation and the saturation conditions for As-bearing PGM. Experiments were done with vacuum-sealed quartz tubes containing a synthetic basalt analogue with Pt metal +/- arsenide melt encapsulated in a natural chromite crucible. Oxygen fugacity was fixed using either solid oxide buffers, or by pre-equilibrating the sample in a gas-mixing furnace. Experiments were done at 0.1 MPa, 1200°C for 1 to 4 days, over an fO_2 range of FMQ-3.3 to +4.3. The trace element content of run-product glasses was measured by LA-ICPMS. We found that the Pt content of As-bearing glasses saturated in Pt metal was essentially identical in comparison to As-free experiments. The dissolved As content of the silicate melt increased significantly with fO_2 , varying from 10 to >10,000 ppm, over the range investigated. This behaviour is consistent with dissolution of As into the silicate melt by a reaction of the form: $As + n/2O_2 = AsO_n$. Regression of the data, and accounting for the variation in the As activity with changes in melt Fe^{2+}/Fe^{3+} , yields an estimated As valence state of 2.4+. This is similar to the valence state of 3+ determined for a natural rhyolitic peraluminous glass using As K-edge XANES (Borisova et al., 2010, *Am. Min.*, vol 95, pp 1095-1104). The somewhat lower valence estimated thermodynamically likely results from uncertainties in the activity-composition relations for the As-species in the composition investigated. To provide a more accurate estimate of As speciation, experiments are planned to measure As L-edge XANES for the run-product glasses from this study, and results will be reported at the conference.

Along-strike variation in HSE, Northern Limb of the Bushveld Complex, South Africa

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Over the last 25 years, the Northern Limb of the Bushveld Complex has been of increasing economic interest due to the low-cost, high-tonnage PGE resources associated with wide reef (contact ?) style mineralisation (e.g. the Platreef). While PGE mineralisation in the Eastern and Western Limbs of the Bushveld Complex is restricted to Critical Zone lithologies (i.e. the Merensky Reef and the UG-2 chromitite), the Northern Limb hosts a range of distinct deposit types. These include Platreef-style PGE deposits, as well as mineralisation hosted in ultramafic 'Lower Zone' cumulates and in more fractionated Main Zone lithologies. The variable stratigraphic setting of these deposits and the variability in local country rock along strike provide the opportunity to test the influence of different magma types and the role of different country rocks in the genesis of mineralisation.

A large volume of data has now been generated by researchers characterising the geology, geochemistry and mineralogy of these Northern Limb deposits. Here, we synthesise existing geochemical and mineralogical data and provide new data (PGE tenors, semi-metal ratios) in sulphides to investigate variations in the concentration and deportment of highly siderophile and strongly chalcophile elements along strike and through the stratigraphy of the Northern Limb of the Bushveld Complex.

Silver isotopes as new tracers of metal sources and ore formation processes

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Silver has two naturally occurring stable isotopes: ¹⁰⁷Ag and ¹⁰⁹Ag. The recent advances in MC-ICPMS techniques using Pd isotopes have led to the detection of natural variability in the Ag isotopic composition of terrestrial samples [1]. The reported range of ¹⁰⁷Ag/¹⁰⁹Ag in volcanic rocks (-9.4 <ε¹⁰⁷Ag<+1.5; [2]) is similar to that in native silver and gold from ore deposits (-6.0<ε¹⁰⁷Ag<+5.3; [3]). In this study, we examined samples of native silver extracted from porphyry Cu-Mo, VHMS, SEDEX Pb-Zn, epithermal and placer Au deposits, which show a range of ε¹⁰⁷Ag from -4.6 to +3.3. The most negative values were obtained for native silver from the Sorskoye porphyry Cu-Mo and Imiter epithermal Ag deposits, and correlate with a mantle source of ore metals. The most positive values were encountered for the sediment-hosted Nochnoye Ag-Pb-Zn deposit and the Broken Hill SEDEX deposit, the latter with a crustal source of ore metals. The ε¹⁰⁷Ag values of the Teutonic Bore VHMS deposit occupy an intermediate position, close to the BSE value of -2.2±0.7. These variations in Ag isotopic composition in mineral systems maybe related with: (1) physico-chemical processes of ore formation (T~150°C); (2) inherited Ag isotopic variability from the protoliths; and (3) nuclear volume decrease due to s-electron removal during the oxidation of Ag⁰ to Ag⁺. These factors may be interconnected: Ag isotopic heterogeneity due to large-scale source variability may be overwritten by fractionation due to chemical processes at a local scale facilitated by hydrothermal fluid circulation or ore precipitation.

Origin of PGM in Bushveld reefs by Re-Os LA data on the micrograins

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The previous Re-Os isotope studies on Bushveld rock and platinum group minerals (PGM) argue for a magmatic process of their concentration (1, 2). This study presents new Re-Os isotope and elemental data in PGM grains from reef horizons of the Platreef obtained by LA MC-ICP-MS measurements at GEMOC ARC (Macquarie University). The Platreef is a composite sill-like body in the northern limb correlative to the Critical Zone in terms of stratigraphic position. The whole Platreef sequence is variably mineralized with a significant hydrothermal overprint. However, reef-style mineralization at the top of the Platreef near the Main Zone boundary shows progressively more pristine magmatic character with depth strongly resembling Merensky Reef mineralization. A key feature that marks a conversion of the Platreef-style ore into the Merensky-style is a more regular appearance of chromite seams with depth. We analysed laurite (RuS₂), hollingworthite (RhAsS), sperrylite (PtAs₂) and Pt-Fe alloys from both the Merensky Reef and the PGE reef of the Platreef. The measured ¹⁸⁷Os/¹⁸⁸Os values vary from 0.1702±0.0015 to 0.1763±0.0003 for laurite and from 0.1718±0.0064 to 0.1786±0.0007 for sperrylite and hollingworthite that is within the known Merensky range. The similar values and the limited variations of the initial Os isotopic ratios of PGMs from the Merensky Reef and Platreef reef-style mineralization suggest their othomagmatic origin from a common source. The data also indicate that observed intergrowths of the analysed PGM, such as hollingworthite exsolution in sperrylite and Pt-Fe symplectites in sulphides, have to be interpreted as primary magmatic textures.

(1) Reisberg L. et al. (2011) Chem. Geol., 281:352-363; (2) Coggon J. et al. (2012) Chem. Geol., 302-303:48-60.

Theme 4:

Tracing Earth's surface geochemical cycles

Rhenium as a tracer of oxidative weathering from the Andes to the lowland Amazon Basin

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Over long timescales ($>10^5$ yrs), the abundance of carbon dioxide (CO₂) in the atmosphere is determined by the balance of the major carbon sources and sinks. Among the major carbon sources, the oxidation of organic carbon contained within sedimentary rocks ("petrogenic" carbon, or OC_{petro}) is thought to result in CO₂ emission of similar magnitude to that released by volcanism. Despite this recognition, there are few data on the rates of OC_{petro} oxidation at Earth's surface. CO₂ release is difficult to track directly due to degassing and carbon cycling in the live biosphere. Rhenium (Re) has been proposed as a proxy for tracing OC_{petro} oxidation. Here we investigate the source, behavior and flux of dissolved and particulate rhenium (Re) in the Madre de Dios watershed (a major Andean tributary of the Amazon River), aiming to quantify the flux of CO₂ released by OC_{petro} oxidation.

The Madre de Dios watershed has a dominantly sedimentary lithology. Erosion rates, acid-hydrolysis weathering reactions, and sulphide oxidation rates have been well-characterized and shown to vary across the mountain to floodplain transition. We seek to understand how mountain erosion controls Re release and whether dissolved Re and other redox sensitive element concentrations are modified during fluvial transit. In addition to quantifying OC_{petro} oxidation, this study will improve our understanding of the source and processes controlling Re in rivers, allowing us to apply trace metal proxies more widely, and potentially in the geological record.

High precision elemental and isotope measurements of dissolved osmium in seawater

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Osmium (Os) isotopes have emerged as a powerful tracer of the changes in ocean chemistry that occur in response to variations in continental weathering, ocean anoxic events, extraterrestrial impacts and anthropogenic contamination. Nevertheless, direct analysis of modern seawater remains challenging, because of the very low Os (femtomolar) concentrations and also because the speciation and oxidation state of Os in seawater remain poorly constrained. Recently it has been suggested that much of the published Os isotope and elemental data of seawater have been compromised. In parallel, it was discovered that widely used pre-cleaned high and low-density polyethylene bottles appear to contaminate seawater Os, where the contamination seems to be caused by the use of ultrapure nitric acid during cleaning.

We conducted a comprehensive comparison of Os isotope and elemental measurements using two different oxidation techniques to achieve tracer-sample equilibration: the low-temperature bromine and high-temperature HPA-S methods on the very same sample. The low Os total procedural blanks (14–18 fg) obtained for both methods together with the high total yield of the chemical procedure (90%) and the high effective ionisation efficiency (6–10%) allowed us to determine the Os elemental and isotope compositions of a seawater profile from the North East Atlantic Ocean (IB13: 60°29.4'N, 19°59.2'W, 2650 m water depth)

Our data show that both techniques can yield an indistinguishable Os isotope composition and Os concentration at the level of precision obtained in this study, $\pm 1.6\%$ for the ¹⁸⁷Os/¹⁸⁸Os ratio and $\pm 3.7\%$ for the Os concentration. There is little variability with depth and the overall average for the whole profile is 1.024 ± 0.031 (3%) for the ¹⁸⁷Os/¹⁸⁸Os ratio and 9.68 ± 0.48 (4.9%) pg kg⁻¹ for the Os concentration, leading us to suggest that at this site, at least, Os appears to behave conservatively.

Enhanced oxidative weathering in glaciated mountain catchments: A stabilising feedback on atmospheric carbon dioxide

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Mountain belts act as sources of carbon dioxide (CO₂) to the atmosphere if erosion and exhumation expose rock-derived organic carbon ('petrogenic' organic carbon, OC_{petro}) to chemical weathering. Estimates suggest 15×10²¹g of carbon is stored in rocks globally as OC_{petro}, ~25,000 times the amount of carbon in the pre-industrial atmosphere. Alongside volcanic and metamorphic degassing, OC_{petro} weathering is thought to be the main source of CO₂ over geological timescales. Erosion in mountain river catchments is thought to enhance oxidative weathering and CO₂ release. However, we lack studies which quantify this process. In addition, it is not clear how glaciation may impact OC_{petro} oxidation. In analogy with silicate weathering, large amounts of fine sediment in glacial catchments may enhance weathering.

Here we quantify oxidative weathering in thirteen catchments draining OC_{petro} bearing rocks in the western Southern Alps, New Zealand. Using rhenium (Re) as a tracer of oxidative weathering, we develop techniques to precisely measure Re concentration at sub-ppt levels in river waters. Using [Re]_{water}/[Re]_{rock} as an oxidative weathering tracer, the weathering efficiency in glacial catchments is >4 times that of non-glacial catchments. Combining this with the OC_{petro} content of rocks and dissolved Re flux, we estimate the CO₂ release by OC_{petro} oxidation. The analysis suggests that non-glacial catchments release similar amounts of CO₂ as catchments in Taiwan where erosion rates are similar. In the Southern Alps, the CO₂ release does not negate CO₂ drawdown by silicate weathering and by riverine transfer of organic matter. Based on our results, we then propose that mountain glaciation may cause enhanced OC_{petro} oxidation rates. Depending on the global fluxes, this would provide a feedback to damp low atmospheric CO₂ levels and cooling. During glacial periods (low CO₂, cold global temperatures) CO₂ emissions by OC_{petro} oxidation in mountain belts could be greatly enhanced.

Emerging Airborne Contaminants in Developing Countries: A case study from India

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Platinum Group Element (PGE) pollution on the Indian subcontinent, likely sourced primarily from automobile catalytic converters, is a growing concern because vehicle sales in India have rapidly increased over the last decade and evidence is mounting that PGE compounds are bioactive. Despite the rapid growth of the Indian automobile industry, the sources and magnitude of PGE contamination in Indian airborne particles has not been studied. In this study we report PGE and mercury (Hg) concentrations, as well as osmium isotope ratios (¹⁸⁷Os/¹⁸⁸Os) of airborne particles (PM₁₀) collected in Kanpur, a large industrial city in India. The study reveals that ~45% and ~71% of the total Os and Pt concentrations are anthropogenic in origin. Combining PGE/Ir and ¹⁸⁷Os/¹⁸⁸Os ratios we further conclude that ~97% of anthropogenic Os is derived from Pt-Pd-Rh-based catalytic converters. Our results therefore indicate that PGE/Ir ratios could be successfully used to quantify the relative proportions of natural and anthropogenic sources in aerosol samples. Mercury and PGE concentrations did not correlate. However, the highest concentrations of particulate Hg correspond to the most radiogenic ¹⁸⁷Os/¹⁸⁸Os isotope ratios (4.6), indicating a fossil fuel emission.

[1] Sen, I. S. *Environmental Science & Technology* (2013), 47, 13,903-13,904

What processes are responsible for excursions to low $^{187}\text{Os}/^{188}\text{Os}$ in the marine Os isotope record?

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The most distinctive and best-characterized features of the marine Osmium isotope record are excursions to low $^{187}\text{Os}/^{188}\text{Os}$. In some instances, these excursions are the result of major extraterrestrial impact events and can be used to assess the response time of the marine Os cycle to external perturbations. Pronounced excursions to low $^{187}\text{Os}/^{188}\text{Os}$ ratios have also been identified in sediments deposited during many different episodes of large igneous province (LIP) emplacement. These excursions have been interpreted as a fingerprint of magma activity; a line of primary evidence in the sediment record used to correlate environmental changes, for example anoxia, with LIP emplacement. Finally, there is a third category of negative excursions in the marine Os isotope record that do not seem to be associated with either an impact event or LIP emplacement. These enigmatic excursions remind us of our incomplete understanding of the surficial Os cycle. Detailed Os isotope records from multiple locations across the the Cretaceous-Paleogene boundary and the Eocene-Oligocene transition reveal geographic variations in the marine $^{187}\text{Os}/^{188}\text{Os}$ record. This spatial heterogeneity adds a new dimension to interpreting the marine Os isotope record that may help identify the underlying causes of negative excursion in the marine Os isotope record. In addition, an Os isotope record from a single site spanning the Cambrian SPICE (Steptoean positive carbon isotope excursion) event will be used to support the speculation that seawater excursions to very low, mantle-like, $^{187}\text{Os}/^{188}\text{Os}$ ratios may not require either the eruption, alteration and weathering of a LIP or a major impact event. Instead, widespread occurrence of anoxic conditions in the global oceans may modify the geochemical cycle of Os, allowing mantle-derived fluxes of Os unrelated to LIP activity to dominate the oceanic Os budget.

Do Os isotopes track glacial interglacial cycling? The strange case of the Benguela Upwelling System

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The possibility of using Os isotopes in hydrogenous marine sediments to track glacial-interglacial variations has been debated for nearly 20 years, with some studies showing excursions to less radiogenic values during glacial intervals [1-5] while others do not [6-7]. Several of these earlier studies may have been affected by factors such as basin isolation, detrital sediment input and low sedimentation rates, potentially biasing the measured Os isotopic compositions of the sediments relative to that of contemporaneous seawater. To clarify this issue, we have undertaken an Os isotopic study of organic-rich sediments from ODP Leg 175, Site 1084, located in the Benguela Upwelling System off the African coast. As this is an open ocean site with a high sedimentation rate and minimal detrital input, the Os isotopic signature of the sediments should closely reflect that of ambient seawater. Re-Os analyses of ~40 samples ranging in age up to 220 ka were performed, and the age model was constrained by new oxygen isotope analyses on benthic forams. Measured Re and Os concentrations were 58-155 ppb and 0.191-0.648 ppb, respectively. The $^{187}\text{Os}/^{188}\text{Os}$ data yield a surprising, bimodal result. Unlike in most [1-5], but not all [7], previous studies, an excursion to less radiogenic values is not observed during the glacial interval MIS 2, with $^{187}\text{Os}/^{188}\text{Os}$ remaining nearly constant at 1.042 ± 0.008 (1σ), a value close to that of modern seawater [8]. In contrast, during MIS 6, a marked decrease in $^{187}\text{Os}/^{188}\text{Os}$ is observed, as has been reported elsewhere. In addition, a minor excursion to lower $^{187}\text{Os}/^{188}\text{Os}$ occurred from 50 to 70 ka, temporally coincident with a similar excursion observed in the Cariaco basin that was previously assumed to be a local feature [4]. Possible explanations of these unexpected results are currently being explored.

[1] Oxburgh (1998) *EPSL* **159**, 181-191 [2] Dalai et al. (2005) *Chem. Geol.* **220**, 303-314 [3] Williams & Turekian (2004) *EPSL* **228**, 379-389 [4] Oxburgh et al. (2007) *EPSL* **263**, 246-258 [5] Burton et al. (2010) *EPSL* **295**, 58-68 [6] Dalai & Ravizza (2010) *GCA* **74**, 4332-4345 [7] Paquay & Ravizza (2012) *EPSL* **349-350**, 126-138. [8] Levasseur et al. (1998) *Science* **282**, 272-274.

Tracking millennial-scale Holocene glacial advance and retreat using Osmium isotopes: Insights from the Greenland Ice Sheet

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Using new high-resolution osmium (Os) isotope stratigraphy from cores adjacent to the Greenland ice sheet we highlight the potential for chemostratigraphy to enhance our understanding of ice sheet dynamics. This study utilizes sediment cores that have excellent chronological controls and demonstrates the role of local and regional weathering fluxes on the marine Os residence time. Distal to the Greenland ice streams core MSM-520 displays a steady lowering of the Os isotope composition during the Holocene. In contrast, proximal to the calving front of Jakobshavn Isbræ (core DA00-06), the Os isotope stratigraphy highlights four stages of ice stream retreat and advance. Our data provide vital benchmarks as we attempt to better constrain the future response of major ice sheets to climate change.

Dating the dramatic and dynamic in the Neoproterozoic: New Re-Os age constraints and paleoweathering proxy data

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The Neoproterozoic Era (1000-541 Ma) witnessed the return of widespread glaciations, major fluctuations in geochemical proxy records, and numerous biological innovations associated with the radiation of eukaryotes that culminated with the emergence of Metazoans. Understanding the drivers and rates of change through this critical transition has been limited by the lack of a robust chronology. Here we present multiple new Re-Os geochronology data from Neoproterozoic sedimentary strata from China and North and South America that refine global correlation schemes and further constrain this critical interval of Earth history. Our new age constraints help define the temporal framework for events including the earliest evidence of eukaryotic biomineralization seen in the fossil record, the Bitter Springs carbon isotope anomaly, large-scale weathering perturbations associated with the termination of the >55 Myr Sturtian glacial epoch, and the “Shuram-Wonoka” carbon isotope anomaly, which is the largest perturbation to the carbon cycle recorded in the geological record.

The Silurian Icehouse: Insights from Osmium and Lithium Isotopes

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The Silurian through to the early Devonian is marked by four large-amplitude positive carbon and oxygen isotope excursions, with the $\delta^{13}\text{C}_{\text{carb}}$ exceeding +5‰ immediately after the Ireviken, Mulde, Lau and Klouk faunal events, indicating that the climate system and carbon cycle were probably more unstable than any other Phanerozoic period when considering the ocean-atmosphere system. Theories behind the cause of these events include changes in ocean circulation, volcanism, sea-level and ice volume. However, despite two decades of research, none has been unequivocally proven.

We have utilised osmium ($^{187}\text{Os}/^{188}\text{Os}$) and lithium ($\delta^7\text{Li}$) isotope values of organic-rich shales and carbonates from geological formations that span these events. These values reflect an interplay between weathering of continental crust and hydrothermal inputs. However, due to the short residence time of Os ($\leq 10\text{kyrs}$) and Li ($\sim 1\text{Myr}$) in the ocean, it is possible to capture short-periodic fluctuations in Earth system processes through the Silurian and help distinguish between these theories.

Os isotope curves for the Ireviken, Mulde, Lau and Klouk events are similar to those published for the Hirnatian glaciation. There is an initial rise in continental weathering associated with the Caledonian Orogeny, drawing CO_2 out of the atmosphere, leading to an expansion of continental ice. Under glacial maximum, weathering rates decline, allowing CO_2 to build up in the atmosphere, inducing rapid deglaciation and exposing rocks to weathering. This is inferred by Li isotope data, that suggests a decline in silicate weathering under glacial maximum.

This data suggests that the Silurian climatic perturbations are associated with glaciation events most likely induced by abrupt uplift during the Caledonian Orogeny.

Theme 5:

Assessing small-scale heterogeneities in Earth materials

Microbeam X-ray imaging of trace PGM phases in cumulate rocks

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A combination of novel techniques based around microbeam X-ray imaging as enabled us to detect PGM phases at sub-ppm concentrations in well-characterised cumulate rock samples, without relying on those grains intersecting the sample surface. Two approaches have been used: microbeam XRF mapping using the Maia detector array on the XFM Beamline of the Australian Synchrotron (Maia-XFM), and high-resolution X-ray computed tomography (HRXCT). Maia-XFM can detect grains of PGE rich phases as small as 1 micron anywhere within a 100 mm thick section, while HRXCT can image dense phases in rock samples in 3D at comparably low voxel resolutions depending on sample size. Neither method by itself can unambiguously identify the detected phases, although Maia-XFM semiquantitatively detects As, Se and Bi as well as first-row transition elements and the heavy PGEs (Ir, Os, Pt) and Au to thousand ppm levels at spatial resolutions of a few mm and milisecond dwell times. Follow up by SEM techniques is commonly required, greatly facilitated by knowledge of the precise 3D location of the particles within the sample. Focussed ion beam milling and simultaneous FEG-SEM has been used to follow up Maia-XFM identification of Pt-rich phases in Pt-enriched (~50 ppb) pyroxenites, revealing complex associations of Cu sulfides with Pt alloys and arsenides at primary cumulus pyroxene grain boundaries. The Maia-XFM data sets enable the location of these assemblages to be related to the growth history of the host cumulate assemblage revealed through subtle minor element (Cr, Ti) zoning in the pyroxenes¹. A combination of Maia-XFM, and HRXCT reveals detailed microtextures of intergrowths of 10-100 nm Cu-rich magmatic sulfide droplets and Pd-Cu and Au-Cu alloy phases in the Platinova Reef of the Skaergaard intrusion. These microtextures indicate collection of both Pd and Au at extremely high partition coefficients by sulfide microdroplets formed by saturation of the parent tholeiite magma with Cu sulfide melt (Holwell et al., this meeting). Ongoing studies include investigation of the spatial relationship of IPGE-rich phases to chromite grains in PGE-enriched chromitites from the Shetland Ophiolite (Prichard, et al, this meeting).

¹Barnes et al., doi:10.1007/s00410-016-1232-1 (2016)

In situ trace element measurements of mantle sulfides by SHRIMP-RG

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We developed a technique to analyze chalcophile and siderophile elements in sulfides using the Cs⁺ beam on the Sensitive High-Resolution Ion Microprobe Reverse Geometry (SHRIMP-RG) at Stanford University. Using a mass resolution of 9000-9500 (at 10% peak height) and calibration curves based on synthetic doped FeS and NiFeS₂ reference materials, we measured ³⁵Cl, ⁸⁰As, ⁸⁰Se, ¹²¹Sb and ¹³⁰Te, ¹⁰⁷Ag, ³²S and ¹⁹⁷Au. Additional elements (¹⁰¹Ru, ¹⁰⁵Rh, ¹⁰⁶Pd, ¹⁰⁷Ag, ¹⁰⁸Pd, ¹⁸⁵Re, ¹⁸⁹Os, ¹⁹³Ir and ¹⁹⁵Pt) are not reported because concentrations were below detection limits or were inaccurate due to overlapping isobaric interferences. The SHRIMP-RG technique provides good spatial resolution and low detection limits (~1 ppm for most elements).

In total we measured 54 unaltered sulfides in 10 abyssal peridotites from the Gakkel and Southwest Indian Ridges. Due to the absence of monosulfide solution, these pentlandite and Cu-bearing sulfides are interpreted as being largely metasomatic in origin, not residual phases. Sulfides contain 4-1000 ppm As, 50-250 ppm Se, 3-300 ppm Sb, 5-400 ppm Te, 4-300 ppm Ag, and 3-300 ppb Au. Se has a narrower range and Au is orders of magnitude lower in concentration than other elements.

The range of Se/Te ratios in our sulfides (0.5 to 27) significantly deviates from the chondritic primitive upper mantle value of 9±1. No significant differences between the two ridges were observed within the limited sample set, however the Gakkel Ridge spans a larger range of Se/Te ratios. The range from subchondritic to suprachondritic Se/Te ratios probably reflects the greater incompatibility of Te during melting compared to Se. Because these sulfides are products of (partial) melting followed by fractional crystallization, Se/Te ratios can be fractionated to higher or lower values. Thus, the trace element systematics of our abyssal peridotite sulfides reflects the effects of mid-ocean ridge processes in mobilizing sulfide melt.

Understanding the timing and nature of diamond-forming events from the study of sulphide inclusions

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Diamond-hosted sulphide inclusions can provide an insight into the original composition of mantle-derived sulphides and some reactions involved in diamond formation. Although their role in the known processes is unclear, sulphides are the main controllers of HSEs and chalcophile elements in the mantle and Re-Os dating of syngenetic diamond-hosted sulphide inclusions is a powerful technique for dating diamond growth and related processes [1-3]. The major and trace element compositions of the sulphides can also be used as tracers for mantle melting processes and formation of ancient continental lithosphere.

In the upper mantle, sulphides commonly exist as a Fe-Ni-Cu-S monosulphide solid solution (MSS) which upon cooling exsolves into a sulphide assemblage of pyrrhotite, pentlandite (\pm Ni-rich) and lastly Cu-bearing sulphides and sometimes other trace phases [4]. Some of these late exsolution products are seen to line the inside of thermal decompression cracks surrounding certain sulphide inclusions. Care must be taken to extract the inclusion entirely for dating (using TIMS): overlooking the complexity of the crack systems and the possible presence of trace sulphides would compromise the accuracy of HSE measurements and dating systematics.

[1] Alard, O. et al. 2000. *Lett. Nature*, 407, 891-894 [2] Westerlund, K.J. et al. 2004. *S. Afr. J. Geol.* 107, 119-130 [3] Harvey, J. et al. 2016. *Rev. Mineral. Geochem.* 81, 579-649 [4] Taylor, L.A. and Liu, Y. 2009. *Int. Geol. Rev.* 40, 663-676

Mineralogical insights on the HSE-Se-Te behaviour during subduction

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Subduction zones are among the sites of the highest mass fluxes between crust and mantle known on Earth. The fluxes are well understood for the lithophile elements and their isotopic systems but the behaviour of strongly chalcophile- (Se, Te) and highly siderophile elements (HSE: Os, Ir, Ru, Pt, Pd, Re) during dehydration of subducting oceanic crust is still poorly constrained, although it likely bears significant implications on the origin of small and large scale HSE-Se-Te and ¹⁸⁶Os-¹⁸⁷Os heterogeneities in the Earth's mantle.

Our samples come from the island of Syros (Greece) and represent fragments of gabbroic- and basaltic oceanic crust subducted in the Eocene. One representative metagabbroic sample contains glaucophane+omphacite+clinozoisite+garnet with accessory rutile, equilibrated at ~1.8 GPa and ~550 °C (blueschist-eclogite facies), which is typical of a subduction geotherm. The common sulphide minerals that host HSE in gabbros (pentlandite-pyrrhotite-chalcopyrite) are absent but pyrite is present, both as inclusions in HP minerals and as intergranular component. Osmium and Ir contents of the bulk rock are comparable to unmetamorphosed gabbros [2] but their Pt, Pd and Re contents are 5-10-fold depleted, suggesting mobilization by hydrothermal/metamorphic fluids. Such fluxings were previously suggested from studies of metabasalts [1], [2], while investigations of metagabbros only indicate Pd mobility [2]. Preliminary HSE data for mineral separates indicate that only <20% of the Ir, Pt and Pd- but ~70% of the Re whole-rock budgets are controlled by HP silicates, while the remaining fractions are probably hosted by pyrite [2]. Highly variable Pt contents within mineral separates and bulk rock replicates suggest the occurrence of Pt-rich micro-inclusions within HP silicates. These current results will be complemented by on-going investigations on Os and the strongly chalcophile elements (Se-Te) for the metagabbro (including analyses of pyrite) and combined with a similar comprehensive study for a representative metabasalt. Our findings will provide new constraints on the fluxes and mineralogical controls of the HSE, Se and Te during subduction as well as the resulting implications on the global cycling of these key geochemical tracers within and in-between the different silicate reservoirs of Earth.

[1]: Becker (2000) *EPSL*, [2]: Dale et al. (2009) *GCA*.

¹⁹⁰Pt-¹⁸⁶Os dating and FIB-TEM investigations of the Pt alloys from the Kondyor mafic-ultramafic massif (Aldan Province, Russia)

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The Kondyor massif is an Ural-Alaskan-type mafic-ultramafic complex having intruded the Archean basement of the SE Siberian craton. It is associated with Mesozoic alkaline intrusions. Its dunite-clinopyroxenite core contains Pt-Fe alloys-bearing chromitites, which are the main source of the Kondyor placer deposits. The age of this chromitite-platinum mineralization and host ultramafites is however poorly constrained limiting our understanding of the conditions of formation of this extremely Pt-rich mineralisation.

Dating of the mafic-ultramafic rocks span from Paleoproterozoic (2477±18 Ma, U-Pb on dunitic zircons) to late Jurassic-early Cretaceous (e.g. 149-137 Ma K-Ar on phlogopite from dunites). Ages obtained on the Pt-Fe and minor Os-Ir-Ru alloys are similarly ranging from Neoproterozoic (658-602 Ma, Re-Os T_{RD} model ages) to Cretaceous (112±7 Ma, ¹⁹⁰Pt-⁴He isochron).

We analysed 13 Pt-Fe alloys from the Pt-rich Kondyor chromitites for Pt-Os isotopic dating. These alloys define a ¹⁸⁶Os-¹⁹⁰Pt isochron yielding an age of 249.8±12 Ma (MSWD 0.81). Internal isochrons indicating similar ages were obtained for 10 alloys. This mm-scale Pt-Os heterogeneity is completed by a nm-scale heterogeneity as shown by the FIB-TEM. Both mm and nm-scale features may provide insights into the origin and history of the mineralisation.

These early Triassic Pt-Os ages are likely more robust age estimates than those obtained previously on both the Pt-Fe and Os-Ir-Ru alloys, as Pt-Os is less sensitive than Pt-He and Re-Os to the long and complex geological history of the Kondyor massif. Interestingly, early Triassic ages are also recorded in the “neighbouring” Siberian super-plume, Noril’sk flood basalt and Guli dunite-clinopyroxenite-carbonatite complex.

Recent development in PGE analysis

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ICP-MS/MS

Measurement procedures for the determination of PGE mass fractions in geological and environmental materials at the pg/g to ng/g range seem to have reached the maturity stage. Most of them employ some sort of analyte/matrix separation after Os removal via the gas phase or liquid/liquid extraction and steps to remove potential elements that cause isobaric and molecular interferences in the ICP-MS. The recent introduction of ICP-MS/MS creates “cleaner” spectra not only through controlled collision and chemical reactions in an octopole cell but also through specific chemical reaction to create compound ions which are measured at a shifted, interference free mass. Chemical reactions within the ICP-MS makes it possible to analyse samples with simple matrices such as moss even without preconcentration and analyte/matrix separation [1].

Reference materials

Recent efforts to better characterise komatiite OKUM and harzburgites MUH-1, reference materials developed for major, trace and PGE certification, demonstrate that the state-of-the-art in PGE analysis is at a lower level than wished. Inhomogeneity issues and incompletely validated measurement procedure due to the lack of matrix matched reference materials still hamper the reduction of the uncertainty of the assigned values to less than 10 %.

[1] Suoranta, Bokhari, Meisel, Niemelä and Perämäki (2016) Geostand. Geoanal. Res, accepted article.

Relating ^{187}Os to PGM located in 3D in different sites in chromitite

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Podiform chromitite-hosted platinum-group minerals from Harold's Grave in the Shetland ophiolite have been imaged in 3D using X-ray computed tomography. Lenses of this chromitite surrounded by dunite in mantle harzburgite are extremely enriched in the IPGE Ru, Os and Ir.

The 3D imaging of the PGM allows them to be divided into three paragenetic groups:- (i) Os-Ir-bearing laurite with Os-Ir-Ru alloys that are totally enclosed in chromite. These probably formed first as the chromite was crystallising. (ii) Os-Ir-poor laurite, and irarsite with ruthenian pentlandite that are interstitial to the chromite grains and often in clusters. The PGE that compose these PGM were probably collected by an immiscible sulphide liquid that crystallised MSS. The PGM then formed by exsolution from the MSS during sulphur loss. (iii) A small group of elongate aligned PGM within chromite grains. The Ir, Ru, Os, Rh and Pt-bearing PGE that form these PGM may have entered the chromite as it crystallised and then exsolved to form PGM during sub-solidus cooling.

Osmium isotope data (n=107) for 2D- and 3D-imaged PGM in the Harold's Grave chromitite define a modal $^{187}\text{Os}/^{188}\text{Os}$ of around 0.1245. This corresponds to a Re-depletion age matching the formation age of the ophiolite (~492 Ma). All PGM belonging to group (iii) have this $^{187}\text{Os}/^{188}\text{Os}$ modal value, consistent with their exsolution from chromite which, in turn, crystallised from a melt derived from ambient mantle at that time.

Rare lower $^{187}\text{Os}/^{188}\text{Os}$ ratios of 0.120 to 0.122 also occur (n=6), the lowest of which corresponds to a Re depletion age of ~1150 Ma. Some PGM with these lower ratios occur in the same polished section of chromitite as those with higher ratios. These PGM are enclosed in chromite, are all composite grains with laurite, and are distinctive because they are accompanied by Rh- and Ni-bearing minerals. They either represent inherited PGM grains, older than the ophiolite, or more likely were formed from a discrete melt sourced from older and more severely depleted mantle.

Re-Os ages of detrital grains from Jack Hills and Mt. Narryer, Yilgarn Craton, Australia

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Renowned for the presence of Hadean zircons [1,2,3], metasediments from Jack Hills and Mount Narryer in the Yilgarn Craton, Australia also host a number of other detrital minerals. Of these metal oxide grains are ideal candidates for Re-Os geochronology. Metasediments from four locations at Jack Hills and two locations at Mt Narryer were crushed and magnetically separated to concentrate phases suitable for Re-Os dating.

EMPA of separates from Jack Hills have revealed an assemblage dominated by chromite, with minor rutile, iron oxides and grains of layered magnetite and quartz. Despite a large range in morphology, from euhedral octahedra to rounded grains, chromites are chemically homogeneous. Their low Mg# (<0.18), high ZnO (0.7-8.4 wt.%) and MnO (0.7-2.8 wt.%) suggest chromites may have been homogenised by the high grade metamorphism which is prevalent throughout the Narryer Terrane [4,5].

Separates from Mt Narryer contain ilmenite, rutile, tourmaline and magnetite with chromite notably absent. Ilmenites contain appreciable MnO (0.2-2.5 wt.%) and low MgO (<0.2 wt.%), indicating they have also been modified by diffusion during metamorphism [6].

Detrital minerals will be analysed to attain Re-Os ages. Preliminary analysis of bulk separates yield high Os concentrations with >14ppb Os for Jack Hills and ~850ppt Os for Mt Narryer. This is consistent with grains originating in mafic crust, and suggests Re-Os ages will be robust. When combined with zircon data, further PGE analysis will provide key information on continental crust generation in the early Archean.

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Highly siderophile heterogeneity in mantle xenoliths and implications for osmium model ages

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Osmium model ages are widely employed to constrain partial melting events in the terrestrial mantle, because of the lesser susceptibility to later stage disturbance of the Re-Os system compared to silicate mineral-hosted isotope systems.

Here we present a detailed mineralogical and geochemical study of sulfides and silicates from a harzburgite xenolith from the Kangerlussuaq area, Greenland. Sample 474527, previously presented by Wittig et al. (2008, 2010) shows clear signs of mantle metasomatism and heterogeneous distribution of highly siderophile element (HSE) concentrations on the thin section scale. Variations in HSE concentration between base metal sulfides (BMS, consisting of pentlandite-pyrrhotite-chalcopyrite) span over three orders of magnitude. Various types of inter-element HSE fractionation can clearly be distinguished in different BMS, and ¹⁸⁷Os/¹⁸⁸Os in individual BMS ranges from 0.104 to 0.194.

This observed small-scale heterogeneity strengthens the notion that mantle samples contain multiple generations of sulfides formed by multiple partial melting and metasomatic melt/rock interaction events. Bulk rock geochemical signatures will thus represent mixtures of these sulfide populations.

The heterogeneity in Os isotopes, largely independent of the mineralogical composition of the BMS, points to the difficulty of interpreting Os isotope data chronologically on both the bulk rock and the individual grain scale. The micro-scale heterogeneity of Os concentration and isotopic composition also points to greater mobility of Os than previously assumed, putting one of the key assumptions for the widespread use of Os model ages into question, and implies the need for caution when assigning chronological validity to Os isotope data, as previously outlined by Rudnick and Walker (2009).

¹⁸⁷Os isotopic composition and HSE variations at the nanoscale

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The Re-Os chronometer has become a fundamental tool for dating partial melting events of the sub-continental lithospheric mantle. Over the past decade it has become increasingly evident that the Re-Os system is controlled by small, distinct mineral phases. Information from these Re-Os-bearing minerals can provide greater insight into the partial melting history of the depleted mantle. Due to the nature of such minerals, and their potential formation during primary partial melting or from secondary re-enrichment, it is essential that the petrological information of the minerals is accurately assessed prior to dating and subsequent interpretation.

A single cratonic peridotite from the Bultfontein kimberlite pipe, South Africa, provides us with a unique opportunity to investigate Re-Os and HSE systematics at variable scales. Through the implementation of novel techniques we have analysed the HSE and Re-Os at the whole-rock, micron and sub-micron scale. We show that the Re-Os system is highly variable across the different Re-Os-host phases, with Pt-alloys displaying a higher Re/Os than their host sulphides. Resulting in T_{RD} ages of 2.9-3.1 Ga and 0.3 Ga-future for the sulphides and alloys respectively. The formation of the alloys as sub-solidus exsolution products dictates that the interpretation of the sulphide ages must therefore relate to the formation of the Pt-alloys and not to Re-depletion during partial melting. Our results emphasize the need for full petrological investigation prior to interpretation of Archean ages.

Constraints on mantle Pb from *in situ* analyses of sulfides

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The isotopic composition of lead provides key constraints on the evolution of the Earth. Sulfide is thought to be the main mineral host for Pb due to the chalcophile behaviour of this element. To explore sulfide Pb, we measured *in situ* Pb concentrations using the Sensitive High Resolution Ion Microprobe, calibrated using a set of synthetic doped sulfide reference materials.

A total of 149 sulfides from 12 peridotites and 1 pyroxenite vein from the Gakkel and Southwest Indian ridges were analysed. These sulfides consist predominantly of pentlandite, with some grains containing discrete or distributed Cu-bearing phases. Hydrothermal sulfides and grains with extensive alteration were excluded from the final dataset. Most grains are interstitial or occur as clusters distributed through multiple silicate phases, with only 12% of grains enclosed in olivine or orthopyroxene. Based on morphology, composition, and the absence of monosulfide solid solution, the sulfides are interpreted as being metasomatic – not residual – in origin. We interpret the sulfides to have formed by fractional crystallization of sulfide melts that were produced by melting of primary mantle sulfides during upwelling beneath the ridge axis.

The average Pb concentration of the pentlandites is 1.8 ± 0.7 ppm ($n=84$ grains, 1σ standard deviation), while Cu-bearing sulfides have an average concentration of 6 ± 7 ppm ($n=31$ grains). As Cu-bearing sulfides crystallize at lower temperatures than pentlandite, the higher Pb concentrations in the Cu-bearing sulfides probably reflect more evolved melt compositions. Using recent estimates for sulfide melt/silicate melt partition coefficients of ~ 30 at 1.5 GPa, these sulfide Pb concentrations correspond to basaltic melts with ~ 0.1 - 0.2 ppm Pb. For comparison, the average Pb concentration in NMORB is 0.5 ppm. This difference may reflect either deeper melt generation, where Pb partitions more favourably into silicate melt, or the removal of some sulfide melt with basaltic melt.

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