V21E-10 1105h

Detecting volcanic eruption precursors: A new method using gravity and deformation measurements

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One of the fundamental questions in modern volcanology is the manner in which a volcanic eruption is triggered; the intrusion of fresh magma into a reservoir is thought to be a key component. The amount by which previously ponded reservoir magma interacts with a newly intruded magma will determine the nature and rate of eruption as well as the chemistry of erupted lavas and shallow dykes. The physics of this interaction can be investigated through a conventional monitoring procedure that incorporates the simple and much used Mogi model relating ground deformation (most simply represented by Δh) to changes in volume of a magma reservoir. Gravity changes (Δg) combined with ground deformation provides information on magma reservoir mass changes. Our models predict how, during inflation, the observed $\Delta g/\Delta h$ gradient will evolve as a volcano develops from a state of dormancy through unrest into a state of explosive activity. Calderas in a state of unrest and large composite volcanoes are the targets for the methods proposed here and are exemplified by Campi Flegrei, Rabaul, Krafla and Long Valley. We show here how the simultaneous measurement of deformation and gravity at only a few key stations can identify important precursory processes within a magma reservoir prior to the onset of more conventional eruption precursors.

V21E-11 1120h

The Seismic Velocity In Gas-charged Magma

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Long-period and hybrid events, seen at the Soufrière Hills Volcano, Montserrat, show dominant low frequency content suggesting the seismic wavefield is formed as a result of interface waves at the boundary between a fluid and a solid medium. This wavefield will depend on the impedance contrast between the two media and therefore the difference in seismic velocity. For a gas-charged magma, increasing pressure with depth reduces the volume of gas exsolved, increasing the seismic velocity with depth in the conduit. The seismic radiation pattern along the conduit can then be modelled. Where single events merge into tremor, gliding lines can sometimes be seen in the spectra and indicate either changes in the seismic parameters with time or varying triggering rates of single events.The differential equation describing the time dependence of bubble growth by diffusion is solved numerically for a stationary magma column undergoing a decompression event. The volume of gas is depth dependent and increases with time as the bubbles grow and expand. It is used to calculate the depth and time dependence of the density, pressure and seismic velocity. The effect of different viscosities associated with different magma types and concentration of water in the melt on the rate of bubble growth is explored. Crystal growth, which increases the concentration of water in the melt, affects the amount of gas that can be exsolved.

V21E-12 1135h

Modelling the Time Dependence of Frequency Content of Long-period Volcanic Earthquakes

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Broad-band seismic networks provide a powerfull tool for the observation and analysis of volcanic earthquakes. The amplitude spectrogram allows us to follow the frequency content of these signals with time. Observed amplitude spectrograms of long-period volcanic earthquakes display distinct spectral lines sometimes varying by several Hertz over time spans of minutes to hours.

We first present several examples associated with various phases of volcanic activity at Soufrière Hills volcano, Montserrat. Then, we present and discuss two mechanisms to explain such frequency changes in the spectrograms: (i) change of physical properties within the magma and, (ii) change in the triggering frequency of repeated sources within the conduit.

We use 2D and 3D finite-difference modelling methods to compute the propagation of seismic waves in simplified volcanic structures: (i) we model the gliding spectral lines by introducing continuously changing magma properties during the wavefield computation; (ii) we explore the resulting pressure distribution within the conduit and its potential role in triggering further events.

We obtain constraints on both amplitude and timescales for changes of magma properties that are required to model gliding lines in amplitude spectrograms.

V21E-13 1150h

Damping and Amplification of Seismic Waves in Gas-Charged Magma

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Low-frequency seismic signals are generated at the interface between a solid medium and a magmatic melt. The existence of gas bubbles in the magma introduces a damping mechanism which depends mainly on the gas volume fraction and on the viscosity of the melt. However, in case of a sudden unloading (e.g. by lava dome failure) a decompressional wave propagates through the magma which becomes now supersaturated. Diffusion of gas into the bubbles leads to an exponential bubble growth which is in general frequency dependent. Such a system can be represented by a negative bulk viscosity which results in a net amplification rather than damping of the decompressional wave. Furthermore, the effects of a harmonically varying pressure on the supersaturated melt is explored, as it is caused by seismic tremor and prolongued conduit resonance.

V22A MC: Hall D Tuesday 1330h

Highly Siderophile Element Chemistry of the Earth, Moon, and Planets (honoring John Morgan) II

(joint with P, HG)

Presiding: **A Brandon,** Johnson Space Center**; C Neal,** University of Notre Dame

V22A-1002 1330h POSTER

Re-Os Isotopic Characteristics of the Earth's Oldest Preserved Oceanic Crustal Fragments (Isua Supracrustals Belt, W Greenland); A Vastly Disturbed System.

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Variably preserved pillow lavas from the Isua Supracrustals Belt (ISB; Western Greenland) exhibit strongly supra-chondritic Re/Os (range from 2 to 45) and highly radiogenic $^{187}Os/^{188}Os$ isotopic compositions (range from 0.3 to 20.5). Re-Os model ages are geologically meaningless and reflect the disturbances invoked by post-formational metamorphic overprinting and by metasomatic events that were associated with the intrusion of various generations of the precursors of tonalitic gneisses into the ISB. Most prominently, a late Archean (c. 2.8 Ga) tectono-metamorphic event has locally reset the Re-Os clock in high strain domains of the ISB. Disturbance of the Re-Os system was initially caused by Re addition in connection with metasomatic fluid flow during the early Archean (3.65 to 3.81 Ga) emplacement of central dome gneiss precursors and tonalite sheets into the supracrustals sequences. The effects of open system behaviour of the Re-Os system are similarly recorded by the U-Pb and Sm-Nd systems of these meta-basalts, principally revealing the influx of U, Th, Re; LREE and alkaline-rich fluids from the gneisses into the oceanic crustal sequences preserved at Isua (Blichert-Toft and Frei, 2001; Frei et al., in press; Frei and Rosing, in press). Ultramafic lenses with komatiitic chemical affinities within the ISB are equally affected by early addition of Re, but the very much higher Os concentrations (more than an order of magnitude higher than those of the meta-basalts with values ranging from 30 to 150 ppt) did efficiently mask the disturbances in the Os isotope compositions, so that reasonable Re depletion ages (T_{RD}) can still be deduced. The least altered of these ultramafic lenses revealed a T_{RD}) of 3725 Ma and a mantle extraction (T_{MA}) age of 3807 Ma, dates which are compatible with independent U-Pb zircon ages from intrusive tonalitic gneisses (Nutman et al., 1997) and Pb-Pb age constraints from metasomatic minerals of strongly altered meta-basalts (Frei and Rosing, in press). They can be regarded as minimum ages of deposition of the supracrustals. The complexity of post-formational overprinting however makes it difficult to investigate and explore the Earth's mantle geochemical evolution before this time.

Blichert-Toft, J. and Frei, R. (2001) Geochim. Cosmochim. Acta, 65, 3177-3187. Frei, R., Rosing, M.T., Waight, T.E., and Ulfbeck, D.G. (in press) Geochim. Cosmochim. Acta Frei,R. and Rosing, M.T. (in press) Chem. Geol. Nutman, A.P., Bennett, V.C., Friend, C.R.L., and Rosing, M.T. (1997) Chem. Geol., 141, 271-287.

V22A-1003 1330h POSTER

Platinum-Group Elements in Basalts Derived From the Icelandic Mantle Plume -Past and Present.

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Paleogene basalts (~55Ma) derived from the ancestral Iceland mantle plume and extruded during continental rifting are exposed along the Blosseville Kyst in central East Greenland. These basalts comprise three intercalated series, viz: a low-Ti, high-Ti and a very high-Ti series. The two Ti-rich series are interpreted to represent continental flood basalts formed by low degrees of partial melting (degree of melting F=3-9%) while the low-Ti series are believed to have formed by higher degrees of partial melting (F:15-25%). All three of the East Greenland basalt series are enriched in the PGE, relative to normal MORB. During differentiation of the low-Ti series, Pd increase from 11 to 24 ppb whereas Pt and Ir decrease from 12 and 0.6 ppb to 3 and <0.05 ppb respectively. The primitive basalts (molar Mg#60) of the dominant high-Ti series contain ~6-10 ppb Pd, ~7-10 ppb Pt and ~0.2 ppb Ir whereas the most evolved basalts (Mg#43) contain 25 ppb Pd, 5 ppb Pt and <0.05 ppb Ir. The PGE-rich nature of these basalts is surprising because low degree partial melts are generally S-saturated and hence strongly depleted in the PGE (cf, Keays, 1995). However, our data indicates that all of the East Greenland magmas were S-undersaturated and as they underwent differentiation, Pd behaved incompatibly while Ir and Pt behaved compatibly. Primitive Holocene Icelandic olivine tholeiites contain 120 ppm Cu, 6 ppb Pd, 4 ppb Pt and 0.2 ppb Ir while their picritic counterparts contain 74 ppm Cu, 17 ppb Pd, 7 ppb Pt and 0.3 ppb Ir. Both the olivine tholeiites and the picrites are believed to have formed by high degrees of partial melting (15-25%) which would have exhausted all of the sulphides in the mantle source region and produced S-undersaturated magmas. In Icelandic samples with 10-14wt% MgO, Cu and the PGEs vary systematically between the primitive picrite and olivine tholeiite compositions given above i.e there is an inverse correlation between Cu and the PGEs. This is best explained by mixing between parental olivine tholeiite and picrite magmas. The low Cu/Pd ratio in the most primitive picrite probably reflect derivation from a depleted mantle where Cu was less efficiently retained in sulphides compared to Pd during previous melt extraction episodes. Whithin the analysed suite of olivine tholeiites, Ir decreases from 0.15 to 0.06 ppb, Pd increases from ~6 to ~15 ppb and Pt/Pd ratio decreases from 0.8-0.2 during differentiation (7-4wt% MgO); these variations provide further evidence that the olivine tholeiite magmas remained S-undersaturated throughout their differentiation.

To summarize, (1) Continental flood basalts and low-Ti tholeiites in the Paleogene East Greenland flood basalt sequence, as well as Holocene Icelandic olivine tholeiites are PGE-rich relative to normal MORB.

(2) Their PGE-contents vary as a function of S-undersaturated differentiation. (3) Cu-PGE variations in Icelandic samples with 10-14 wt% MgO suggest that they represent mixtures between distinct tholeiitic (Cu/Pd: 20000) and depleted picritic (Cu/Pd: 4400) parental liquids.

Reference: Keays RR (1995) The role of komatiitic magmatism and S-saturation in the formation of ore deposits. Lithos 34:1-18.

V22A-1004 1330h POSTER

Unique Behaviors of Highly Siderophile elements

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Platinum group elements, Re and Au are called highly siderophile elements (HSE) because they have very high metal/silicate partition coefficients. Determination of their metal/silicate partition coefficients, however, is not easy. Low concentrations of HSE in silicates are not the only hamper. The suboptical size nuggets formed by HSE in silicate melts under reducing conditions are another factor affecting true determination of HSE in the silicates (1). The mechanism of formation of HSE nuggets is still under discussion.

In this study a fire assay technique was used to extract metal elements from geological reference material BCR-1. Similar amounts of highly pure FeNi metal and BCR-1 were mixed and melted in a furnace at 1550°C and at a CO/CO_2 controlled oxygen fugacity. After fusion a big metal ball formed. Some tiny metal grains (∼100 mm) were also found in the silicate glass. The big metal and several tiny metals were collected for neutron activation analysis. While the major compositions of the big metal and tiny metals are similar, concentrations of trace elements in the two sizes of metal are very different: trace elements are highly enriched in the tiny metal fraction. Cobalt and Cr come mainly from the BCR-1 reference material and their fractionation between big and tiny metals is reduced along with increasing melting time. Platinum, Au and Ir come from Pt wire used to hold corundum containers. The tiny/big metal concentration ratios of Pt, Au and Ir, however, increased with increasing melting time. A likely explanation is Pt, Au and Ir dissolved in the silicate melts via vapor forms and the dissolved Pt, Au and Ir are disseminated in the silicate and easily caught by tiny metal grains. If so the appearance of HSE nuggets is an experimental design problem. Avoiding formation and condensation of HSE vapors may eliminate the occurrence of HSE nuggets.

Reference: (1) Borisov A and Palme H. GCA, 4349-4357, 1997.

V22A-1005 1330h POSTER

Siderophile Element Compositions of Lunar Impact Breccias: Implications for the Cataclysm and Early Earth

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Highly siderophile element signatures of the two main textural and compositional groups of Apollo 17 impact melt breccias (poikilitics and aphanites) are consistent with EH chondrite impactor(s). Similar siderophile element signatures in both types of breccias implies either that multiple EH chondritic impactors were delivered to the Serenitatis region of the Moon within a narrow time interval, or that the two groups of breccias are petrogenetically related to a single impact event. To the extent that these breccias can be linked with the Serenitatis basin-forming event, this identifies one type of planetesimal responsible for creating a large nearside lunar basin, possibly during a terminal cataclysm.

Owing to its larger size and greater gravitational focusing, the Earth would have experienced a significantly greater cratering rate (20x) and mass accretion rate (100x) compared to the Moon. If there was a terminal cataclysm, the Earth must have been hit by several large impacts during the crucial period in which the oldest preserved continental crust was forming and early life was evolving. If EH chondrites are found to be an important population for creating the 3.8 to 4.0 Ga lunar basins, their fractionated HSE pattern may have contributed to mantle heterogeneity on Earth. However, the dry and highly reduced nature of EH chondrites would preclude a significant contribution from these planetesimals to the volatile budget of the Earth and the oxidation of the terrestrial mantle. Additional studies of highly siderophile elements in lunar impact breccias and ancient terrestrial rocks are needed to establish the composition of infalling planetesimals on the early Earth and Moon, and the contribution of large impact events to the subsequent evolution of the Earth and other terrestrial planets.

V22A-1006 1330h POSTER

Metal-Silicate Interactions at High Pressure and Temperature

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Laser-heated diamond-anvil cell (LHDAC) experiments were carried out to determine the partition coefficients of Ni and Co between iron metal and several silicates. One challenge of these experiments is to analyze accurately small samples from the LHDAC with sub-micrometer spatial resolution. We used diamond anvils with 500 microns culets, and stainless-steel gaskets preindented to a thickness of 40μm and drilled to a diameter of 200μm. We used both compacted powders with several silicate glass compositions (ranging from SiO_2 to basaltic composition simulating that of model C1 chondrite) and a 25μm thick Fe-Ni-Co alloy foil. Thermal insulation from the diamonds was achieved by 10μm-thick pure Al_2O_3 and solid argon pressure medium. Pressures were measured at room temperature before and after laser heating, with the ruby-fluorescence method. The samples were heated by a multimode YAG laser for an average of 10-15 minutes. Temperatures were determined spectro-radiometrically with a fit to a grey-body Planck function. Samples recovered after the runs were polished down to the heated surface and analyzed by electron microprobe (the electron beam is less than 1μm and the resolution is about 1μm), or characterized by Transmission Electron Microscopy (TEM). In addition, we have analyzed our samples using secondary ion mass spectrometry (SIMS) analysis. A successful overlap of results of these different analysis techniques will substantially increase confidence in the extension of experiments to lower-mantle conditions. Our preliminary results in the system Si-Al-Fe-Mg-Ca-Ni-Co-O, show a good agreement with those of multianvil experiments at low pressures (5-12 GPa) [1], and with increasing pressure until 50 GPa we observe the expected decrease of the partition coefficients of Ni and Co for the same redox conditions. The partition coefficients determined in our work at high pressures (5-50 GPa) and constant temperature (2500 ± 200 K), $D^M = X^M_{metal}$(wt%) / $X^M_{silicate}$(wt%) (M = Ni or Co) decrease from 20 at about 13 GPa to values below 10 at pressures higher than 25 GPa. These experiments will help constrain the partition coefficients of Ni and Co at the core-mantle boundary conditions.

[1] Thibault and Walter (1995), Geochim. Cosmochim. Acta, 59, 991.

V22A-1007 1330h POSTER

Online Rhenium Fractionation Correction Using Tungsten-Doping Technique on a Magnetic Sector ICP-MS.

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Precise Re concentrations are commonly analysed by ID-NTIMS. The use of multicollector ICP-MS may alternatively be more time effective for similar precisions. One major drawback with ICP-MS is the lack of control concerning instrumental mass bias, which tends to be time dependant for a given machine setting.

The mass discrimination in the ICP-MS is a sum of numerous phenomena, mainly the space charge effects within the plasma, the supersonic gaseous expansion between the cones, and the fractionation related to the hexapole , in the case of the IsoProbe (Micromass ICP-MS). Rhenium possesses only two isotopes, so an internal fractionation correction is not possible at least for spiked samples. A standard bracketing technique would be efficient to resolve this problem if the fractionation effects were evolving regularly with time; we have evidence that it is not always the case for our instrument.

Similarly to the Pb-Tl systematics, we added some W to a Re standard solution. These two elements are neighbours in the Mendeleiev table and do not have any isobars. This allows us to measure 184W, 185Re, 186W and 187Re simultaneously (static mode, 188Os is also monitored) and compare the 186W/184W and 187Re/185Re. Repeated analyses of this mixture yielded different fractionation factors (that is the beta value from the exponential law, normalised to 187Re/185Re=1.67398, Gramlich et al, 1973 and 186W/184W=0.927633, Lee and Halliday, 1995) for these two metals. However these beta values evolve together with time. The relationship between the beta-Re and beta-W is linear, with a slope of one and a non-zero intercept within instrumental precision. The slope indicates that these elements behave similarly in the ICP-MS. The intercept is most likely a result of inconsistent normalising values for the measured ratios : the Re reference value currently used may have to be reconsidered.

In conclusion, empirical results allow to calculate an accurate on-line fractionation factor to apply to the Re data from the simultaneously mesured beta-W. This is the case both for pure standard solutions as well as natural spiked samples (i.e. with a somewhat dirty matrix due to imperfect chemical separation). Most significant is the observation that the Re standard isotopic ratios obtained with this W-technique are at least 3 times more reproducible than with the standard bracketing technique.

V22A-1008 1330h POSTER

Tracking Melt-Rock Reaction Using Os Isotopes: Maqsad Diapir (Oman Ophiolite)

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The exceptional exposure of the Oman ophiolite allows to study in detail the mantle processes occurring beneath a spreading centre. We have carried out a Re-Os pilot study focussed on the Maqsad diapir in the western part of the Sumail massif. The Maqsad diapir is roughly constituted of 3 petrographic units: 1, the main harzburgitic domain (MHD); 2, the diapir harzburgite (DH) showing plunging lineation; 3, a thick dunitic, mantle-crust transition zone (MTZ) topping the DH section. The MHD samples are characterised by Os content about 4 ppb and $^{187}Os/^{188}Os$ down to 0.1210. These features are in agreement with a >15% melt extraction. These unradiogenic Os compositions yield a model Re-depletion age ca. 1 Ga, similar to other Re-Os model age obtained for other oceanic related mantle samples worldwide. Samples from the DH domain despite similar range in Al_2O_3 content show more radiogenic Os composition ($0.1240 < {}^{187}Os/^{188}Os < 0.1298$). The MTZ dunites show even more radiogenic Os composition ($0.1352 < {}^{187}Os/^{188}Os < 0.1399$). The MTZ dunite are further characterised by low Os content (<1.5 ppb) not in agreement with the well know high compatible nature of Os. These observations are inconsistent with a residual origin after melting for these dunites. In contrast, Os systematic indicate than the MTZ dunites as well as the diapir harzburgites are not a mere product of melt depletion but rather result from extensive melt-rock reaction as previously demonstrated (e.g., Kelemen et al., 1995; Godard et al., 2000). Those authors have postulated that dunites are the product of melt-rock reaction leading to the crystallisation of olivine and Fe-enrichment (leading to low Mg-number) similar but less extensive process has been envisaged for the diapir harzburgite. $^{187}Os/^{188}Os$ is inversely correlated with the Mg-number of the MTZ and DH samples. Suggesting that indeed the petrographic and geochemical characteristics of both domains are due to the same process occurring at various extend. The processes leading to the overprinting of the Os isotopic signature in the DH and MTZ domain is currently under investigation but could be related to the dissolution and precipitation of sulphides and to the S-saturation and under-saturation of the percolating melt.

These preliminary results suggest that the Re-Os system could be a very efficient tracer of melt-rock reaction occurring at large melt-rock ratios and indicate that a fair amount of melt-rock interaction occurred. Such processes may have important bearings for the Os-systematic of MORB.

Kelemen et al., Nature, 375, 747-753, 1995; Godard et al, Earth Planet. Sci. Lett., 180, 133-148, 2000.

V22A-1009 1330h POSTER

Highly siderophile elements and Os isotopes in mantle xenoliths from the Eifel volcanic field and the Vogelsberg volcano (Germany)

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Mantle derived peridotite xenoliths, ranging from unmetasomatised fertile lherzolites (La/Yb_N = 0.85 to 1.63; Al_2O_3 = 2.61 to 4.61 wt%) to increasingly depleted metasomatised harzburgites (La/YbN = 3.35 to 14.75; Al_2O_3 = 0.73 to 2.04 wt%), including pyroxenites (La/Yb_N = 5.02 to 5.16; Al_2O_3 = 4.30 to 5.30 wt%) from the Eifel volcanic field and the Vogelsberg volcano, have been analyzed for their highly siderophile elements (HSE), including six platinum-group elements (PGE: Os, Ir, Pt, Ru, Rh, Pd), Re and Au, and some other trace elements (e.g. REE) and Os-isotopes to investigate the behaviour of HSE and Os-isotopes during melt extraction and metasomatism. Comparison of PGE abundances and patterns between anhydrous fertile xenoliths and hydrous harzburgitic xenoliths shows that PGE-ratios are not significantly fractionated between both groups, although some harzburgites are up to ~30% melt depleted. No systematic dependence of the contents of PGE on the degree of fertility of the host rock have been found. There Os contents range from <0.1 to 6.5 ng/g. Two pyroxenite samples show large variabilities in there PGE contents, with Ir contents of 0.23 and 4.30 ng/g. Some harzburgites have significantly higher concentrations of all PGE in comparison to samples of similar fertility reflecting the mobility of these elements in a metasomatized mantle. Approximately unfractionated PGE-patterns indicate that these elements were apparently transported with mobile phases (metasomatic components), presumably sulfides, which dominate the budget of highly siderophile elements in the mantle. Most samples show variable depletions in Os (Os/Ir; <0.03 to 1.26) with no systematic correlation between degree or type of metasomatism or degree of melt extraction. The harzburgites from the Eifel indicate that metasomatism can significantly modify the PGE chemistry of mantle rocks obscuring the original signature of melt loss. The presence of a plume-like structure beneath the Eifel may cause thermal erosion at the base of the lithosphere. Ascending plume melts could be responsible for heating, partial melting and metasomatism, resulting in enhanced sulfide mobility in the overlying mantle.

Os isotopic systematics of these mantle xenoliths provide insight into the effects of melt extraction and metasomatism on Os isotopes and place constraints on the evolution of the lithospheric mantle component beneath central Europe. Variable Os isotope compositions ($^{187}Os/^{188}Os$ = 0.1237-0.1420) at approximately similar Al_2O_3 contents indicate that portions of the Eifel lithospheric upper mantle have been variably overprinted by the addition of radiogenic Os and the loss of the primary mantle Os which was presumably present. Samples with Os contents >1.5 ng/g have relatively unradiogenic Os isotope compositions ($^{187}Os/^{188}Os$ = 0.1208-0.128) and Al_2O_3-Os isotopic systematics consistent with ancient melt depletion and isolation from the convecting asthenospheric mantle for time periods similar to the age of the overlying crust (~1.6 Ga). The high statistical significance of this correlation leads us to infer that it does indeed convey useful geologic information about the timing of the formation of the central European crust and mantle. This is consistent as well with results from other peridotite massifs in the European region.

V22A-1010 1330h POSTER

Os Isotopic Composition of Late-Archean Komatiites From Alexo in the Abitibi Greenstone Belt, Canada

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We have examined the Re-Os isotope systematics and major and trace element characteristics of a suite of komatiitic flows from Alexo area in the Abitibi greenstone belt. The objective of this study was to determine the initial Os isotopic composition of the late-Archean mantle source(s) of these rocks. Most of the samples have high Os concentrations and low Re/Os ratios. Moreover, some of these rocks have high Cr concentrations, and, therefore, direct determination of initial Os isotopic composition from primary chromites is possible. The Re-Os isochron results for whole rocks and chromites yield an age of 2760 ± 79 Ma. This age is in general agreement with Pb-Pb and Sm-Nd isochron ages of 2690 ± 15 Ma and 2752 ± 87 Ma, respectively (Dupre et. al., 1984). The initial Os isotopic composition ($^{187}Os/^{188}Os_{(I)}$ = 0.1081 ± 0.0016) obtained from this isochron is essentially chondritic (γ_{Os} = −0.5 ± 1.5). Our results, therefore, suggest an absence of any large-scale heterogeneity in initial Os isotopic composition of the mantle source(s) of these komatiites. Duplicate analyses of a differentiated (Mg# 0.66) and yet presumably cogenetic basaltic komatiite ($^{187}Re/^{188}Os$ > 8.14 and Os < 0.46 ppb) yield relatively radiogenic initial γ_{Os} values of +15.9 and +12.6. Such radiogenic initial isotopic compositions in an otherwise chondritic association may indicate: [1] open-system behavior due to hydrothermal alteration and low-grade metamorphism and/or [2] crustal contamination. The latter interpretation is consistent with recently studied komatiites and associated magmatic ores from this area (Lahaye et. al., 2001).

V22A-1011 1330h INVITED POSTER

Melt Percolation Monitored by Os-Isotopes and PGE Abundances: A Case Study From the Mantle Section of the Troodos Ophiolite

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Melt-mantle interaction is monitored by Os isotopes, PGE abundances, REE in cpx and Cr# in spinel in a single melt channel of the mantle section from the Troodos Ophiolite Complex. The melt channel is composed of a central dunite (6 cm wide) which is surrounded by harzburgite. In both lithologies spinel has a Cr# of 0.58 ± 0.01. Cpx in the dunite and harzburgite have similar and extremely depleted REE patterns with $(Gd/Yb)_N$ values from 0.03 to 0.07. Therefore, the lithophile elements suggest that harzburgite and dunite interacted with the same melt during the percolation process.

The Os isotopic composition of the dunite in the center and near the rim is radiogenic ($^{187}Os/^{188}Os$=0.138 and 0.139, respectively), compared to the harzburgite 4, 15 and 20 cm away from the dunite center ($^{187}Os/^{188}Os$=0.128, 0.132 and 0.129, respectively). The harzburgite has a rather flat PGE pattern, which is typical for mantle peridotites. In contrast the dunite shows mantle melt-like patterns, which are similar to those of boninites from the Troodos Ophiolite Complex. Osmium, Ir and Ru concentrations in the dunite are lower than those of the primitive mantle. This implies that these metals do not behave compatibly during the melt percolation process in the dunite. In addition, PGE ratios such as Pd/Ir and Os/Ir vary systematically in the melt channel. They depend on the melt/rock ratio and monitor the progressing reaction of the melt with harzburgite to form dunite.

We suggest that in the dunite the mantle sulfides containing the PGEs were completely dissolved by the percolating melt. Eventually the melt percolation ceased and the Os isotopic composition and PGE abundances of the dunite are controlled by the melt signature. In contrast, in the harzburgite dissolution of mantle sulfides by the percolating melt is insignificant and the remaining mantle sulfides still dominate the Os isotopic composition and PGE abundances.

V22A-1012 1330h POSTER

A Primordial and Highly Radiogenic Osmium Isotope Reservoir in Earth's Mantle

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The discovery of coupled enrichment of $^{186}Os/^{188}Os$ and $^{187}Os/^{186}Os$ ratios in Hawai'ian and Noril'sk lavas led to the suggestion that the associated mantle plumes originate at the core-mantle boundary where radiogenic osmium from the outer core can mix into the lower mantle[1−5]. We show that mantle-derived iridosmine (Os-rich Os-Ir-Ru alloy) grains from peridotite-bearing ophiolites in the Klamath mountains have extremely radiogenic $^{186}Os/^{188}Os$ ratios and very old Re-Os model ages (from 256 to 2644 Ma). This osmium can not have been derived from the (initially chondritic) outer core. Instead, the iridosmine data demonstrate the existence of a primordial and distinctly non-chondritic highly siderophile element reservoir in Earth with a high initial $^{186}Os/^{188}Os$ ratio. This reservoir is residing in the lower mantle and periodically mixes into the chondritic upper mantle, self-consistently explaining both the Os isotope composition of the iridosmine grains and the coupled $^{186,187}Os$ enrichments in the Hawai'ian and Noril'sk lavas and removing the requisite for these deep mantle plumes to originate at the core-mantle boundary. [1] Walker, R. J. et al. Geochim. Cosmochim. Acta 58, 4179-4197 (1994). [2] Walker, R. J., Morgan, J. W. & Horan, M. F. Science 269, 819-822 (1995). [3] Walker, R. J. et al. Geochim. Cosmochim. Acta 61, 4799-4807 (1997). [4] Brandon, A. D. et al. Science 280, 1570-1573 (1998). [5] Brandon, A. D., Norman, M. D., Walker, R. J. & Morgan, J. W. Earth. Planet. Sci. Lett. 174, 25-42 (1999).

V22A-1013 1330h POSTER

The Ontong Java Plateau: Evidence of Sulfide Involvement Using Platinum Group Elements.

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Ontong Java Plateau (OJP) basalts in the SW Pacific have been produced by large degrees of partial melting (Mahoney and Spencer, 1991, EPSL, 104:196-210; Neal et al., 1997, AGU Mono. 100:183-216), consistent with decompression melting of a surfacing plume head originating at the core-mantle boundary (CMB) (Coffin and Eldholm, 1993, Sci. Am., 269:42-49). Due to significant fractional crystallization (up to 50%, Neal et al., ibid.) and the resulting low Os abundances of the OJP basalts, Os isotope techniques used to demonstrate a CMB origin for other plumes (Walker et al., 1995, Science, 269:819-822 and 1997, GCA, 61:3145-3160) cannot be easily applied to the OJP. Geophysical modeling suggests chemical interactions across the CMB would occur (3-6%) (e.g., Kellogg and King, 1993, GRL, 20:379-382; Boehler et al., 1995, Chem. Geol., 120:199-205), which would produce enriched siderophile signatures in the resulting lower mantle-core mixture. The high degree of partial melting (>20%)(Michael, 1999, Geochem. Geophys. Geosyst.) supports the view that any platinum group elements (PGEs) as well as sulfides would be partitioned into the OJP plume rather than remaining in the source (Barnes et al., 1985, Chem. Geol. 53, 303-323).

PGE abundances (excluding Os) have been analyzed in OJP basalts from the islands of Malaita and Makira. Melting models using spinel peridotite demonstrate the PGE abundances in the OJP basalts cannot be generated from typical upper mantle. Melting models using primitive mantle mixed with a small amount of bulk core material can produce the PGE patterns and abundances present in OJP basalts (Ely and Neal, 1999, EOS, 80:F1103).

Adjacent samples from separate flows indicate that magma chamber fractional crystallization had little effect on PGE abundances. PGE abundances are also remarkably uniform across sequences of flows, except for the variable removal of Pd by weathering. Primitive mantle-normalized patterns using PGEs and trace elements demonstrate that there may have been PGE removal by sulfides in some samples. However, any sulfide removal of PGEs argues for even higher PGE abundances in the source, assumed to be a small amount of bulk core material mixed into the OJP plume source.

V22A-1014 1330h POSTER

Platinum Group Element Abundances in Mare Basalts: Sulfide Immiscibility in the Lunar Magma Ocean

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The platinum group element (PGE) budget of lunar or mare basalts has always been considered lower than that for terrestrial basalts. Generally only Ir has been quantified and has been considered the typical highly siderophile element and abundances greater than about 100 ppt (pg/g) have been termed spurious and attributable to contamination. However, Ir is the most depleted PGE (excluding Os) in basalts from Earth. Recent work has shown that this is also the case for mare basalts and that high-Ti basalts generally contain greater PGE abundances than the low-Ti basalts. These differences are a function of sulfur content and not directly related to crystal fractionation.

Plotting Y/Cu vs. PGE/Y ratios highlights samples that have experienced sulfide immiscibility, as chalcophile elements would be depleted relative to the lithophiles. All mare basalts analyzed show elevated Y/Cu and depleted PGE/Y ratios, consistent with sulfide immiscibility. By contrast, ocean island basalts and basalts from large igneous provinces on Earth have moderate values for these ratios, consistent with not having experienced sulfide immiscibility.

As both high-Ti and low-Ti basalts show evidence for sulfide immiscibility, we suggest this occurred during the creation of the mare source (i.e., during the lunar magma ocean). If the lunar magma ocean underwent sulfide immiscibility followed by overturn of the cumulate pile, the mare sources would possess an overall PGE-depleted signature. Perhaps most significantly, this process would also account for the extremely high U/Pb ratios observed in mare basalts.

V22A-1015 1330h POSTER

Insights into The PGE and Re-Os Systematics of the Lithospheric Mantle from in-situ Analysis of Sulfide Phases.

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The highly siderophile element (Platinum Group elements (PGE)+ Au+Re) form a coherent group which behave very differently to lithophile elements and thus provide a different perspective on the formation and evolution of the lithospheric mantle. In addition, the Re-Os isotopic system may provide reliable melt depletion ages. However, the distribution and behaviour of the HSE in the mantle is poorly understood. Although base metal sulfides are thought to be the main host for HSE, little attention has been paid to sulfide abundance, distribution, mineralogy and microstructural sites in mantle. Further understanding of HSE behaviour in the mantle will depend on the studies of the relationships between HSE distribution, ReOs isotope systematic, and sulfide petrographic characteristics. In-situ techniques as LA-ICPMS or LA-MC-ICPMS allow to investigate the distribution of HSE and variability of Os isotopes in mantle sulfides. The main results of these studies are: 1, the extreme variability of the chondrite-normalised HSE patterns; 2, Base metal sulfides control the PGE budget of mantle rocks; 3, The HSE patterns define two sulfide groups, which reflect also differences in major element chemistry and microstructural position. Silicate-enclosed MSS show arch-shaped primitive mantle normalised HSE patterns with low PdIr, suggesting that they are residual after melting. Unradiogenic Os isotope compositions, agree indeed with ancient melt depletion and long-term isolation from the convecting mantle. In contrast, interstitial sulfides, typically S-poor and Cu-rich have lower Os-Ir contents but high PdIr. Petrographic and geochemical features indicate that they have been metasomatically introduced. Their ^{187}Os/^{188}Os display usually radiogenic values and show variable ^{187}Re/^{188}Os. Both types of sulfide often occur in the same sample; such samples have normal sulfur contents (e.g. S< 200ppm). The in-situ analysis of PGE and Os isotopes provides crucial information on the behaviour and distribution of the HSE and on the evolution of the lithosphere. Although the in-situ Re/Os method is subject to larger errors than TIMS analysis, its spatial resolution preserves petrographic information allowing the data to be interpreted with less ambiguity. Since many of the mantle samples studied contain the two types of sulfide we therefore suggest that many of the whole-rock analyses reflect mixing between several sulfide generations. It is thus hazardous to draw conclusions on Earth formation and differentiation processes based upon whole rock PGE abundances or Os isotopes without at least basic information on sulfides. These data suggest that sulfide could become a key phase in unravelling the formation and evolution of the mantle lithosphere.

V22A-1016 1330h POSTER

Diffusion of Siderophile Elements in Iron Meteorites

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Preliminary results for diffusion of siderophile elements (Cu, Os, Pd, Re, Os, and Mo) in an iron meteorite analog were obtained at 1400°C and 1GPa from diffusion couple experiments in a piston-cylinder apparatus. Alloys were prepared by synthesizing mixtures of pure metal powders. The alloys were made from a 90 wt% Fe and 10 wt% Ni base mixture, and approximately 1wt% of the various siderophile elements was added (individually) to the same base mixture to make the doped alloys. The powders were packed in predrilled holes (1 mm dia. by 8 mm deep) in MgO cylinders, and run in a piston cylinder apparatus at 1400°C and 1GPa for 48 hours. The resulting homogeneous alloys were then sectioned into wafers approximately 1mm thick, and the faces were polished to prepare for the diffusion experiments. A diffusion couple experiment was conducted by mating a pure alloy wafer and a doped wafer, and placing the couple into an MgO capsule for pressurization and heating in the piston cylinder. The duration of the diffusion experiments ranged from 33 hours to 72 hours. Upon run completion, the diffusion couples were extracted, sectioned lengthwise, and polished for analysis. Diffusion profiles were measured using an electron microprobe. From these experiments it was found that at 1400°C and 1GPa the diffusion coefficient of Os is 1.6E-14 m^2/s, the diffusion coefficient of Re is 2.8E-14 m^2/s, for Pd it is 9.2E-14 m^2/s, for Cu it is 1.2E-13 m^2/s, and for Mo it is 2.3E-13 m^2/s.

These preliminary results raise the possibility that significant diffusive fraction of siderophile elements may occur in metal-silicate systems that fail to equilibrate fully, or under disequilibrium crystallization in pure metal systems.

V22A-1017 1330h POSTER

Platinum-Group Elements in Kerguelen Plateau Basalts: a Tale of Crystal Fractionation, the Core-Mantle Boundary, and no Sulfide Segregation.

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Basalt samples from the Kerguelen Plateau in the southern Indian Ocean (ODP Leg 183) were analyzed for major and trace elements including the platinum-group elements (PGEs: Os, Ir, Ru, Rh, Pt, Pd). PGE abundances range from 0.1 (Os-, Ir, Ru) to 5 times primitive mantle (i.e., Pt). Olivine and Cr-spinel were fractionating phases, which probably accentuated the depletion of Os, Ir, and Ru relative to Rh, Pt, and Pd in primitive mantle-normalized profiles. Primitive mantle-normalized profiles show a relatively flat transition form Pt and Pd to Y, although a slight negative Pd anomaly is present in some samples. Sulfide immiscibility has the potential to preferentially remove Pd, but would also deplete all of the PGEs relative to Y. Plots of PGE/Y vs. Y/Cu demonstrate that the Pd anomaly was not caused by separation of a sulfide-rich fluid. Downhole variation of Pt in the Site 1138 basalt sequence is similar to that of other incompatible elements demonstrating that Pt is behaving as a lithophile element and from which we infer that the magma is undersaturated with respect to S. Finally, if sulfide immiscibility had occurred, Ru/Ir ratios would increase due to the greater affinity of Ir for sulfide liquid (vs. silicate melt), but these ratios are within error of the primitive mantle value. The depletion in Pd is attributed to it being preferentially removed during secondary alteration of the KP basalts.

There seems to be very little consistent variation in PGE concentrations between ODP Sites 1136, 1137, 1138, 1141 and 1142. The PGEs in Sites 1136, 1141, and 1142 samples are generally lower in abundance than those from Sites 1137 and 1138. Overall, the PGEs in the Kerguelen plateau basalts are present in relatively high abundances. When plotted with MORBs, for example, all of the Kerguelen basalts are much higher in abundance, even though the KP basalts are derived from a much higher degree of partial melting. Most MORBs, however, appear to have experienced sulfide saturation, as evidenced a pronounced jump from Pt and Pd to Y when normalized to primitive mantle. Nevertheless, PGE abundances in the KP basalts are higher than can be produced from even an undifferentiated primitive mantle source. The elevated PGE abundances are proposed to be the result of Kerguelen plume source originating at the outer core.

V22A-1018 1330h POSTER

Kinetic Controls on the Distribution of Chalcophile Elements Between Silicate and Metal-Rich Liquids

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The partitioning of trace elements such as the Platinum-Group Elements (PGE) between finite reservoirs of silicate and sulphide or metal liquid has traditionally been described in terms of equilibrium distributions. The relative sizes of the reservoirs are expressed in terms of the ratio R=(mass of silicate melt)/(mass of sulphide melt). Application of experimentally determined partition coefficients K to genetic models for natural occurrences of PGE-rich sulphide mineralization hosted by igneous rocks has been largely successful. However, there are a number of examples of stratiform PGE mineralization (e.g., Great Dyke, Skaergaard Intrusion, Munni Munni Intrusion) where the horizons of maximum enrichment of the various PGE appear at different stratigraphic levels offset by as much as tens of meters. These instances have proven impossible to model using models of magmatic sulphide fractionation at equilibrium without proposing radical temporal variations in K and have led to considerable debate about the possible role of hydrothermal processes either in the original process of PGE concentration or in subsequent local migrations of these elements. I have derived equations describing the flux of trace elements between coexisting liquids both at rest and undergoing convection, and show that the rate at which each element is transferred between reservoirs depends on its diffusivity. In the hypothetical situation that sulphide droplets are growing from a quiescent silicate magma by diffusive transfer of FeS into the droplets, any element that diffuses rapidly compared with FeS will show near-equilibrium distributions between silicate and sulphide melt, giving the impression of having formed at high R-factor. Any relatively slow-moving element will accrue to the droplet slowly, becoming diluted by the continued rapid addition of FeS, and will apparently record a very low R-value. Accumulation of sulphide droplets at the base of a magma chamber characterized by continued slow removal of sulphide under conditions of slight sulphide supersaturation will thus cause the early stripping of more mobile PGE and base metals, followed later by the removal of the less mobile constituents. A stratiform sulphide horizon thus formed will be enriched in rapidly diffusing chalcophile elements in its lower portion and in more slowly diffusing chalcophile elements in its upper portions. Quantitative modeling of the formation of the offset PGE horizon at the Archean Munni Munni Intrusion in Australia shows that the observed offsets can faithfully be reproduced by a purely magmatic model including kinetic effects, requiring no temporal variation in partition coefficients and no participation by hydrothermal processes.