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Quiescently degassing (not exploding) volcanoes inject into the troposphere plumes that have remarkably high concentrations of ordinarily-rare, volatile trace metals. In pre-industrial times, these emissions appear to have accounted for the strong "enrichments" (relative to concentrations in crustal material or in ocean solute) of many such trace metals in the material deposited from the atmosphere. This has been shown by measuring the source strength of the emissions of metals from volcanoes, and comparing that to the amounts of the metals (excess over amounts accounted for by rock dust and sea salt) deposited onto high-latitude ice sheets: volcano degassing outputs of metals and deposition masses of metals to ice are comparable, on the basis of the masses (fluxes) and proportions of the metals, and from the proportions of lead (Pb) isotopes. There is indication that in modern industrial times the elevated trace metal fractions in the atmospheric material that has small particle size and long atmospheric residence time is still more strongly influenced by volcano emissions than by industrial emissions. Throughout earth's history it is likely that volcano emissions were a major control on the environmental background levels of trace elements, in which plants and animals evolved their tolerances to these mostly-poisonous substances.

V12H-07 1730h

Element fluxes from Copahue Volcano, Argentina

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Copahue volcano in Argentina has an active volcano-magmatic hydrothermal system that emits fluids with pH=0.3 that feed a river system. River flux measurements and analytical data provide element flux data from 1997 to 2003, which includes the eruptive period of July to December 2000. The fluids have up to 6.5 percent sulfate, 1 percent Cl and ppm levels of B, As, Cu, Zn and Pb. The hydrothermal system acts as a perfect scrubber for magmatic gases during the periods of passive degassing, although the dissolved magmatic gases are modified through water rock interaction and mineral precipitation. The magmatic SO₂ disproportionates into sulfate and liquid elemental sulfur at about 300 C; the sulfate is discharged with the fluids, whereas the liquid sulfur is temporarily retained in the reservoir but ejected during phreatic and hydrothermal eruptions. The intrusion and chemical attack of new magma in the hydrothermal reservoir in early 2000 was indicated by strongly increased Mg concentrations and Mg fluxes, and higher Mg/Cl and Mg/K values. The hydrothermal discharge has acidified a large glacial lake (0.5 km³) to pH=2 and the lake effluents acidify the exiting river. Even more than 100 km downstream, the effects of acid pulses from the lake are evident from red coated boulders and fish die-offs. The river-bound sulfate fluxes from the system range from 70 to 200 kilotonnes/year. The equivalent SO₂ output of the whole volcanic system ranges from 150 to 500 tonnes/day, which includes the fraction of native sulfur that formed inside the mountain but does not include the release of SO₂ into the atmosphere during the eruptions. Trace element fluxes of the river will be scaled up and compared with global element fluxes from meteoric river waters (subterranean volcanic weathering versus watershed weathering).

V12H-08 1745h INVITED

Sources, Fluxes and Cycling of Trace Metals on Global and Regional Scales

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The latest assessment of anthropogenic sources of trace metals globally and the results of the 2000 emission estimates for these sources are presented. Stationary fossil fuel combustion continues to be the major source of Cr, Hg, Mn, Sb, Se, Sn, and Tl with respect to the coal combustion and the major source of Ni and V with respect to oil combustion. Combustion of leaded, low-leaded and unleaded gasoline continues to be the major source of atmospheric Pb emissions. The third major source of trace metals is non-ferrous metal production, which is the largest source of atmospheric As, Cd, Cu, In and Zn. The largest anthropogenic emissions of atmospheric trace metals were estimated for Asia. This can be explained by growing demands for energy in the region and increasing industrial production. As a result, the Asian emissions are not only larger than the emissions on other continents, but also showing an increasing trend. Another factor contributing to high emissions in Asia is the efficiency of emission control which is lower than in Europe and

North America. Concerning the two latter continents, emissions of trace metals show a decreasing tendency over the last two decades. A comparison of global anthropogenic emission estimates with the global natural emission estimates suggests that anthropogenic emissions of Pb and V are by one order of magnitude higher than the natural emissions of these metals. Anthropogenic emissions are a factor of 2 to 3 higher than the natural emissions for Cd and Ni, while they are comparable for Cu, Hg, Mo, Sb and Zn. The comparison also indicates that global natural emissions of As, Cr, and Se are larger than the global anthropogenic emissions of these elements by a factor of 2 to 3. Finally, the natural sources are far more significant than the anthropogenic sources for Mn.

V12I MCC: 3010 Monday 1600h

Many Facets of Garnet: Recorders of Crust and Mantle Dynamics II (joint with T)

Presiding: D Vance, University of London; R Spiess, Universitat di Padova

V12I-01 1600h

Combined High-Precision Garnet Ages and Garnet Ionprobe Data from Granulite-Facies Migmatites and Granites -Implications for Element Redistribution During High-Grade Metamorphism and Melting

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Migmatitic and metapelitic garnet from the granulite-facies (5-6 kbar/750oC) part of the Damara orogen (Namibia) has been used to date high-grade regional metamorphism and yielded high-precision Sm-Nd grt-whole rock ages that range from 523 to 509 Ma similar to the U-Pb monazite ages (531 - 517 Ma) from the same rock. All garnet species show significant variation in Pb isotope composition, Nd/U-Th/U and U/Nd-Sm/Nd space suggesting a significant contribution of minute accessory phases (i.e. monazite and zircon). Trace element variations in the metapelite garnet show no core-rim REE variation. The negative Eu anomaly is less pronounced than in migmatite garnets. These garnets show no pronounced core-rim variations in Zr (9-6 ppm) and Sr (0.12 ppm) and moderate concentrations of Ti (30 ppm), V (40 ppm) and Cr (100 ppm) suggesting variable contributions of zircon, monazite and ilmenite during garnet growth. Garnets from in-situ migmatites show REE, Sr, Zr, Ti and Cr depletion and increasing negative Eu anomalies from core to rim suggesting the presence of a REE and HFSE-enriched granitic melt during melting. Garnets from intrusion-related migmatites show REE, Zr and Sr depletion from core to rim similar to garnet from in-situ migmatites. The decreasing negative Eu anomaly from core to rim is a result of decreasing LREE concentrations relative to HREE concentrations at constant Eu. These garnets have overall low concentrations of V, Cr and Sr similar to igneous garnets. These features suggest initial growth of garnet during in-situ melting with plagioclase present followed by growth of garnet in an intrusive trace element-depleted granitic melt. Igneous garnet is one order of magnitude less enriched in REE than the other garnet species but shows enrichment in HREE and depletion of LREE in the core relative to the rim. This igneous garnet is depleted in Sr, Zr, V and Cr compatible with the trace element-depleted nature of the host leucogranite. All garnet species show distinct (Sm/Gd)N and Eu/Eu* covariations which are discussed together with previously published trace element systematics of amphibolite-facies, granulite-facies and igneous garnets.

V12I-02 1615h

Isotope Dilution and LA ICPMS Study of Trace Elements in Garnets: Implications for Sm-Nd and Lu-Hf Dating.

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One of the main advantages of garnet geochronology is a possibility of establishing a direct link between isotopic ages and PT conditions. However, both Lu-Hf and Sm-Nd garnet dating can strongly be affected by submicroscopic inclusions capable of dominating the Sm-Nd and Lu-Hf budget. We investigated possible effects of various inclusions on Sm-Nd and Lu-Hf systems by combined isotope dilution and LA ICPMS studies. Internal isochrons obtained for 6 high-grade blocks of metabasites from the Franciscan complex yielded highly precise Lu-Hf ages ranging from 114 to 170 Ma, but failed to provide Sm-Nd dates. The main reason for failure of the Sm-Nd dating was a rather large amount of matrix silicate inclusions, which contained > 100 times more Nd than analyzed "impure" garnet fractions. The same inclusions had very limited influence on the Lu-Hf budget. This is mainly due to strong enrichment of garnets in heavy REE and due to much lower Hf concentrations in rock forming silicates. The ¹⁷⁶Lu/¹⁷⁷Hf ratios obtained for the analyzed garnets are typically between 1.5 and 8, but for two samples with spessartine-rich garnets, values range between 21 and 28 and are the highest yet reported. Small amount of zircon and rutile inclusions did not notably suppress ¹⁷⁶Lu/¹⁷⁷Hf ratios. This is mainly due to their small size (<10 μm) and low abundance, but also because of their limited dissolution during sample digestion on a hotplate. Our results demonstrate that even samples with significant amounts of inclusions can yield precise and accurate Lu-Hf dates. For upper amphibolite facies metapelites from Vietnam, we obtained well defined Sm-Nd ages of 52.1±2.5 and 31.4±1.0 Ma, which are grossly discordant with the corresponding Lu-Hf dates of 84.1±1.6 Ma and 77.9±1.6 Ma, respectively. We therefore conducted LA ICP MS measurements on 4 selected samples.

Sm/Nd ratios show rather flat zonation profiles throughout most of the crystal, with an up to 30% increase in the rims. The zonation closely follows Fe and Mn profiles. Lu/Hf ratios, on the other hand, show very large variations with low values in the rims reaching up to several hundreds in the cores and shows closer association with Y, Ca and Mg. Preservation of very strong zonation pattern of heavy REE together with Lu-Hf ages significantly older than corresponding Sm-Nd dates suggest higher closure temperature for the former system and possible inheritance problems in the analyzed samples.

Sm/Nd ratios obtained by isotope dilution for garnets leached with sulphuric acid (SAL) were only about 10% lower than those estimated by LA ICPMS. This demonstrates high efficiency of SAL leaching in purifying garnets from monazite inclusions, which is of fundamental importance for achieving reliable ages. The same leaching technique had very different influence on Lu-Hf system. Garnets with ¹⁷⁶Lu/¹⁷⁷Hf ratios >20 after leaching yielded even higher ratios after leaching. On the other hand, SAL applied to garnets with more typical ¹⁷⁶Lu/¹⁷⁷Hf ratios were brought down even by up to 50% relative to the unleached fractions. The latter case demonstrates removal of inclusions with Lu/Hf ratios higher than those in garnet. The most likely mineral with such high ratio in analyzed metabasites is apatite and in the case of metapelites- xenotime.

V12I-03 1630h

Sm-Nd Dating of Spatially Controlled Domains of Garnet Single Crystals

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Ganguly and Tirone have recently presented a method of determining the cooling rates of rocks from the difference between the core- and bulk-ages of a crystal as determined by a single decay test. We present the first application and successful test of the method using the core and bulk ages of garnet single crystals, according to the Sm-Nd decay system, in two rock samples with contrasting cooling rates, which can be constrained independently. The samples belong to the metamorphic core complex, Valhalla, British Columbia, and the granulite facies mid-crustal magmatic arc of the Salinian terrane, California. We have micro-sampled the garnet crystals over specific radial dimensions, and measured the Nd isotopes of these

small sample masses, as NdO₂ via conventional solid source mass spectrometry, to determine the Sm-Nd age difference between the core and bulk crystals. Using a peak metamorphic P-T condition of 8 kb, 820 C, the core (67.3 Ma) and bulk (60.9 Ma) ages of the British Columbian garnet sample yield a cooling rate of 8 C/Myr, which is in very good agreement with the cooling rates that we have derived by modeling the retrograde Fe-Mg zoning in the same garnet, and resetting of the bulk Sm-Nd garnet cooling age with respect to the U-Pb zircon age. Propagating the uncertainties of the inferred peak metamorphic condition, the three independent methods yield a cooling rate of 4-8 C/Myr for the British Columbian sample. The Salinian sample, on the other hand, yields indistinguishable core (78.2 ± 2.7 Ma) and bulk (77.9 ± 2.9 Ma) ages, as expected from its fast cooling history, which can be constrained by the results of earlier studies. Since the Sm-Nd decay system in garnet has relatively high closure temperature (usually more than 650 C), the technique developed in this paper fills an important gap in thermochemistry since the commonly used thermochronometers are applicable only at significantly lower temperatures.

V12I-04 1645h INVITED

The Rates and Timescales of Collisional Orogenesis; Insights From Metamorphic Monazite and the Importance of Garnet

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Much of our understanding of the processes involved in the prograde portion of the orogenic cycle comes from physical and computational models, rather than from geological observation. Although significant progress has been made in the numerical and physical simulation of orogenesis, few constraints exist that permit these models to be rigorously tested. Tools, reliant principally upon metamorphic garnet, that allow the prograde pressure and temperature history to be determined have been applied successfully to a number of orogenic systems. However, it appears the major stumbling block is the necessary time constraints. Traditional methods involve either accessory phase or rock-forming mineral chronometry. Both methods have their drawbacks, for instance, it is difficult to attach an accessory phase age to P-T, and conversely it is notoriously difficult to get precise and accurate ages from rock-forming mineral chronometers (although several new methods have proved successful). To ameliorate this situation, several workers, including ourselves, have been actively seeking methods that allow accessory phase chronometers to be linked to P-T, with particular success being achieved with monazite and xenotime. Fundamentally these methods are of two types: (i) those that are based on detailed textural and chemical studies of the samples in question, or (ii) the empirically or experimentally calibrated accessory phase thermometers. Metamorphic garnet is fundamental to both these methods. Through a combination of these approaches with *in situ* accessory mineral dating (SHRIMP, LA-MC-ICPMS) we have been able to constrain the timing of prograde metamorphism, and determine heating and burial rates for several orogenic regions, including the Asian and Indian Himalaya and the Canadian Cordillera.

V12I-05 1705h INVITED

Garnet Deformation Microstructures: TEM vs. EBSD

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The development of electron backscatter diffraction (EBSD) and orientation contrast (OC) analysis enable us to study the microstructure of minerals and to measure the orientation of all crystallographic axes in thin sections with resolution down to sub micrometer scale. One of the great advantages of this methods is that it is now possible to study cubic crystals, such as garnet, which are isotropic for light. The application of this new technique to the study of garnets revealed an unexpected wide variety of microstructures, which are

not all related to the deformation of garnet. The orientation distribution analyses help to distinguish between brittle or plastic deformation, grain or subgrain boundaries and growth defects. Garnet microstructures related to plastic deformation are characterized by the development of rotation axes if a transect across several garnet subgrains is measured with small crystallographic mismatches (< 3°) across cell boundaries. Each specific rotation axis is directly related to the activated slip system. If more than one slip system is involved, the identification of individual is not always possible. In order to fully characterize the deformation microstructure additional transmission electron microscopical (TEM) work is needed. Here we present new data on garnet deformation microstructures characterized by EBSD and TEM techniques. In some cases a connection between cell boundary and chemical composition is observed by comparing OC, BSE and element mapping. The same area is studied by analytical TEM and shows subgrain boundaries as well as indications for brittle failure with subsequent refilling of a newly grown garnet. In the case of subgrain boundaries a higher diffusivity is expected along dislocation cores. In order to get a more general view about the net effect of microstructuring of garnet, bulk diffusion calculations were performed for homogeneously distributed defects and a network of subgrain boundaries. Assuming the same enhancement of diffusion by microstructuring as in metal, garnet remains an open system for homogeneously distributed defects below 600 to 650°C at strain rates in the order of 10-12 s⁻¹. A closely spaced network of subgrain boundaries will affect bulk diffusion at even higher temperatures. Our data suggest that deformation microstructures in garnet are more frequent than previously assumed and that microstructures may significantly enhance bulk diffusion coefficients. As a consequence the microstructure of garnet must be considered when applying geo-chronological or thermo-barometrical techniques.

V12I-06 1725h

Crystallographic-Preferred Orientation vs. Shape-Preferred Orientation of Mineral Inclusions in Garnet

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Mineral inclusions in garnet are used to infer assemblages and textures that existed prior to entrapment and equilibration, and may be used to establish P-T conditions and paths. These applications rest on the assumption that inclusion shape and composition represent pre-entrapment features. If inclusions are texturally modified during syn- to post-entrapment processes, inclusion textures that appear to represent structural fabrics passively overgrown by garnet may instead represent textural and chemical interaction of inclusions with host. It is therefore necessary to determine the relationship, if any, of the crystallographic-preferred orientation (CPO) and shape-preferred orientation (SPO) of inclusions in garnet. An example of a case in which inclusion SPO might not correlate with CPO, and therefore may not represent a pre-entrapment fabric, is observed in high-grade metamorphic rocks in which the inclusions develop facets parallel to garnet crystallographic axes; that is, the inclusions are negative crystals. Because the inclusion shapes result from post-entrapment modification, the SPO defined by the facets has no meaning as a fabric indicator. Preliminary electron back-scattered diffraction (EBSD) data collected from faceted quartz and plagioclase inclusions in a sillimanite gneiss (peak T > 725 degrees C) indicate no correlation between the facet-defined SPO and the CPOs of the inclusions. Ongoing work examines the relationship between SPO and CPO for rocks representing a range of metamorphic grades and P-T-t-deformation histories.

V12I-07 1740h

Unravelling Garnet Aggregate Microstructures: Multiple Nucleation and Coalescence Versus Brittle Deformation

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Very particular garnet porphyroblast microstructures relating to a growth process that implies multiple nucleation plus grain-boundary energy minimisation driven rotation of individual garnet grains during coalescence to a single crystal (Spiess et al., 2001) have the capability to constrain the step limiting factors of reaction progress during metamorphism. Indeed, the degree of coalescence, and hence the type of microstructure that evolves by this process, relates to significantly different ratios of interface reaction rates vs. diffusion rates (Dobbs et al., 2003), and reasonably to differences in the metamorphic settings. The main importance of these coalescence microstructures might indeed be in the recognition of such interrelationships. However, similar garnet microstructures can also form by brittle deformation of a single porphyroblast, rather than by coalescence of an aggregate of individual grains. Because the implications from such deformation microstructures are totally different, there is need to unambiguously recognising their distinguishing features. We have analysed the microstructure of a garnet porphyroblast that has been deformed to an ellipsoidal aggregate of garnet grains during brittle deformation within a mylonite zone. We have used EBSD and OC to analyse the garnet substructures as well as the degree of crystallographic misorientation between adjacent grains, and we have used X-ray mapping plus quantitative EDS microchemical analysis to unravel any significant compositional zoning. The data we have obtained clearly show that coalescence microstructures are completely different from brittle deformation microstructures. Specifically, for the brittle deformed garnet porphyroblast we have observed that: 1) X-ray mapping does not reveal zoning patterns that support multiple nucleation and the setting up of growth rate differentials throughout the ellipsoidal porphyroblast domain; 2) OC images do not show substructures of microfaceted sub-domains that relate to impingement; 3) Uncorrelated EBSD data are statistically random, and the crystallographic orientation of adjacent grains do not show any tendency for a reduction in misorientation. In addition, our data also suggests that during brittle deformation fracturing of garnet to an aggregate of grains is controlled by the existing stress field, the distribution of quartz inclusions, and the crystallography of garnet. This latter aspect is also confirmed by the dispersion path of EBSD data plotted within pole figures. References: Spiess R., Peruzzo L., Prior D.J. and Wheeler J., 2001. Development of garnet porphyroblasts by multiple nucleation, coalescence and boundary driven rotations. *Journal of Metamorphic Geology*, 19, 269-290. Dobbs H. T., Peruzzo L., Seno F., Spiess R. and Prior D. J. 2003. Unravelling the Schneeburg garnet puzzle: a numerical model of multiple nucleation and coalescence. *Contributions to Mineralogy and Petrology* (published online first).

V12J MCC: 3006 Monday 1600h

Crustal and Mantle Processes in Ophiolites and Ocean Crust Generation II (joint with GP, OS, T)

Presiding: Y Dilek, Miami University;
W Bach, Woods Hole Oceanographic Institution

V12J-01 1600h

Unconformities in Slow-Spread Oceanic Crust: Implications for Spreading Processes and Dismembered Ophiolites

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Parallel studies of ophiolites and oceanic lithosphere have provided progressively more sophisticated and complex views of processes at mid-ocean ridge spreading centers. Investigations of major seafloor escarpments in slow-spread lithosphere provide tectonic windows into the geology of oceanic crust that may be interpreted in terms of spreading processes. Traditional models of oceanic crust, largely based on the internal structure of ophiolite complexes, anticipate a laterally persistent, predictable layered assemblage of rock units including the familiar sequence of pillow basalts, sheeted dikes, and gabbroic rocks overlying mantle peridotites. However, direct observations in slow-spread oceanic crust of the Mid-Atlantic Ridge commonly reveal a diverse array of crustal structures generated at a slow-spreading rate and variable magma supply. One of the most common features of crustal sections found in these settings are unconformities in which relatively fresh basaltic lavas and/or sedimentary rocks directly overlie other variably deformed and metamorphosed crustal or upper mantle rock units. Crustal sections in different areas document these types of unconformities over serpentinized peridotites, metagabbros, and lava/dike units. Despite the common exposure of relatively deep crustal and