

65.3 and 63.7 respectively were found in two microdiamonds. One Cr-spinel possesses exceptionally high Mg# of 88.5, and another has anomalously high NiO content (0.26 wt.%) and low Mg# of 58.1. Olivines with anomalously high NiO (up to 0.64 wt.%) along with relatively low forsterite (Fo 86-89) were also detected. Wehrlitic pyrope-uvavovite garnet of unique composition (Cr₂O₃ 13.5 wt.%, CaO 12.1 wt.%) was found in one microdiamond. Two microdiamonds contain unusual E-type garnets, one with 17.1 wt.% CaO and another with exceptionally low Mg# of 30. Both these compositions plot outside of E-type garnet inclusions field (Meyer, 1987). We conclude that mineral inclusions in microdiamonds are more variable in their compositions compared with inclusions in macrodiamonds. This feature may be related to the specific composition of a part of microdiamonds source.

V12C-1005 1330h POSTER

Syngenetic Diamond Mineral Inclusions: Are They Really?

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Diamonds are time capsules containing mineral inclusions from long ago and far away. The major assumption made in almost all studies of diamond inclusions (DIs) is that they are formed at the same time and by the same process as the host diamond - i.e., syngeneis. Evidence in support of such an assumption is usually omitted or weak at best. However, recent studies have documented extreme chemical variations of multiple DIs in individual diamonds (Sobolev et al., 1998, *Intl Geol Rev*; Taylor et al., 2000, *Intl Geol Rev*) that are contrary to derivation from a fractionating melt, and which are definitely not of a syngenetic origin. Indeed, the criteria for syngeneis are weak and not unambiguous.

To further investigate this issue of syngeneis, garnet mineral inclusions in unusually large diamonds (~20-108 carats) from Udachnaya, Mir, and Aikhal kimberlite pipes of Yakutia were analyzed for major and trace-element compositions. The most striking chemical feature is the sinusoidal REE patterns of harzburgitic garnet DIs, similar to those reported widely in the literature. Such sinusoidal REE patterns suggest a garnet petrogenesis that began with a partial-melting event, followed by metasomatic enrichment, particularly in REEs. Equilibration with the metasomatic fluids was established with respect to the LREEs in the garnets, whereas the M-HREEs were only partially re-equilibrated due to their slower diffusion rates. Negative anomalies of Ba and Sr in the garnets indicate that the fluids were not carbonatitic. The host diamonds must have grown after these events.

There is a large amount of evidence that effectively demonstrates that diamonds and their mineral inclusions in many, if not most, cases did not form at the same time, definitely not by the same processes. This casts serious doubts on the universal axiom in the literature that diamonds and their DIs are syngenetic. Interpretations based largely on 'assumed syngenetic relationships, therefore, require serious re-evaluation.

V12C-1006 1330h POSTER

In-Situ Chemical Analyses of Mineral Inclusions in Diamonds in Kimberlitic Eclogites From Yakutia

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Mineral inclusions in diamonds (DIs) are stated to provide P-T-X-t information regarding the formation of the diamonds and the nature of the upper mantle. In an endeavor to further understand the importance of diamonds and their DIs in relation to their host rocks,

we have investigated several diamondiferous eclogites from Yakutia, first by HRXC tomography (Taylor et al., 2001, this meeting) and then by dissection of the eclogites into their individual minerals. The mineralogy of the host eclogite is presented by Misra et al. (2001, this meeting).

Two of the diamondiferous eclogite xenoliths, although weighing but 66 g and 42 g, contain 74 and 47 macro-diamonds, resp. Based on HRXC imaging, appropriate sections were selected in the eclogite to extract diamonds with minimum loss of material. In the majority of cases, diamonds occur as perfect octahedron with well developed crystal faces. In some cases, however, diamonds occur as macles (twinned xls). The size range of the diamonds is 1-6 mm. Optical examination reveals the sulfides as the most common DIs in these diamonds, followed by clinopyroxenes and garnets. Each diamond was cut and polished along relatively soft directions parallel to either (001) or (110) faces so as to expose DIs for *in-situ* analyses. Examination by cathodoluminescence (CL) on an EMP demonstrated that the majority of the diamonds have minute, optically invisible, cracks from the DIs to the surfaces of the diamonds - i.e., the possibility of an open system. These diamonds show complicated growth histories and contain DIs that are in some cases, found to be associated with secondary alteration. In addition, the DIs in each diamond, examined *in-situ* are of different composition from the host and different from DIs in other diamonds, a relationship reported earlier (Taylor et al., 2000, *Intl Geol Rev*).

These observations raise serious doubts about the significance of DIs and the *pristinity* and *syngeneis* of DIs removed by the typical *diamond crushing* procedure. Therefore, extreme caution must be taken when interpreting any of the P-T-X-t conditions of diamond growth, based on DIs.

V12D MC: Hall D Monday 1330h Hydrothermal Systems

Presiding: P Larson, Washington State University

V12D-1007 1330h POSTER

Oxygen isotope evolution of the lower ocean crust: an in-situ study by UV-laser-ablation oxygen isotope microprobe

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Systematic analysis of mineral oxygen isotope compositions in gabbro has the potential to constrain the effects of cooling processes in the lower ocean crust. For this reason we measured three representative samples of gabbro from Hole 735B of Leg 176 by UV-laser microprobe for the oxygen isotopic compositions of their constituent minerals. Sample 28, from 514.79 mbsf, is located between two cataclastic faults, with both high and low temperature alteration; sample 1 (880.31 mbsf) is within a high-temperature deformation zone, and sample 16 (1402.16 mbsf) is in the lower part of the core, which is far away from both the crystal-plastic shear zone or from any fault. The measured results show that respective minerals in the three samples have very similar $\delta^{18}\text{O}$ values, although their geological settings and whole rock $\delta^{18}\text{O}$ values are quite different. Clinopyroxene and olivine have normal values for NMORB, $+5.5 \pm 0.4^\circ/\text{oo}$ and $+5.2 \pm 0.3^\circ/\text{oo}$ respectively, while plagioclases have heavier $\delta^{18}\text{O}$ values ($+6.6 \pm 0.3^\circ/\text{oo}$) than that of plagioclase in NMORB ($+6.0^\circ/\text{oo}$). This suggests that all three gabbros have encountered similar cooling histories from one source magma by a single intrusion. The large inter-crystal $\delta^{18}\text{O}$ difference in sample 28 between the unaltered plagioclase with $\delta^{18}\text{O}$ values about $+6.0^\circ/\text{oo}$ and the altered ones with $\delta^{18}\text{O}$ values about $+7.6^\circ/\text{oo}$ is most probably due to low temperature alteration by seawater. Considering the unaltered constant $\delta^{18}\text{O}$ values of olivine and clinopyroxene, the modification of the O-isotope composition of plagioclase must occur near the time of crystallization and the temperature should be higher or equal to the closure temperature for O-isotopes in plagioclase but lower than that for olivine and clinopyroxene.

V12D-1008 1330h POSTER

Petrology of a Calcic Skarn from Al-Madhiq, SW Saudi Arabia

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A new skarn occurrence, located in the SW Arabian shield in the country rocks of Neo-Proterozoic age, displays features typical of calcic skarns that host W-deposits. It is an exoskarn of the proximal type related to a granitoid contact with the regional rocks of mixed sedimentary and volcanic derivation. The skarn minerals include both the prograde (brownish red grossular, hedenbergite, aluminian sphene, albite), and retrograde (epidote, quartz and hornblende) assemblages. Grossular composition reflects a mildly reduced genetic environment. The garnet components range: grossular, 58.27 - 83.54 %; andradite, 6.5 - 21.6 %; uvarovite, 0 - 0.15 %; pyrope, 0 - 0.47 %; almandine, 4.33 - 18.75 %; spessartine, 0.4 - 8.58 %. A step-scan across a grossular crystal showed the sympathetic decrease of Mn and Fe in the core, concomitant with Ca decrease towards the rim. This variation trend deviates from the generally-known Fe-decreasing and Mn-increasing inwards trend of most metamorphic and igneous garnets. The aluminian sphene composition resembles that described only recently from the low-pressure calc-silicates.

V12D-1009 1330h POSTER

Decline of a Hydrothermal Vent Field Escanaba Trough 12 Years Later

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Hydrothermal venting was discovered in Escanaba Trough, the southern sediment-covered portion of the Gorda Ridge, in 1988. Large pyrrhotite-rich massive sulfide mounds are abundant at each of the volcanic/intrusive centers that have been investigated in Escanaba Trough, but the only area of known hydrothermal venting is the NESCA site along the ridge axis at 41°N. Hydrothermal fluids venting at 217°C and 108°C were sampled in 1988 on two sulfide mounds separated by about 275 m. The end-member fluid compositions were indistinguishable within analytical errors. Several sulfide mounds were observed in 1988 which had diffusely venting low temperature (< 20°C) fluids that supported extensive vent communities dominated by fields of Ridgia.

Nine holes were drilled in the NESCA area in 1996 on ODP Leg 169, including Hole 1036I that penetrated to basaltic basement at 405 m below sea floor (mbsf). Surveys of the area using the drill string camera located only one area of active venting at the same mound where 217°C vent fluids were sampled from two active vents in 1988. Drill hole 1036A was spudded between the two active vents on this sulfide mound (approximately 4 and 8 m away) and penetrated to 115 mbsf.

The NESCA site was revisited in 2000 using MBARI's *R/V Western Flyer* and *ROV Tiburon*. The hydrothermal vents appeared essentially identical to observations made from the drill string camera in 1996 despite the presence of a drill hole within meters of the two vents. The maximum vent temperature measured in 2000 was 212°C. Fluid samples have major element and isotopic compositions very similar to those collected in 1988. The vent fluids have higher methane (~19 mmol/kg) than those from the geologically similar Middle Valley vent field, but lower values than those at Guaymas Basin. Drill hole 1036A was weakly venting, but the diffuse hydrothermal fluids could not be sampled with the equipment available. The walls of the drill hole were colonized by palm worms, limpets, and snails. Four other drill holes showed no hydrothermal flow nor visible evidence of down hole recharge.

Mapping with Tiburon confirmed that the extent of hydrothermal venting at NESCA decreased dramatically since 1988. Formerly extensive colonies of Ridgia had vanished leaving no trace of their presence. Although hydrothermal venting has collapsed to a single mound, the temperature and composition of the fluids remained nearly unchanged. This is curious given that

sediment pore fluids analyzed on Leg 169 included both high salinity and low salinity components of phase separated hydrothermal fluids in the shallow subsurface indicating that the hydrothermal field must have had a relatively recent (relative to the rate of pore fluid diffusion) high temperature history. Hydrothermal fluids presently venting at this site must be derived from an essentially homogeneous, approximately 215fluid reservoir that has declined in its fluid output on a decadal scale, but has not undergone significant changes in temperature and composition. Venting at the seafloor does not seem to have been affected by drilling in the hydrothermal field.

V12D-1010 1330h POSTER

Using SEM and EDS Data to Evaluate the Evolution of Secondary Minerals in Incipiently Altered Volcanic Rocks of Southeast Guatemala

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Secondary processes such as weathering and hydrothermal alteration are known to affect the geochemistry of volcanic rocks following emplacement. Data suggest that even at the earliest stages of these processes, secondary products such as clays and zeolites develop. These secondary minerals may serve as the host for trace elements that are mobilized from the glassy matrix and primary minerals. Phenocrysts exhibiting different degrees of weathering were compared using EDS scans and secondary-electron imaging, in order to better characterize the secondary products, and their role in element mobility.

Three geologic units from Tecuamburro volcanic complex in southeast Guatemala were sampled to examine secondary mineral formation in incipiently weathered rocks. The samples range in age from 0.8 to 2.6 Ma and in composition from basalt to dacite. Samples are petrographically characterized by plagioclase, pyroxene, and oxide phenocrysts, and a glassy groundmass containing microlites similar to the phenocrysts. Each hand sample (approx. 10-20cm diameter) was divided into 3 zones: core, intermediate, and rind.

In core plagioclases, EDS data show no obvious variation in Ca-Si ratios across the grains. Accessory phases such as phosphates and Fe-Ti oxides are also present, and randomly distributed in the core plagioclase grains. Secondary-electron images of a plagioclase from the core reveal fractures already filled with secondary material (e.g. clays). Core pyroxenes contain Fe-Ti oxides both randomly distributed throughout the grains, and along fractures and cleavages. In the intermediate zone, the edges of plagioclase grains are depleted in Ca relative to the grain centers. Fractures in the intermediate plagioclases contain Fe-Ti oxides along with clays, while pyroxene fractures contain both Fe-Ti oxides and phosphates. In the rind, plagioclase Ca-Si ratios vary greatly within individual grains. These variations are interpreted as secondary when contrasted with the homogenous core plagioclase grains. Fractures in rind pyroxenes contain kaolinite, and Fe-Ti oxides are abundant in fractures and along grain edges. Phosphates in the rind are uncommon, and are not associated with either plagioclase or pyroxene. Secondary images of a rind plagioclase show etch pits, clay minerals in fractures and on the surface, and possible zeolites along large fracture walls.

The nature and abundance of secondary material does increase within the profile of these incipiently weathered rocks. However, even the relatively fresh cores contain clays and oxides in fractures. Ca-Si ratios in plagioclase grains dramatically change from core to rind, and strongly suggest alteration. Clays, oxides, and phosphates are common in fractures and edges of phenocrysts from the intermediate zone. Fractures in the grains from the rind contain abundant clays and oxides. The occurrence of secondary phases even in the least altered samples leads us to believe that trace elements may also be mobile at these early stages of alteration. Further study of the early-forming secondary phases will clarify their role in the mobility of these elements.

V12D-1011 1330h POSTER

Geochemistry of Metals from mine tailing in Taxco Mexico

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The mining district of Taxco in Central Mexico has been exploited since prehispanic times. The processing of metals produced tailings with high heavy metal concentrations. Those tailings constitute a potential risk to the environment. To assess the effects of the mine tailing on water quality, tailing samples and water samples from rivers, wells and tailing effluents were collected and analyzed for Cu, Zn, As and Pb. Metals were analyzed with by ICP-MS. Tailing samples were leached with water to determine pH and sulfate concentration. The highest metal contents were found in the samples with a pH acid. As, Pb and Zn are over the drinking water standards in some of the water samples.

V12D-1012 1330h POSTER

Isotopic Studies of Gypsum in the Macquarie Island Ophiolite: Tracing Hydrothermal Reactions

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The O, S, and Sr isotopic compositions have been determined for 17 samples of gypsum from the sheeted dike complex of the Macquarie Island Ophiolite to trace chemical reactions during hydrothermal recharge. Macquarie Island is a sliver of N-MORB ocean crust tectonically exposed on the Australian-Pacific plate boundary. The gypsiums have $\delta^{18}O$ values of 12.5-14.4‰, which precludes formation from meteoric water and confirm their formation, initially as anhydrite, from seawater fluids beneath the seafloor. The gypsiums have elevated $\delta^{34}S$ values (26.2-29.0‰) compared to seawater (21‰), as the result of sulfate reduction. If in oxygen isotopic equilibrium with normal seawater the minerals formed at temperatures of 137-158°C. At these temperatures, inorganic sulfate reduction is kinetically inhibited, and fractionation between sulfate and sulfide is too large (~35‰) to yield ^{34}S -enriched hydrothermal sulfide in the dike wall-rocks. The gypsiums have $^{87}Sr/^{86}Sr$ ratios of 0.70446-0.70524 reflecting highly reacted solutions compared to modern seawater (0.7092). Kinetic effects on oxygen isotopic exchange in sulfate or ^{18}O -depletions of the fluid resulting from water-rock interactions would decrease the calculated formation temperatures of gypsum, and could put temperatures in the range where microbial sulfate reduction could occur. In this scenario, formation waters residing in the volcanic section at temperatures of ~100°C underwent significant seawater-rock interaction and sulfate in solution was reduced to sulfide by microbial activity. Supporting evidence includes negative $\delta^{34}S$ values of sulfide minerals in the lavas, consistent with microbial sulfate reduction there. Tectonic activity at the spreading ridge allowed ingress of evolved formation waters from the lavas into hot dikes, and resulted in precipitation of anhydrite during heating of these fluids. Anhydrite was hydrated to gypsum as the dikes cooled during subsequent aging of the crust. Alternatively, anhydrite may have formed within the dikes by a complex process of mixing high-temperature hydrothermal fluids with cooler seawater fluids.

V12D-1013 1330h POSTER

O and H Isotope Ratios of Syenite Blocks in the El Abrigo Ignimbrite, Tenerife, Canary Islands: A Hydrothermal Fingerprint for Assimilation

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As part of an ongoing project investigating assimilation in ocean island magmas, we are measuring stable isotope ratios of hydrothermally altered lithic fragments in phonolitic pyroclastic deposits from Tenerife, Canary Islands. Nepheline syenite blocks occur in the 0.196 Ma El Abrigo ignimbrite of the Diego Hernandez Formation (DHF). The DHF is the most recent of at least three caldera-forming magmatic cycles on Tenerife. The blocks are fragments of evolved plutons that are chemically similar to phonolites but extend to more strongly differentiated compositions. Distinct major and trace element concentrations suggest that the blocks derive from two intrusions, here referred to as A and B. The B syenites have chemical affinities with the El Abrigo phonolite, and some blocks contain small pockets of residual glass, suggesting that the B pluton may have been coeval with the El Abrigo magma. O isotope ratios of the B syenites lie within the range 4.8 to 7.0 per mil. The B samples are mostly fresh, and their higher O isotope ratios are near pristine magmatic values. Lower values occur in rocks with mild hydrothermal mineralogical alteration, and their values reflect limited high-temperature water-rock isotope exchange. O isotope ratios for A blocks are lower (0.1 to 6.3 per mil, most less than 2.0 per mil), and some samples show extensive mineral alteration. Near-uniform alteration among the A samples, distinct major and trace element compositions, and lack of glass show that this syenite was older than, and unrelated to, the El Abrigo magma. Syenite D/H ratios range from 90 to 120 per mil. O vs H isotope relations indicate that an ^{18}O -depleted meteoric water was the most important reservoir for the high-temperature hydrothermal fluid. Assimilation of altered syenite should provide a distinct stable isotope fingerprint that would be inherited by the product magma. DHF phonolites yield O ratios in the range 5.5 to 7.0 per mil, which may be this fingerprint. Assimilation of variably altered syenites, with accompanying fractionation, is a viable mechanism for producing this stable isotope variability in the magmas.

V12D-1014 1330h POSTER

Arsenic Fractionation in Tailing Piles in Zimapán, Hidalgo, México

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Zimapán, Hidalgo, is located in a semi-arid region in the central part of México and has been one of the main mining districts of this country.

As a result of the mining activities, residual material has been deposited in the surroundings of town. Arsenic ground water pollution has been reported produced by natural and anthropogenic sources. X-ray diffraction showed presence of sulfide minerals in tailing piles, such as arsenopyrite.

To determine the arsenic mobility, samples from tailings were analyzed by sequential extraction procedure. Arsenic was determined on extraction solutions at each step by HG-AAS. The extraction was done with different chemicals to determine As exchangeable, As bound to carbonates or specifically adsorbed, As bound to Fe-Al oxides, As bound to organic matter and sulfides, and As residual. Most of the arsenic was contained in the Fe-Al oxides a residual fractions. Nevertheless The As content in the exchangeable fraction was found to be of environmental risk.

V12D-1015 1330h POSTER

Factors to be Considered in Long-Term Monitoring of a Former Nuclear Test Site in a Geophysically Active and Water-rich Environment

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The US Department of Energy (USDOE) is currently undertaking an ambitious program of environmental remediation of the surface of Amchitka Island

in the western Aleutians, where three underground nuclear tests were conducted during 1963-1971. Among these tests was Cannikin, at approximately 5 megatons the largest nuclear device ever exploded underground by the United States and equivalent in seismic energy release to a magnitude 7 earthquake. The blast caused about 1 m of uplift of the Bering Sea coastline in the 3-km-wide fault-bounded block within which it was detonated. The impending final transfer of stewardship of this area to the US Fish and Wildlife Service as part of the Alaska Maritime National Wildlife Refuge raises anew the question of the potential for transport of radionuclides from the shot cavity, located at 1791 m depth in mafic lahatic breccias, into the accessible environment. In particular, there is concern about whether such contaminants could become concentrated in the marine food chain that is used for subsistence by Alaskan Natives (and by the broader international community through the North Pacific and Bering Fisheries). Both possible transport pathways in the form of faults and transport medium in the form of abundant water are present.

Since the pre-plate tectonics paradigm days of active testing, the scientific community's understanding of the tectonic context of the Aleutian Islands has grown tremendously. Recently, the first direct measurements of motion within the arc have been made. How this new understanding should guide plans for long-term monitoring of the site is an important question. Convergence due to subduction of the North Pacific plate beneath North America ranges from near-normal at the Alaska Peninsula and eastern Aleutian islands to highly oblique in the west. Amchitka itself can be seen as a subarcial portion of a 200-km-long Rat Island arc crest segment. This fragment has torn from the Andreanof Islands to the east at Amchitka Pass and has rotated 25 degrees clockwise about a pole near Kiska Volcano, in the right-lateral shear of the western arc. The island is cut by ENE trending normal faults that are down-dropped to the northwest and reflect arc-parallel extension. Quaternary-age normal faulting decreases in intensity northwestward from Amchitka Pass, but is nevertheless present in the vicinity of and was activated by the nuclear tests. Westward translation of the island is probably more than the rate of 1 cm/year measured at Unmak Island 900 km to the east, and less than 3 cm/year measured at Attu 400 km to the west. The University of Alaska is receiving support under the USDOE-funded CRESPII program (Consortium for Risk Evaluation with Stakeholder Participation; IRM, New Brunswick, NJ.) to develop a research plan leading to long term stewardship of the site in collaboration with key researchers and stakeholders. A GPS network was established by us to define movement of and deformation within Amchitka; the present state of test-induced ground fractures, up to 2 km in length and 5.7 m in vertical displacement, was documented; and deep core samples from the shot region, acquired 30 years ago, were shipped to the mainland for further analysis.

V12D-1016 1330h POSTER

The Influence of PH and Oxygen Fugacity on the Hydrothermal Transport of Pb and Zn by Carboxylate Complexes.

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A chemical model was developed to evaluate the influence of log p H conditions on Pb and Zn complexation by acetate and malonate in 100°C basinal brines with bulk chemical compositions similar to diagenetic ore fluids and modern petroleum-field brines of moderate salinity (TDS = 180 g L⁻¹). In the model composite brine, acetate with a concentration of 7,700 mg L⁻¹ (0.13 m) represents the major monocarboxylate ligands detected in basinal brines, while malonate with a concentration of 300 mg L⁻¹ (0.0029m) represents the dominant dicarboxylate ligands. Total Pb and Zn concentrations (constrained by galena and sphalerite solubility, respectively) and Pb and Zn speciation were calculated as a function of log and pH for the model composite fluid.

The 1.0 and 10 ppm isopleths of total Pb and total Zn in carboxylate (acetate + malonate) complexes illustrate that the ore fluid of Giordano (1994) for red-bed related base metal deposits and Anderson's (1975) Mississippi Valley-type ore fluid are potentially capable of transporting sufficient amounts of Pb and Zn in the form of carboxylate complexes to form economic deposits of Pb and Zn. Both of these fluids are oxidized, have very low total reduced sulfur, and have pHs in the range 5.5 to 6.5. On the other hand, the reduced ore fluid models of Sverjensky (1984) (projected to 100°C) and Giordano and Barnes (1981), both for Mississippi Valley type deposits, can at best transport amounts of Pb and Zn as carboxylate complexes that are many orders of magnitude below the 1 to 10 ppm minimum required to form economic deposits. The speciation results show that the log p H conditions most favorable for carboxylate complexation are the same conditions under which chloride complexation dominates Pb and

Zn speciation. Furthermore, the results show that basinal brines and related ore fluids characterized by temperatures near 100°C, high oxidation states (i.e., low total reduced sulfur), and high but reasonable concentrations of carboxylate anions can mobilize up to 3 percent of the total Pb and up to 1.3 percent of the total Zn as carboxylate complexes. These percentages, under the most favorable conditions, correspond to approximately 1 to 100 ppm of those metals in solution; concentrations that are adequate to form economic deposits of these metals. However, the field evidence from modern petroleum-field brines suggests that these optimal conditions, at 100°C, for carboxylate complexation are rarely met.

V12D-1017 1330h POSTER

Mineralogy and Geochemistry of Vanadium-Bearing Black Shales at Zhangcun and Zhengfang, Eastern Jiangxi Province, China

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As a member of Hetang Formation, lower Cambrian, the Zhangcun-Zhengfang vanadium-bearing black shales are spread in the sea basin outside of the Ancient Jiangnan Island Arc. The composition of black shales is silicite + siltstone + detrital carbonate. A large amount of hyalophane has been discovered in the shales and the hyalophane-rich rock is the major type of vanadium-host rock. The barium content in the hyalophane is up to 18.91%. The vanadium mainly exists in vanadiferous illite and several Ti-V oxides, possibly including a new mineral. The chemical formula of this kind of Ti-V oxide is V₂O₃nTiO₂, n=49, according to the electronic microprobe studies. The micro X-ray diffraction studies show the new mineral may be triclinic. The shales are rich in Ba, K, V and contain only trace Na and Mn while all the compositions of the shales except carbonate have a low content of Mg and Ca. According to the authors study, V obviously has a relationship with Ba and Se, which are from the volcano or hydrothermal activities, and the basic elements Cr, Co, Ni, Ti and Fe. It may present that they are from the same source. Thus, it seems that they are not from the normal sedimentary environment and may be from the hydrothermal deposition. The REE models show that silicite may be the hydrothermal deposit that does not mix with seawater while the REE models of hyalophane-rich rock is similar to some modern hydrothermal deposits in the seafloor. The subtle negative anomaly of Yb may reflect the REE model of basalt in the seafloor.

The geology and geochemistry of the shales indicate that the shales may be of hydrothermal genesis. Silicite may be the typical pure hydrothermal sediment and hyalophane-rich rock may be the product of hydrothermal activity while the hydrothermal fluid passes the continent source material in the sedimentary process. V, Ti, Ba and Si may be from the volcanic rock in the seafloor and the Al and K may be from the continent.

V12D-1018 1330h POSTER

Formation of Hydrothermal Vents in Volcanic Basins: the Karoo Basin, South Africa

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Injection of magmatic melts in sedimentary basins leads to rapid heating of the intruded sediments and their pore fluids. Numerical modeling of the temperature and fluid pressure fields around a magmatic sill shows that boiling of pore fluids may cause it to rise explosively towards the surface shortly (a few years) after sill emplacement. This fluid expulsion may be associated with fluidization of sediments and hydrothermal vent formation.

The Paleozoic Karoo Basin was intruded by voluminous basaltic melts at ca. 183 Ma. The basin

is a unique natural laboratory to study the formation and effects of hydrothermal systems as the entire sedimentary and intrusive volcanic succession is exposed. Planar sill intrusions are identified in the deep sequences (Ecca Group), whereas transgressive sheets and rings are common in intermediate sequences (Beaufort Group). The upper sequences (Stormberg Group) are characterized by few intrusions and numerous hydrothermal vents.

Recent fieldwork has focused on mapping the structures and morphology of the hydrothermal vents in the Karoo Basin. The vents range from being almost purely volcanic to almost purely sedimentary. Sand-rich hydrothermal vents represent positive erosional remnants with inward dipping surrounding sedimentary strata. Numerous potholes and sandstone dikes suggest mobilization of sediments towards the palaeosurface. Microcrystalline pore-clogging silica is associated with these potholes, suggesting precipitation from a silica-oversaturated fluid. Petroleum shows and calcite-asphaltene veins are further found in a few hydrothermal vents. The presence of very high pore fluid pressure during the volcanic phase is documented by the identification of partly molten sandstone veins and dikes in the dolerites sills located below the hydrothermal vents.

Seismic data from the Vring and Mre volcanic basins in the Norwegian Sea show abundant circular, eye-shaped reflections near the top-Paleocene time horizon. We interpret these features as hydrothermal vents similar to the ones identified in the Karoo Basin. The seismic data reveal that the hydrothermal vents are always located above the termination of sills that were intruded prior to, and during, continental breakup in the NE Atlantic.

We propose the following model based on the fieldwork, seismic interpretation and numerical modeling: 1) intrusion of magma leads to heating, and locally boiling, of pore fluids in the intruded sediments; 2) increased fluid pressure may cause hydrofracturing likely starting at the tip of the intrusion; 3) fluid decompression may lead to an explosive hydrothermal eruption at the paleosurface, forming a hydrothermal vent; 4) the fracture system created during the explosive phase is later re-used for circulation of hydrothermal fluids during cooling of the magma; and 5) the hydrothermal fracture system can later be re-used as fluid migration pathways as shown by the high permeability of hydrothermal vents drilled in the Karoo Basin and the presence of seismic seep anomalies above hydrothermal vents in the Norwegian Sea.

V12D-1019 1330h POSTER

Hydrogeochemistry of geothermal waters in the Magusan and Bugok area, southern part of Korea

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Hydrogeochemical and environmental isotopic studies of geothermal waters in the Bugok and Magusan area were conducted to understand the subsurface evolution of geothermal system in South Korea. Hydrochemically, the Bugok thermal waters (BTW; outflowing temperature = 45.8-78.0 degree in centigrade) belong to the Na-SO₄ type, whereas the Magusan thermal waters (MTW; 27.5-54.8 degree in centigrade) represent the Na-Cl type. Peripheral groundwaters (17.2-22.4 degree in centigrade) in both areas belong to the Ca-HCO₃ type. Both BTW and MTW show a good correlation between TDS and SiO₂ content. The thermodynamic calculation using SOLVEQ indicates that all the BTW and MTW are saturated or supersaturated with respect to albite, quartz, calcite, kaolinite, anorthite, muscovite and paragonite, and are under-saturated with respect to gypsum, anhydrite and chalcidony. A good correlation among in-situ temperature, oxygen (and hydrogen) isotope values, and tritium content is observed for BTW and MTW. The high chlorine concentration of MTW reflects the substantial mixing of paleoseawater in the geothermal system, as also suggested by Na, Br, SO₄, and Cl concentrations. We propose a hydrogeochemical model for MTW, which includes the paleoseawater mixing and addition of sedimentary SO₄ by water-rock interaction during the descent of meteoric recharged water and the calcite dissolution and successive CO₂ degassing during the ascent of heated waters. In the case of BTW, we propose an alternative model which includes complex processes such as the recharge of meteoric waters at higher elevation,

the prolonged water-rock interaction including the dissolution of sedimentary (evaporitic?) sulfates, the reduction of sulfate to form H₂S, the CO₂ degassing and associated calcite precipitation, and the re-oxidation of H₂S to SO₄. We consider that the geothermal system responsible for both MTW and BTW are located nearer to a deep heat source, compared to the other geothermal systems found in South Korea. The application of silica and various cation geothermometers as well as multi-component geochemical modeling suggests the temperatures of a deep thermal reservoir of up to about 120 to 130 degree in centigrade. Accordingly, a potential geothermal anomaly (40-85 mW/square meters) is expected to exist beneath the Magumusan and Bugok area.

V12E MC: 304 Monday 1330h

Trench to Subarc: Diagenetic and Metamorphic Mass Flux in Subduction Zones (GERM/MARGINS Subduction Factory Session) II (joint with OS, T, MR)

Presiding: G E Bebout, Lehigh University; J Ryan, University of South Florida

V12E-01 1335h

Comparative Thermal Structures of Circum-Pacific Subduction Zones

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Subduction zone thermal structure influences Benioff Zone (BZ) seismicity, slab dehydration/metamorphism, geochemical fluxes, and arc magma production. To evaluate effects of relative differences in slab-surface temperature (SST), we have simulated thermal structures of ten circum-Pacific cross-arc transects (Andean, Central American, Cascades, E Aleutian, Kurile, NE Japan, and Mariana arcs) showing large variations in slab age (9-134 Ma), convergence rate (2-10 cm/yr), duration (40-226 Ma), slab length (200-1200 km), and slab geometry.

A finite-element method was used to simulate mantle convection and a finite-difference solver used to compute heat transfer. A staggered grid for discretization enhanced accurate modeling of mantle convection. All models assume realistic curved slab geometries as constrained by BZ earthquake hypocenters. Shear-heating is evaluated using rheology of wet quartzite to simulate the presence of a veneer of subducted sediment near upper slab surfaces. Error propagation analysis indicates that the major uncertainty in SST profile is associated with (1) uncertainty in thickness of the overriding lithospheric plate, which determines the size of the convecting wedge domain, and (2) shear-heating contributions. Assuming constant lithosphere thickness (100 km), we estimate a nearly two-fold range in SST (300 to 600 °C) at BZ depths below the respective volcanic fronts. Moreover, for most transects similar SSTs (800±50 °C) are predicted at depths of the deepest BZ earthquakes. Even where slow subduction of young slabs occur, Ts approaching the wet solidus of oceanic crust or sediments are predicted only if the lithospheric lid is relatively thin or there is very strong shear-heating. Thus, we consider direct melting of subducted materials unlikely in any of the model transects.

Assuming that highly fluid-mobile B is derived largely from subducted slabs, B-enrichment data help constrain our thermal models. We show that B-enrichment (e.g., B/Zr ratios) in arc volcanic rocks is anti-correlated with SSTs at 100 km depth. This relation is consistent with progressive loss of fluids and fluid-mobile elements as descending slabs warm, and with variation in slab thermal structure from arc to arc.

V12E-02 1350h INVITED

Quantification of Subduction Zone Metamorphic Devolatilization From Computed High Pressure Phase Equilibria

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Devolatilization in subduction zones is essential to arc magmatism, seismicity and volatile recycling. A premise of our research is that realistic modeling of metamorphic devolatilization of subducted lithologies is only possible with phase equilibria for chemical systems that closely approximate actual bulk compositions. Volatile components are introduced into subduction zones by three contrasting lithologies: marine sediments, and hydrothermally altered mantle ultramafic rocks and oceanic metabasalts. Using free energy minimization (Perplex programs - web address: erdw.ethz.ch/~jamie/perplex), phase equilibria were computed to 6 GPa (~160 km) to quantify the evolution of CO₂ and H₂O by prograde metamorphism of these lithologies. Geotherms for NW and SE Japan [1] were adopted as thermal extremes along the tops of subducted slabs. The following summarizes our conclusions regarding the correlation between the depth of devolatilization, bulk rock composition and P-T locations geotherms. Serpentinites: for carbonate-bearing serpentinites (ophicarbonates) little CO₂ is released; for high-temperature (high-T) geotherms complete dehydration occurs under forearcs, and for low-temperature (low-T) geotherms major dehydration occurs under subarcs. Siliceous limestones: little devolatilization for all geotherms. Marls: with high-T geotherms devolatilization is complete under subarcs; in contrast, little devolatilization occurs with low-T geotherms. Carbonate-free pelites and turbidites: with high-T geotherms most dehydration occurs under forearcs, whereas along low-T geotherms substantial H₂O is released under subarcs. Carbonate-bearing oceanic metabasalts: decarbonation is negligible along low-T and intermediate-T geotherms and is limited along high-T geotherms; dehydration is complete under forearcs for high-T geotherms, significant under subarcs for intermediate-T geotherms, and very limited along low-T geotherms. Carbonate-free oceanic metabasalts: dehydration is complete under forearcs for high-T geotherms, and widespread under subarcs for intermediate-T and low-T geotherms. Metamorphic devolatilization of subducted metabasalts and metasediments is continuous; thus, we do not expect pulses of fluid release (corresponding to univariant devolatilization) for these lithologies. Our study emphasizes that because of differences in the bulk compositions of volatile-bearing lithologies and in the P-T location of geotherms, generalized modeling of subduction zone volatile recycling is questionable.

References: [1] Peacock, S.M. and Wang, K. (1999) Science, 268, 937-939.

V12E-03 1410h

The influence of subduction zone thermal structure on arc magma chemistry: B and fluid-mobile elements

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It is postulated that contents of B and other highly fluid-mobile elements (HFMs) in primitive arc lavas are sensitive to thermal structures of subducting slabs (sensu lato), which are the principal sources for these elements in subduction zones. Initial slab HFM inventories may be variably depleted in proportion to progressive fluid release as a consequence of gradual warming and metamorphism of descending slabs. Also, some variation in the rate of slab heating is expected from arc to arc due to differences in subduction rate, slab age, Benioff Zone (BZ) geometry, etc. Thus, a greater fraction of the initial slab HFM inventory will be available to modify subarc mantle domains in relatively cool subduction zones, and vice versa. Nearly 100-fold variation in B-enrichment (e.g., as monitored by B/Zr or similar ratios normalized to constant B content) is observed for volcanic front (VF) basalts from arcs worldwide. B-enrichment is highly correlated with the above measurable subduction parameters and with other temperature-sensitive parameters such as slab length (= down-dip extent of BZ seismicity). B-enrichment is also well correlated with slab-surface temperatures (SSTs) below the VF, as determined from numerical models (Huang et al., this volume). These relations suggest that slab HFM fluxes are strongly influenced by slab thermal history, and probably controlled by stability of HFM host minerals as well as the availability of fluid transport media. Different behavior is expected for various elements depending on their fluid-solubility and/or P-T stability of relevant host phases in which case geochemical fractionations are readily feasible and may explain some of the geochemical variability among arc magma suites. Moreover, B/Zr and similar ratios potentially can be used to infer aspects of slab thermal structure. However, care must be taken that the ratios are representative of the most primitive mafic magmas and not modified

by shallow crust-level processes. For example, interaction with lower crust rocks can lower normalized B/Zr values for relatively evolved lavas.

V12E-04 1425h

Mineral Solubility in Aqueous Fluids at High Pressure: Implications for Metasomatism in Subduction Zones and the Mantle Wedge

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Subduction zones are regions of profound fluid-controlled mass transfer (metasomatism). However, the physical chemistry of fluid-rock interaction in this environment remains poorly understood because there are few measurements of mineral solubility at the relevant pressures and temperatures. We have carried out a program of experimental and theoretical studies of mineral solubility in H₂O-NaCl-HCl-H₂S fluids at 5-20 kbar and 350-900 °C. Experiments are performed in a piston-cylinder apparatus; mineral solubilities are determined based on weight changes of encapsulated minerals or analysis of extracted quench fluids. When combined with theoretical predictions, these studies provide a basis for modeling metasomatism in subduction zones and the mantle wedge.

Experimental studies on quartz, diaspore, corundum, albite-paragonite-quartz, calcite, forsterite and enstatite show that, as a general rule, mineral solubility increases strongly with pressure at constant temperature in pure H₂O. In some cases solubility is 3-4 orders of magnitude higher at subduction zone conditions than in shallow crustal environments. Silica, alkalis, and Al dominate the solute load relative to alkaline earths and transition metals. NaCl profoundly enhances the solubility of calcite and Al and other metal oxides, but decreases SiO₂ solubility significantly. Studies of HCl dissociation show it to be a weaker acid at >5 kbar than anticipated from low-pressure experiments. H₂S does not strongly influence the solubilities of Si, Al, and Na, but is expected to enhance metal solubility. Experimental results agree well with theoretical predictions of solubility based on the observation that the quantity ΔV_r/βH₂O RT is isothermally constant with increasing pressure. This gives a foundation for predicting thermodynamic properties of aqueous species that have not been studied experimentally. Results of our studies confirm that aqueous subduction-zone fluids will be rich in alkalis, Al, and Si. Metal contents will be low, unless additional components (NaCl, HCl, H₂S) are present.

V12E-05 1440h

Experimental Study of Slab-Mantle Geochemical Exchange in Subduction Zones

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Aqueous fluids derived from subducting oceanic crust play an important role in the material transport leading to the production of arc lavas, and in the long-term chemical evolution of the Earth's mantle and crust. In order to determine the geochemical evolution of both the subducting slab and the overlying mantle wedge, a series of dehydration/hydration experiments was carried out at conditions of 0.8-4.0 GPa and 650-900 °C appropriate for subduction zones. Blueschist facies rocks/minerals, and olivine (Fog₁) were used for starting materials, as analogue materials of slab and mantle, respectively. Finely ground metabasalt (H₂O = 5.9 wt%) and glaucophane (H₂O = 2.3 wt%) were separately sealed in gold capsules with an olivine grain (1mm diameter), and then run in a piston-cylinder apparatus. Polished sections of run products were observed and analyzed for major element compositions with an electron micro-probe. Trace elements of selected run-products were determined using an ion probe (Cameca-5f).

At subsolidus conditions, the metabasalt was transformed into amphibolite-facies mineral assemblages