

provide continuous geochemical coverage of the hole and agree well with ICP-ES and ICP-MS K, Th and U core analyses. Because K/Rb, Rb/Cs and Th/REE ratios are fairly constant within each lithologic unit, bulk estimates are accurate for these elements as well. The Site 1149 sedimentary column is 20% lower in K than the Site 801 column (due to the lack of alkalic volcanics), but enriched by 60% in Th (due to the Asian dust). Taking into account the 25% lower mass flux of material due to the thinner Izu section, the mass flux for most elements is of similar magnitude (within 40%) for the Izu trench and Marianas trench. Although in the right direction for some elements (e.g., K), the magnitude of the flux difference falls way short of explaining the very low concentrations of the Izu volcanic front. However, submarine lavas erupted 100-150 km behind the Izu volcanic front have the appropriate composition for the sediment input fluxes, including Pb isotopes, Ce anomalies, Th/La, and Th/Na. This suggests that the Izu subduction factory has a delayed delivery system, with most sedimentary slab material missing the arc, but feeding the back-arc region. Both the Izu and Mariana arcs are consistent with subducted sediment components derived from > 175 km in these cold slabs, but the near vertical slab beneath the Marianas allows these components to contribute to the volcanic front. Thus, sediment input accounts for some contrasts in the two arcs (Pb isotopes and Th/La), while slab dip accounts for others (the delivery system).

T22D-11 1635h INVITED

Why are the Arc Volcanoes Where They are?

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The depth to the top of the intermediate-depth seismicity beneath the arc volcanoes is constant to within a few kilometres along individual segments of volcanic arcs, but varies between arc segments by tens of kilometres. The total range in this depth is from 65 km to 130 km, inconsistent with the common assumption that the volcanoes directly overlie regions where the slabs release fluid by dehydration of amphibole at roughly constant pressure. However, this depth varies inversely with the descent speed of the subducting plate, which is the controlling factor in the thermal structure of the subduction zone. Interpretation of this observation, using simple analytical solutions for the temperature structure in and above subducting slabs, suggests that the locations of the volcanoes are controlled by a mechanism requiring that some part of the slab, or the mantle wedge, should exceed a critical temperature. Plausible mechanisms include the release of fluids in strongly temperature-dependent reactions occurring near the top of the slab, or a temperature-induced change in the mode of melt migration in the wedge, such as the focusing of flow into cracks once the temperature falls below a critical value.

T22D-12 1650h

A Dangling Slab, Amplified Arc Volcanism, Mantle Flow and Seismic Anisotropy in the Kamchatka Plate Corner

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The Kamchatka peninsula in Russian East Asia lies at the junction of a transcurrent plate boundary, aligned with the western Aleutian Islands, and a steeply-dipping subduction zone with near-normal convergence. Seismicity patterns and *P*-wave tomography argue that subducting Pacific lithosphere terminates at the Aleutian junction, and that the downwind extension (>150km depth) of the slab edge is missing. Seismic observables of elastic anisotropy (*SKS* splitting and Love-Rayleigh scattering) are consistent with asthenospheric strain that rotates from trench-parallel beneath the descending slab to trench-normal

beyond its edge. Present-day arc volcanism is concentrated near the slab edge, in the Klyuchevskoy and Sheveluch eruptive centers. Loss of the downwind slab edge, whether from thermo-convective or ductile instability, and subsequent "slab-window" mantle return flow is indicated by widespread Quaternary volcanism in the Sredinny range inland of Klyuchevskoy and Sheveluch, as well as the inferred Quaternary uplift of the central Kamchatka depression. The slab beneath Klyuchevskoy has shallower dip (35°) than the subduction zone farther south (55°) suggesting a transient lofting of the slab edge, either from asthenospheric flow or the loss of downwind load. Such lofting may induce pressure-release melting to supply the Klyuchevskoy and Sheveluch eruptive centers. Petrologic indicators of high magma-peridotite equilibrium temperatures, long residence times for the hydrous arc-volcanic component, and weak expression of subducted sediment flux support the lofting hypothesis, and discourage an alternate interpretation in terms of accelerated slab rollback and/or a heightened influx of subducted volatiles. Over the late Cenozoic, the Komandorsky Basin subducted beneath northern Kamchatka and produced arc volcanics in the Sredinny Range. Several lines of evidence suggest the north-east migration of a plate triple junction (North America/Pacific/Komandorsky) along the southern Kamchatka coast in Oligocene-Miocene times. Three "cape terranes" (Shipunsky, Kronotsky, Kamchatka) along the coastline are exotic, with geologic similarities to present-day Western Aleutian islands, and may have accreted in a "caulking-gun" process as the triple junction migrated NE. The late Cenozoic transfer of arc volcanism from the Sredinny range to the eastern volcanic front of Kamchatka may have been facilitated by the progressive replacement of a shallow-dipping Komandorsky slab with a steeply-dipping Pacific slab.

T22E MC: 309 Tuesday 1345h

Fortieth Anniversary of the Synthesis and Discovery of Stishovite II (joint with P, V, DI, MR, HG)

Presiding: C T Prewitt, Carnegie Institution of Washington; R J Hemley, Carnegie Institution of Washington

T22E-01 1345h INVITED

The Discovery of High-Density Silica

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I was a graduate student at Moscow State University in the period 1960-1962, and developed an interest in the problem of the interior of the Earth and its constituents. I decided to look for the high-pressure phase of silica predicted by Francis Birch in 1952. Finally with much help from S.V. Popova I was able to perform experiments with a high-pressure apparatus at the Institute of High-Pressure Physics in Moscow, and in 1961 I obtained the new phase. Some special circumstances, which led to first synthesis a high-density form of silica, are described. In some sense this discovery may illustrate the role of chances in science.

T22E-02 1400h

Packing Systematics of Stishovite

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Thompson and Downs (2001) devised an algorithm to quantify the distortion of the anion skeleton in a crystal structure from ideal closest-packing. Application of this algorithm to pyroxenes, olivines, spinels, wadsleyites, and kyanite shows that they all become more efficiently packed with pressure, and less so with temperature. In spite of Megaw's (1973) assertion that the rutile structure is not based on the closest-packing

of anions, we find that it can be interpreted as a distorted HCP structure. However, the observed structure of stishovite becomes more distorted with increasing pressure. Based upon structures determined by theory, this trend is reversed above 70 GPa. Theoretical determinations in the calcium-chloride structure show that silica is slightly more efficiently packed than stishovite at the transition pressure and becomes rapidly more closely-packed as pressure increases. Theoretical high pressure polymorphs of silica, such as the α -PbO₂ structure, are all close to ideal closest-packed.

It has been observed that rutile-structured compounds do not exhibit the usual pressure-temperature inverse relationship (Hazen and Finger, 1981). This is also true of the packing efficiency of rutile and SnO₂, as they become more distorted with both pressure and temperature. Stishovite, however, becomes less distorted with temperature. This presentation will shed light on anion-anion interactions in the stishovite structure.

Megaw, H.D. (1973) *Crystal Structures: A Working Approach*. W.B. Saunders Company, Philadelphia. Thompson, R.M. and Downs, R.T. (2001) Quantifying distortion from ideal closest-packing in a crystal structure with analysis and application. *Acta Crystallographica B* 57, 119-127. Hazen, R.M. and Finger, L.W. (1981) Bulk moduli and high-pressure crystal structures of rutile-type compounds. *The Journal of the Physical Chemistry of Solids*, 42, 143-151.

T22E-03 1415h

Electron-Density Analysis and Phase Transition of SiO₂ under Pressures over 50GPa using Single-Crystal Diffraction Study

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Single-crystal structure analysis of SiO₂ stishovite, (rutile type, P4₂/mnm z=2) was carried out using the newly devised DAC. Electron-density distribution was investigated at high pressures up to 50GPa. A new DAC was devised especially for the single-crystal structure analyses under high pressure. The cell is characterized by large single-crystal diamond window plates about 4 carats set on the table planes of diamond anvils. The wavelength of E=30.388keV emitted from bending magnet of SR source with 8GeV 100mA at SPring-8 was used for the diffraction intensity measurement. The new assembly presents the precise electron density distribution as a function of pressure. The detailed specification of the new DAC was reported (Yamanaka et al. 2001). The charge distribution reveals a significant admixture of covalency in the chemical bonds of SiO₂ rutile-type oxides and the appropriate charge of the cations turns out to be far from a formal charge of Si⁴⁺ configuration. Our results are well consistent with energy band calculation and cluster-model calculation. The difference Fourier synthesis reveals The significant d-electron population indicates that some degree of non-sphericity of valence electron distribution around cation. The bonding electrons are related to the overlapped orbits of s, p and d electrons. We also carried out the molecular orbital calculation in order to investigate the density of state of valence electron. Dipole moment was experimentally determined by summation of product of charge and interatomic distance. The result of the apparent relative ionicity of Si⁴⁺ is +2.12(8) for 1atm and +2.26(15) for 29.1GPa. The electronic orbital overlapping causes the deformation of octahedral coordination SiO₆ of the rutile-type structures and the bond character about the covalency/ionicity. The d-electron of cations increases the degree of d-p-pai bond in Si-O. The ratio between shared and unshared edge distance of O-O has a strong relation with the interatomic repulsive force between two cations Si-Si and the degree of pai-bond of Si-O. Stishovite transforms to CaCl₂ structure at 58GPa. The bonding nature induces the symmetry change.

T22E-04 1430h

Stishovite Equation of State to Megabar Pressures

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