T41F MCC: 3007 Thursday 1020h

The Structure and Physical Properties of Grain Boundaries in Rocks II *(joint with V)*

Presiding: **S ten Grotenhuis,** HPT-Lab/Inst Earth Sciences**; T Hiraga,** Tohoku University

T41F-01 1020h INVITED

Measurement of Grain Boundary Partitioning of Ar and He

Ethan F Baxter[1,2] (617-358-2844; efb@bu.edu)

Paul D Asimow[2] (asimow@gps.caltech.edu)

Kenneth A Farley[2] (farley@gps.caltech.edu)

[1]Department of Earth Sciences, Boston University 685 Commonwealth Ave, Boston, MA 02215, United States

[2]Division of Geological and Planetary Sciences, California Institute of Technology MC 170-25, Paasadena, CA 91125, United States

An experimental procedure has been developed that permits measurement of the partitioning of Ar and He between crystal interiors and the grain boundary region between crystals (GB) in synthetic polycrystalline diopside aggregates. ^{37}Ar and ^{4}He are introduced into solid glass samples via neutron irradiation, eliminating issues of possible atmospheric gas contamination. Samples are then crystallized in sub-solidus conditions from a pure diopside glass in a piston cylinder apparatus. During crystallization, noble gases simultaneously diffusively equilibrate between the evolving crystal and grain boundary reservoirs. After equilibration, GB Ar and He is differentiated from that incorporated within the crystals by means of step heating analysis. An apparent equilibrium state (i.e. constant equilibrium partitioning) is reached after about 20 hours of crystallization in our experiments. Data for longer durations show the predicted systematic trend of decreasing GB Ar and He with increasing grain size. These data yield values of effective grain boundary surface partitioning, $K_{(Ar)surf}$, in units of (mol Ar/m3 of crystal)/(mol Ar/m^2 of GB) of 6.8 x 10^3 to 2.4 x 10^4 m^{-1}. Using a nominal GB thickness of 2-3 nm (corroborated by TEM imaging of experimental samples) a true partition coefficient (units of (mol Ar/m^3 of crystal)/(mol Ar/m^3 in GB)), $K_{(Ar)}$, may be determined: 1.4 x 10^{-5} to 7.1 x 10^{-5}. This value is about an order of magnitude lower than Ar partitioning between diopside and glass. He partitioning data provide a less robust constraint with $K_{(He)}$ between 10^{-4} and 10^{-5}. These data suggest that grain boundaries constitute a significant, but not infinite, reservoir, and therefore bulk transport pathway, for noble gases in the lower crust and mantle.

T41F-02 1040h INVITED

Equilibrium Grain Boundary Segregation in Mantle Rocks: Grain Boundaries as Reservoirs of Incompatible Elements

Takehiko Hiraga[1] (hirag001@umn.edu)

Ian M Anderson[2] (andersonim@ornl.gov)

David L Kohlstedt[3] (dlkohl@umn.edu)

[1]Tohoku University, Department of Machine Intelligence and Systems Engineering, Aramaki-Aza, Aoba 01,, Sendai 980-8579, Japan

[2]Oak Ridge National Laboratory , 1 Bethel Valley Road, Oak Ridge, TN 37831-6064, United States

[3]University of Minnesota, Department of Geology & Geophysics, 310 Pillusbury Dr S.E, Minneapolis, MN 55455, United States

The classical model developed by McLean describes segregation of solute or impurity atoms to grain boundaries in binary alloy systems using the absorption analogue. This thermodynamic model has not been applied to grain boundaries in Earth materials; grain boundaries have simply been treated as possible sinks for impurities in rocks. To test if the model describes segregation to grain boundaries in mantle rocks, the chemistry of olivine grain boundaries in many types of olivine aggregates annealed at 1373-1523 K and in natural peridotites was analyzed using energy dispersive X-ray (EDX) profiling obtained with a scanning transmission electron microscope (STEM) with a probe size of < 1.4 nm. Profiles across grain boundaries reveal a substantial segregation of Ca, Al and Ti. High-resolution transmission electron microscopy (HREM) observations reveal that the boundaries do not contain a grain boundary phase. Moreover, an equilibrium thermodynamic model, assuming that the solute is confined entirely to the grain boundary plane, is quantitatively consistent with the level of Ca grain boundary segregation and its temperature dependence. Strain energy minimization and space charge compensation are two important thermodynamic driving forces for segregation to grain boundaries. A survey of all elements measured in the grain boundary profiles indicates that differences in ionic radius and valence state from that of host elements (i.e., Mg and Si) control the enrichment of elements at grain boundaries. The magnitude of the partitioning is explained well by regarding the segregation energy as the misfit strain energy calculated for substitution of Ca for Mg in olivine grains. Therefore, we can predict the value of the partition coefficient for different elements and different minerals with parameters such as ionic radius and Young's modulus for the crystals. Based on this calculation, we conclude that grain boundaries can be primary storage sites for the elements with large ionic radii such as Sr, Ba, K and Rb in mantle rocks.

T41F-03 1100h

The Composition of Olivine Grain Boundaries

John Fitz Gerald[1] (john.fitzgerald@anu.edu.au)

Ulrich Faul[1] (uli.faul@anu.edu.au)

Martin Cmiral[1] (cmiral@iol.cz)

[1]Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

As an integral part of the characterisation of microstructures of experimentally produced olivine-rich samples, we have systematically studied grain boundaries in a conventional 300KV TEM by imaging and EDS analysis. Grain boundaries examined have misorientations > 10° and show none of the arrays of dislocations present in either subgrain walls or grain boundaries in metals. In the TEM each grain boundary is oriented exactly parallel to the electron beam to produce the sharpest image of the grain boundary, and then TEM EDS analysis is performed with a beam ca. 20nm wide and 200nm long parallel to the grain boundary. Each grain boundary EDS spectrum is then compared to a spectrum acquired under the same conditions in the adjoining olivine grain. A large range of samples have been examined, including olivine aggregates derived from natural rocks and fully synthetically produced (trace element free, sol-gel origin). The samples were quenched from temperatures between 1100 and 1400°C after being run either under hydrostatic conditions from 0.3 to 3 GPa or after deformation in a Paterson gas-medium apparatus. The apparent width of the grain boundary region in high resolution TEM images is not detectably different for any of these samples, but significant EDX spectral changes show differences in composition of the grain boundaries that depend on bulk composition and sample treatment. For example, olivine in fully synthetically produced samples is trace element free, and correspondingly no trace elements are detectable in grain boundaries by TEM EDS. When a basaltic melt is added, EPMA WDS analyses show that the olivine grain interiors equilibrate with the melt by incorporating a small amount of Ca, Ti and Al as trace elements. Using TEM EDS we observe that the grain boundaries in these samples are now enriched in these elements relative to olivine grain interiors. Levels of trace elements in grain boundaries also appear to be affected by strain history: grain boundaries in newly recrystallised regions (deformed aggregate of San Carlos olivine + basaltic melt) have very low levels of trace elements immediately after deformation, yet after a long hydrostatic anneal (1300°C, > 500 hrs) have re-equilibrated and contain significantly higher levels of trace elements. We conclude that the trace element enrichment in olivine grain boundaries relative to grain interiors reflects equilibrium partitioning between grain interiors, grain boundaries and other phases such as melt. This leads us to expect that olivine grain boundaries in natural rocks will also be enriched in trace elements depending on bulk chemistry.

T41F-04 1115h

Electrical properties of polycrystalline olivine: evidence for grain boundary transport

Saskia M Ten Grotenhuis[1] (31-30-2531177; saskiatg@geo.uu.nl)

Martyn R Drury[1] (martynd@geo.uu.nl)

Colin J Peach[1] (cpeach@geo.uu.nl)

Chris J Spiers[1] (cspiers@geo.uu.nl)

[1]Utrecht University, Department of Earth Sciences P.O. Box 80021, Utrecht 3508 TA, Netherlands

The physical and chemical properties of grain boundaries are known to play an important role in determining the electrical properties of polycrystalline oxides. Grain boundaries can either enhance conductivity if the transport of charge carriers along the grain boundaries is faster than through the lattice, or grain boundaries can reduce conductivity if the grain boundaries block the transport of charge carriers. The purpose of the experiments presented here is to deduce the mechanisms responsible for electrical conductivity in fine-grained forsterite, the Mg-end member of olivine, in order to get a better understanding of the contribution of grain boundary transport, of the properties of the grain boundaries, and to determine any relation between grain size and conductivity. A relationship between grain size and conductivity at high temperature could potentially be used to interpret zones of anomalous conductivity in the upper mantle. The materials studied consist of fine-grained forsterite (Mg2SiO4) with a minor amount (5%) of enstatite (MgSiO3) added. The electrical conductivity of three melt-free synthetic polycrystalline samples, with grain sizes between 1.1 and 4.7 mm, was measured at temperatures up to 1470°C. The complex impedance plots display one clear arc, indicating a single dominant conduction mechanism. Bulk conductivity is inversely proportional to the grain size of the different samples. This relation suggests that grain boundary diffusion of the charge carriers is controlling the electrical conductivity of the samples. The activation energy for diffusion of the charge carriers lies between 315 and 323 kJ/mol. This resembles previous data on grain boundary diffusion of Mg in forsterite and grain boundary diffusion creep. A geometrical model of less conducting cubic grains and more conducting grain boundaries agrees well with the experimental data. This model is applied to a natural mantle shear zone to predict the conductivity contrast between fine-grained shear zones and less deformed regions in the lithosphere. Upper mantle shear zones are predicted to have 1.5 to 2 orders of magnitude higher conductivity than less deformed regions in the lithosphere. This may mean that fine-grained shear zones can be detected using magnetotelluric methods.

T41F-05 1130h

Does the electrical conductivity of partially molten rocks depend on grain-boundaries?

Frank R. Schilling (++49 331 288 1875; fsch@gfz-potsdam.de)

GeoForschungsZentrum Potsdam, Division 4 Telegrafenberg, Potsdam D-14473, Germany

In the active orogenic systems of the Central Andes and the Himalayas, extremely high electrical conductivities are observed and attributed to partially molten rocks within the crust. Laboratory experiments in combination with numerical calculations show that the conductivity behaviour of partially molten rocks can be explained by a complete interconnectivity of the melt phase for melt fractions > 20 vol.%. Furthermore, a comparison of laboratory experiments and numerical modelling reveals an excellent agreement between observations and models. This holds true for Hashin-Shtrikman as well as a modified brick-layer model. In these models, only one conductivity mechanism is assumed for both, crystals and melt phase. However, there is experimental evidence that the conductivity mechanism in the solid matrix is dominated by electrons whereas ionic charge transfer dominates the conductivity in the melt phase. At the high frequencies applied in laboratory studies, the effect of charge transfer from crystals to melt will not - or slightly - affect the bulk-conductivity of the composite. However, at lower frequencies as used in field studies, the different charge transfer mechanisms in crystals and melt will lead to a blocking of charge transfer between solid and melt. This enhances the resistivity of partially molten rocks at low frequencies compared to laboratory studies using high frequencies. Therefore, grain-boundaries will influence the electrical conductivity of partially molten rocks. In other words, in partially molten rocks processes at grain-boundaries hinder a direct scaling of laboratory observations to field studies. However, the knowledge of the underlying mechanisms of charge transfer in crystals and melts allow an extrapolation of laboratory observations to field studies, if models are used which take the grain-boundary effects into account. Such a model will be presented and discussed.

T41F-06 1145h

Hart's Mechanical Equation of State in Rock-Salt: Data and Theoretical Model Based on Subgrain Boundary Migration

Donald S. Stone[1] (608-262-8791; dsstone@facstaff.wisc.edu)

Thawatchai Plookphol[1] (plookphol@wisc.edu)

Reid F. Cooper[2] (401-863-2160; Reid_Cooper@Brown.edu)

[1]University of Wisconsin-Madison, Department of Materials Science and Engineering 1509 University Ave, Madison, WI 53706

[2]Brown University, Department of Geological Sciences, Providence, RI 02912

There are a wide variety of materials that exhibit behavior consistent with Hart's mechanical equation of state. For such materials, constant structure "hardness curves" can be generated using load relaxation experiments, which sweep out a spectrum of stress vs. strain rate at nearly constant strain. Hardness curves generated at different levels of work hardening scale with each other: that is, they can be translated in log-log space along lines of fixed slope so that they fit on top of each other. Despite the ubiquity of scaling among many varied materials, there has never been an experimental effort to establish a microscopic basis for it until now. And until now, there has never been a careful effort to establish the relationship between data generated from load relaxation and those obtained from creep tests. One benefit of such efforts would be to provide experimenters a tool for extending experimental techniques to lower strain rates - short duration load relaxation experiments can routinely achieve 10^{-8} s^{-1} and, with effort, 10^{-10} s^{-1}. Such efforts might also lead to a better understanding of power law creep itself, for which there is no universally accepted microscopic model. In this work we investigate mechanical equation of state in single crystal rock-salt at 673K and 973K deformed under compression in the [100] orientation. We find that different hardness states correspond to different average subgrain sizes and that subgrain size distributions obtained at different levels of stress are similar to each other, i.e., they have the same shape. We compare the experimental data with a model based on the partitioning of the crystal between dislocation glide in large subgrains and subgrain boundary migration in small ones; the distinction between "large" and "small" is based on strain rate. In the model, subgrain boundary migration is governed by the same kind of law that governs Nabarro-Herring creep (with subgrains substituting for grains), except that the numerical coefficient is much smaller in the case of subgrains owing to constraints between the migration of neighboring subgrain boundaries. Subgrain boundary migration is also responsible for dynamic recovery. The model is able to mimic all aspects of the data including load relaxation, transient creep, and steady state power law creep. Moreover, the model is able to account for a transition from power law creep at high temperature (973K) and low stress into power law breakdown at low temperature and high stress (673K) without resorting to additional mechanisms.

T41F-07 1200h

Grain Size Reduction and Deformation Mechanisms in Ultra-Fine-Grained Shear Zones From the Lherz Peridotite

Gill M. Pennock[1] (gpennock@geo.uu.nl)

Martyn R. Drury[1] (martynd@geo.uu.nl)

Hans G. Ave Lallemant[2] (ave@rice.edu)

[1]Department of Earth Sciences, Utrecht University, PO Box 80.021, Utrecht 3508TA, Netherlands

[2]Department of Geology and Geophysics,Rice University, PO Box 1892, Houston 77251-1892

We have used SEM and Electron backscattered diffraction to investigate the petrology, microstructure and lattice preferred orientation (LPO) of narrow (5-10 mm wide), high strain, ultramylonitic shear zones exposed in the Lherz peridotite body, N. Pyrenees, France. The wall rock is a protomylonite with a normal olivine LPO ([100] parallel to the stretching lineation). Fractures occur in the wall rock and terminate at the shear zone margin. There is a systematic step-like grain-size decrease (2 mm, 0.1 mm, 0.02 mm, 0.01 mm, 0.005 mm) at the margin of the shear zone. In the shear zone grains are elongated with a good alignment of grain boundaries. The mineral assemblage consists of olivine, pyroxene, spinel and amphibole clasts in a matrix of olivine, pyroxene, spinel, magnesite (MgCO3). An olivine LPO occurs in the matrix similar to the type-B LPO reported by Jung and Karato(Science, 293,1460, 2001). The narrow ultramylonite zones may initially have formed as fractures that were subsequently infiltrated by CO2 derived from adjacent limestones. If this hypothesis is correct then the initial grain-size reduction probably involved some cataclasis with shear zones forming during crustal emplacement of the peridotite. Microstructures and mineral assemblages indicate that recrystallization and the reaction (ol + CO2 = opx + magnesite) have also contributed to grain size reduction. The decrease of matrix grain size into the shear zone may reflect increasing cataclastic strain, decreasing temperature during reaction or increasing stress during dynamic recrystallisation. The ultra-fine grain size and aligned grain boundaries suggest an important role for sliding along interfaces. Granular flow is the most likely deformation mechanism in such fine-grained rocks, unless deformation occurred at very high stress and strain rate. The presence of LPO in these ultra-fine grained shear zones is unexpected. The type-B LPO may be (a) a relict from early dislocation creep (b) produced by high stress-high strain rate dislocation creep or (c) could be characteristic of granular flow in aggregates with an elongated grain shapes.

T42A MCC: Level 1 Thursday 1330h

The Structure and Physical Properties of Grain Boundaries in Rocks III Posters *(joint with V)*

Presiding: **A Schubnel,** Lassonde Institute**; S Majumder,** University of Minnesota

T42A-0265 1330h POSTER

Mechanical compaction of Bleurswiller sandstone : elastic wave velocities and permeability evolution

Jerome Fortin[1] (fortin@geologie.ens.fr)

Alexandre Schubnel[1,2] (schubnel@geologie.ens.fr)

Yves Gueguen[1] (gueguen@geologie.ens.fr)

[1]Laboratoire de Geologie, ENS Paris, 24 rue Lhomond, Paris 75005, France

[2]Lassonde Institute, 170 College Street, Toronto, ON M5S 3E3, Canada

Field observations and laboratory experiments have recently documented in porous sandstones the development of compaction bands sub-perpendicular to the direction of maximum principal stress. These compaction bands have been preferentially observed in relatively homogeneous sandstones of high porosity, such as Bentheim sandstone studied by Wong et al. [2001] and Baud et al. [2003], but also in a heterogenous sandstone of high porosity, such as Diemelstadt sandstone Fortin et al. [2003]. Rock deformation, fluid transport, and acoustic velocity are coupled together. On one hand, Scott et al. [1993] showed that acoustic velocities across the brittle-ductile transition are clearly being affected. On the other hand the relation between permeability evolution and compaction of sandstone was demonstrated by Zhu et al [1999]. To understand better the complexity of damage resulting from compaction band formation and its effect on permeability, we performed series of experiments on Bleurswiller sandstone of porosity 25%. This vosgian sandstone is made of 50% quartz, 30% feldspars, and 20% of oxides and micas. Hydrostatic and conventional triaxial compression experiments were conducted at room temperature on saturated samples under drained conditions, with a constant pore pressure of 10 MPa. The samples were deformed in the range of confining pressure from 60 to 300 MPa Compressional wave velocities, shear waves velocity, and permeability have been measured during both hydrostatic and triaxial experiments.

T42A-0266 1330h POSTER

Reduction of ionic diffusivity in nanopore water of geomaterials

Tetsuro Hirono[1] (+81-46-867-9328; hirono@jamstec.go.jp)

Satoru Nakashima[2] (+81-3-5734-3544; satoru@geo.titech.ac.jp)

Chris J. Spiers[3] (+31-30-2534972; cspiers@geo.uu.nl)

[1]Japan Marine Science and Technology Center, Natsushima 2-15, Yokosuka 237-0061, Japan

[2]Tokyo Institute of Technology, Ookayama 2-12-1, Tokyo 152-8551, Japan

[3]Utrecht University, Budapestlaan 4, PO Box 80.02, Utrecht 3508 TA, Netherlands

Recent molecular dynamics simulations and spectroscopic approaches indicated that water molecules confined in nanometre scale has a constrained structure with shorter hydrogen bond distances. In order to verify a hypothesis that ionic diffusivity in rocks should be affected by the constrained molecule structure of water in nanopore, we measured the effective diffusion coefficients of iodine ion in undeformed rocks by through-diffusion experiments. We also studied the quantitative relationship between the diffusion coefficients and the pore structures. Most of effective diffusion coefficients (De) for rocks can be explained by the power law with effective porosity (p), while De values for the sample involving abundant nanopores were much lower than this relation. These could be resulted from that De depends not only on porosity and tortuosity (t) but also on inonic diffusion coefficient in nanopore water (Dn). By simultaneous equation of Dn and t with known De and porosity in two nanopore-type rocks, Dn and t can be deduced independently, leading the equation (De = 9.0 x 10^{-10} x p^3). This means that Dn is 9.0 x $10^{[-10]}$ $m4^{24}$/s. This Dn values is about two-times lower than the diffusivity in free pure water. This result can be applied for hydraulics, structural geology and new discipline of nano technology.

T42A-0267 1330h POSTER

An Experimental Study of Pressure Solution of Halite Under the Confocal Microscope

Zvi Karcz[1,3] (845 365 8463; zvi@LDEO.columbia.edu); Einat Aharonov[2] (einata@wicc.weizmann.ac.il); Deniz M Ertas[3] (deniz.ertas@exxonmobil.com); Robert J Johnston[3] (robert.j.johnston@exxonmobil.com); Richard S Polizzotti[3] (richard.s.polizzotti@exxonmobil.com); Christopher H Scholz[1] (scholz@LDEO.columbia.edu)

[1]Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University , 61 Route 9W, Palisades, NY 10964, United States

[2]Department of Environmental Science and Energy Research, Weizmann Institute of Science , POB 26, Rehovot 76100, Israel

[3]Corporate Strategic Research, ExxonMobil Research and Engineering Company , 1545 Route 22 East , Annandale, NJ 08801, United States

We present an experimental study of pressure solution of halite under a confocal microscope designed to resolve conflicting results in previous experiments. Two pressure solution mechanisms, thin film diffusion and undercutting, were conceptually proposed (Weyl, 1959) and later experimentally shown to operate under similar conditions (Tada & Siever, 1986; Hickman & Evans 1992, 1995; Schutjens & Spiers, 1999). However, a transition between these mechanisms was never observed, and it is not clear what may induce it. Our experimental setup consists of a halite beveled indenter pressed against a flat quartz window. The contact is viewed in-situ through the window with the confocal microscope. We hypothesize that changing the angle of the bevel may change the relative magnitude of the driving forces, consequently inducing a transition in pressure solution mechanisms. The confocal microscope allows a 3D reconstruction of the microstructures at the contact.

T42A-0268 1330h POSTER

Mobility of Water Molecules on Brucite and Talc Surfaces by *Ab Initio* Potential Energy Surface and Molecular Dynamics Simulations

Hiroshi Sakuma[1,3] (81-3-5734-2617; hsaku@geo.titech.ac.jp)

Taku Tsuchiya[2] (takut@cems.umn.edu)

Katsuyuki Kawamura[1] (kats@geo.titech.ac.jp)

Kenshiro Otsuki[3] (otsuki@dges.tohoku.ac.jp)

[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 1528551, Japan

[2]Department of Chemical Engineering and Materials Science (CEMS), University of Minnesota, 421 Washington Av. SE, Minneapolis, MN 55455, United States

[3]Institute of Geology and Paleontology, Graduate School of Science, Tohoku University, Aoba, Aramaki, Aoba, Sendai 9808578, Japan

The interaction between minerals and water molecules is a fundamentally important property that influences fluid distribution and migration in the earth's crust, and transportation of H_2O into the earth's mantle. In this work, we focused attention on the mobility of water molecules on the cleavage surfaces of brucite and talc, and performed the molecular dynamics simulations. Brucite is in most common as an alteration product of periclase in contact metamorphosed dolomites. It is also found as a low-temperature hydrothermal vein mineral in serpentinites and chlorite schists. Talc occurs most frequently as a product of metamorphism of hydrothermal alteration of ultramafic rocks and is an important phase in the oceanic crust. The first step in performing the simulations of mineral-water interfaces is to develop a reliable and consistent model for the interaction of water molecules with solid surfaces. Fundamental understanding of such interaction often requires physico-chemical knowledge at a molecular level, which is not easily obtained