

Misasa International Student Intern Program 2008



Abstract

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Participants of the Misasa International Student Intern Program 2008

Geochemistry and geochronology group:

Name	Univ.	Intern Supervisor(s)	Intern Project
NOACK Niels	University of Cologne, Germany	PML members*	Time decoding for the subduction and exhumation processes in an ancient convergent plate margin: Multichronology of the Paleozoic eclogites in Japan
COLLINS Ana	University of Texas at Austin, UAS		
SAPAH Marian Selorm	University of Ghana, Ghana		
KIMURA Yumiko	Kwansei Gakuin Univ., Japan		
ROSZJAR Julia	Westfälische Wilhelm Universität Munster, Germany	PML members*	An application of comprehensive geochemical analysis onto carbonaceous-chondrite constituents
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High-pressure experimental mineral physics group:

Name	Univ.	Intern Supervisor(s)	Intern Project
DellaGIUSTINA Daniela	Univ. Arizona, U.S.A.	T. Yoshino	The effect of H ₂ O on the electrical conductivity of orthopyroxene
SAWYER Ryan	Univ. Western Ontario, Canada	T. Katsura	Synthesis of single crystal majorite-garnet with pyrolyte minus olivine composition
HAMASAKI Masahiro	Kumamoto Univ., Japan	A. Yoneda	High frequency resonant ultrasound spectroscopy (RUS) on a small single crystal specimen

High-pressure crystal chemistry and magmalogy group:

Name	Univ.	Intern Supervisor(s)	Intern Project
CHEVRELMagdalena Oryaelle	Universite Paul Sabatier, France	M. Kanzaki	In-situ Raman and IR spectroscopic study of hydrous GeO ₂ glass under pressure
REIBSTEIN Sindy Andrea	Institut für Mineralogie TU Bergakademie Freiberg, Germany	X. Xue & M. Kanzaki	Synthesis and structural characterization of high-pressure AlPO ₄ phases

Time Decoding for the Subduction and Exhumation Processes in an Ancient Convergent Plate Margin: Multichronology of the Paleozoic Eclogites in Japan

Ana Collins, Yumiko Kimura, Niels Noack, and Marian Selorm Sapah*

Abstract

This multigeochronological study focused on the evaluation of mineral dating in disequibrated metamorphic rocks as well as constraining the metamorphic history of Paleozoic eclogites in the Renge Schist of the Hida Belt, SW Japan. The eclogites occur as boudin structures within a pelitic schist host rock and are unique in that they are transitional between the eclogite and blueschist facies. Such conditions, while essential for reconstructing a metamorphic history, are problematic for isochron dating which assumes equilibrium conditions. The applicability of certain geochronometers was evaluated on the basis of petrographical observations.

The eclogite sample was identified to be derived from a MORB basalt as shown in major and trace element compositions, while the protolith of the pelitic schist was a semipelagic sediment. Petrographic observations combined with delta ^{18}O data confirmed equilibrium paragenesis at peak metamorphic conditions of garnet and omphacite. Chlorite alteration in microfractures and other impurities could effect isotopic ages. X-ray maps of garnets reveal prograde zoning with increasing Mg and decreasing Mn towards the rim. This is also good evidence for disequilibrium in our samples. Inclusion trails in the garnets reveal that growth was synchronous with deformation.

U-Pb, Sm-Nd, Rb-Sr, and K-Ar isotopic systems were utilized in order to obtain the ages from peak metamorphism to cooling during exhumation. Each isotopic system has a different closure temperature within each mineral allowing us to track the metamorphic history of the Paleozoic eclogite and pelitic schist samples. Zircons yielded a U-Pb age of 366 ± 14 Ma. A K-Ar cooling age of 319 ± 8 Ma was obtained using phengites from both samples. However, other mineral constituents show great variation, with each mineral recording a different closure temperature and isotopic ratios that do not fall neatly along an isochron line. We obtained a U-Pb concordia age of 366 ± 14 Ma. This correlates well with the thermobarometric calculations of Tsuijijimori (2002) based on the peak eclogite mineral assemblage. P-T conditions of $550 - 600$ °C and 2.0-2.2 GPa were obtained. Rb-Sr and Sm-Nd isotopic systems were also utilized to further constrain the timing of subduction and exhumation processes. The results show that the applicability of these isotopic systems to disequibrated LT rocks is constrained by mineral equilibria conditions and the insufficiently known closure temperatures of the applied isotopic systems.

Based on U-Pb and K-Ar ages, estimations of slow exhumation took place over a timeframe of 50 Ma years. Moreover, an exhumation rate of 1-2 km per 1 Ma could be estimated.

*Names are in alphabetical order

An application of comprehensive geochemical analysis onto carbonaceous-chondrite constituents

Julia Roszjàr and Miles M^cCammon

August 8, 2008

Abstract

A chondrite, which is a piece of an asteroid, is a mechanical mixture of high- and low-temperature components and is heterogeneous both in elemental and isotope abundances within/among mineral phases in micron scale. Based on past meteorite studies, asteroids have reacted with aqueous fluid after formation of their parent asteroids.

To investigate the first geologic fluid-related processes, elemental distribution of asteroid-constitute phases in three carbonaceous chondrites (CO, CV, and CM) are examined. In order to estimate elemental abundances in phases that are sensitive to aqueous fluid, leaching technique was applied to powdered bulk chondrite and leachate-, residue-, and bulk-elemental abundances are compared.

Chondrules, that are the most abundant components in chondrites (up to 50%), are especially interesting targets to advance understanding the fluid-related processes in the asteroid. Chondrules are a few micron to millimeter-sized igneous spheres and believed to have formed from clumps of precursor dust by repeated transient heating events in the early solar nebula. Chondrules comprises of various high-temperature phases that likely respond differently to interaction with fluids. The glassy mesostasis likely is susceptible to alteration processes, whereas silicate minerals (e.g., olivine and pyroxene) are much more resistant to fluid alteration.

Besides determination of elemental abundances in phases that have chemically different properties, elemental abundances in chondrule consisting phases were determined using in-situ technique. Three chondrules from three meteorites were picked up and petrographic analysis of thin sections, using optical microscope, scanning electron microscopes (SEM), and energy-dispersive X-ray analyzer (EDX) as well as with quantitative analysis using electron microprobe analyzer (EMPA) for major elements and ion micro-probe (SIMS) for trace elements were conducted.

A comprehensive petrologic and geochemical approach shows that trace elements distributed heterogeneously among meteorites and among/within chondrules, and revealed complexity of asteroidal history.

The Effect of H₂O on the Electrical Conductivity of Orthopyroxene

Della GIUSTINA Daniela

This project was motivated by the Yoshino et. al. 2006 *Nature* paper “Hydrous olivine unable to account for conductivity anomaly at the top of the asthenosphere”. In this work Yoshino and colleagues tried to account for anomalously high measurements of electrical conductivity in the North Pacific oceanic asthenosphere by examining hydrated olivine as a possible source of the anomaly. Their work concludes that this anomaly cannot be accounted for by olivine hydration. Therefore this project evaluated the possibility that the hydration of another important mantle constituent, Al-bearing orthopyroxene, may be responsible for the observed anomaly.

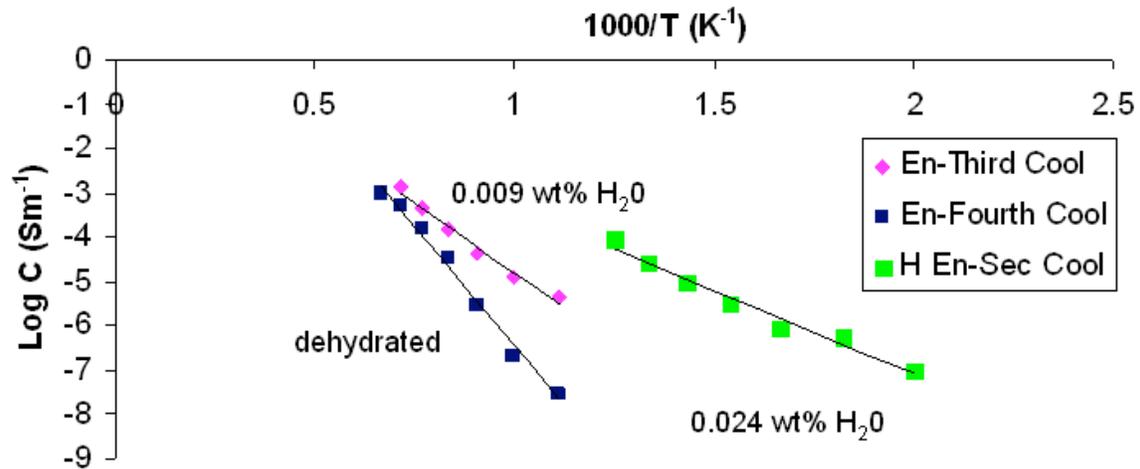
In order to evaluate the effect of hydration on the conductivity of Al-bearing orthopyroxene this project was divided into 3 separate processes: sample preparation and synthesis, high pressure in-situ electrical conductivity measurements, and finally FTIR (Fourier transform infrared spectroscopy) analysis of samples to constrain H₂O content.

Sample preparation was completed by mixing dry oxide powders in the correct proportions to establish an Al-En composition with 3 wt. % and Mg# of 92. After a dry oxide mixture with near-ideal composition was created, the oxide powder was baked in a furnace and subsequently quenched to create an amorphous glass. From this glass two different aggregates of Al-En were synthesized under 1.5 GPa in a piston cylinder apparatus. This included a hydrogen doped Al-En aggregate and a non-doped Al-En sample. Both of these samples were used to perform high pressure in-situ electrical conductivity measurements.

The Kawai-Type Multi Anvil 1000 Ton Press in the HACTO Lab was utilized for high pressure experiments. A 25-15 cell design was constructed to perform the experiment. After cell assembly was completed and the sample was placed in the high pressure apparatus, the experiments were performed under 1.5 GPa. A practice experiment was performed with MgO to gain familiarity with both cell assembly and to measure the resistance associated with the insulation materials. The second experiment included the undoped hydrogen sample; resistance of the sample was measured by applying an alternating current, between the temperatures of 330-1600 K. The third experiment included the hydrogen-doped sample; resistance of the sample was measured by impedance spectroscopy, between the temperatures of 500-800 K. The hydrogen-doped sample was kept at low temperatures to prevent hydrogen escape. This data was then plotted and fitted to a linear curve; using the Arrhenius equation the activation energy and pre-exponential term can be obtained from experimental data.

After these measurements were performed FTIR analysis was conducted to constrain the amount of hydration in each sample. A summary of the measurements performed as well as some comparative work (Xu and Shackland, 1999) are included in the table and figure below.

Sample	C _{OH} (wt%)	Log σ_0 (S m^{-1})	E _a (eV)	T (K)
En #1	0.009	1.51	1.25	900-1400
En #2	***	4.41	2.16	900-1500
Hydrous En	0.024	0.43	0.75	500-800
Similar En (Xu et. Al)	NA	3.72	1.80	1000-1400



From this experimental data it is clear that a low temperatures hydrated samples are electrically conductive primarily by proton migration, while at higher temperatures dehydrated samples are electrically conductive via small polaron conduction. Small polaron conduction is exhibited by the data obtained during the fourth cooling cycle of the undoped sample, while proton conduction is strongly exhibited by the data obtained during the second cooling cycle for the H-doped sample.

Based on this data it can be concluded that hydrated Al-bearing orthopyroxene can not account for high electrical conductivity anomalies in the Northern Pacific asthenosphere. Therefore this anomaly is most likely due to the presence of partial melt and not hydrated silicate minerals.

Synthesis of Single Crystal Majorite-Garnet with Pyrolite minus Olivine Composition

Ryan SAWYER

The composition of the Mantle Transition Region (MTR), an area located between ~400 km and ~660 km depth, remains controversial. A recent study by Irifune et al. (2008) revealed that a larger temperature dependence on elastic wave velocity exists in majorite-garnet with a pyrolite-minus-olivine composition. This temperature dependence has led to elastic wave velocities which are much lower than those predicted by other studies, particular in the case of shear wave velocity. Also, due to this temperature dependence, a large discrepancy in shear wave velocity was found to exist between laboratory measurements of pyrolite and piclogite mantle compositional models and seismological models such as PREM and AK135 in the region between ~500 km and ~660 km. Since the experiments of Irifune et al. (2008) were the first of their kind to measure the elasticity of majorite-garnet in situ at realistic MTR pressure and temperature conditions, it is necessary to study the elasticity of majorite using a different method.

One such method is Brillouin scattering. Brillouin scattering uses high energy photons to bombard a sample and create lattice vibrations, from which the elasticity of the sample can be measured.

The goal of the project was to synthesize polycrystalline and single crystal samples of majorite-garnet with a pyrolite-minus-olivine composition which will then be sent to Dr. Bass and Dr. Sinogeikin at the University of Illinois, who will conduct Brillouin scattering measurements in an attempt to verify the findings of Irifune et al. (2008).

Samples of a pyrolite minus olivine glass starting material were made and then high pressure experiments were conducted. Polycrystalline synthesis took place at a pressure of 18 GPa and a temperature of 1523°C. Single crystal synthesis experiments were conducted at 18 GPa and 2323 °C. Experiments were performed using a Kawai-type multi-anvil apparatus. A 14/6 octahedral cell assembly was used (14 mm edge length, 6 mm truncation).

A polycrystalline sample of majorite-garnet was successfully synthesized; however a single crystal sample was not due to instability of the resistive heater in the high pressure cell during heating. The recovered polycrystalline sample was found to be homogeneous and agreed with the composition of the starting glass, except for a small presence of stishovite. SEM analysis indicated the presence of stishovite along possible grain boundaries with average grain size ranged from 10 – 20 μm . The polycrystalline sample will now be sent to undergo Brillouin scattering measurements.

High frequency Resonant Ultrasound Spectroscopy (RUS) on a small single crystal specimen

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Abstract

Earth's layered structure has been investigated by means of the seismic velocity profile. Therefore, the elastic properties of the high-pressure phase minerals are indispensable for the research of the Earth's deep interior. However, the elastic moduli of the high-pressure minerals have been insufficient. They have been determined by Brillouin scattering method, because the available sample's size of high-pressure minerals is limited less than 1 mm. However, it is well known that opaque sample is not suitable for Brillouin scattering method.

Resonant ultrasound spectroscopy (RUS) is one of the typical techniques to measure elastic moduli, especially, of relatively small sample; it is based on natural vibration mode analysis on detected peaks in the frequency domain. We can detect peaks of natural frequencies higher than 10 MHz frequency by new RUS method. However it is not clarify how small sample can be measured in the RUS. For the progress of research in the Earth's interior, it is necessary to establish measurement by small sample.

In the present research, I made the sample of cylinder. Its diameter and height are as small as $\sim 250\mu\text{m}$, although the sample shape was not perfect cylinder, In order for this achievement, I made three improvements on ultrasound drilling machine which I used to make the sample. The first improvement is replacing broken valve to new one. The next one is making new stage with flat surface by thicker aluminum plate. The last one is attaching a dial gauge to monitor the depth of horn against work during processing. I tried to measure the sample on RUS by means of the measurement program developed by myself during this Internship program.

Although there still remains little problem on the cylinder sample newly processed, its characteristics are enough for us to think the cylinder shape as the first choice for the high frequency RUS.

In-situ Raman and IR spectroscopic study of hydrous GeO₂ glass under pressure

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Introduction

During the six weeks program I have done in-situ Raman and infrared (IR) spectroscopic measurements on hydrous germanium dioxide (GeO₂) glass under pressure. GeO₂ is mainly used because it is known that crystalline GeO₂ is a structural analog of silica, and transforms to the octahedrally coordinate Ge form at much lower pressures than silica. The project consisted in making dry and hydrous glasses from GeO₂ powder and then doing in-situ Raman and IR spectroscopic measurements. The measurements were performed under pressure (until 12GPa) in order to know structural evolution of anhydrous and hydrous GeO₂ glasses by means of vibrational changes.

Experimental

The first step was to make the hydrous glasses. After three days of sampling and one day IHPV experiment, we didn't succeed to get hydrous glasses (the capsules burst). We decided to use glasses produced in precedent works. The dry glass was produced by quenching at ambient pressure and 1400°C, the hydrous glass was quenched from 2kbar and 1400°C, which contains 0.4 OH for one Ge (2wt% of water). High pressure in-situ Raman and IR measurements were performed using diamond anvil cells (DAC). The gasket hole was 300µm in diameter with about 100µm in depth. Glass chips and small ruby chips were sandwiched between KBr pressure medium layers. Fluorescence spectrum from the ruby was used for pressure measurement.

Results and discussion

The Raman spectrum of hydrous GeO₂ glass at ambient pressure shows a main band at 426cm⁻¹. This peak corresponds to the vibrational frequency of Ge-O-Ge bending. The Ge-O-Ge stretching is shown by two low intensity bands at higher frequency (ca 840 and 950cm⁻¹). The hydrous glass displays other bands at ca 770cm⁻¹, representative of the Ge-OH stretching, and ca 3500cm⁻¹, representative of the O-H stretching. The main band shows a clear positive Raman shift with pressure. Major changes of the spectra shape happen circa 6GPa: right shoulder of the 400cm⁻¹ band gets higher in intensity, the peak broadens out and lost intensity, the three high frequency peaks are not really discernible anymore. From 6 to 12 GPa the shape keeps going in the same way (broaden and shift), the high pressure shape is thus characterized by three broad bands at 280, 550, 880 cm⁻¹. During the decompression we note that there is no major change until 2 GPa. At 2 GPa the spectrum starts to be recovered. Once the pressure is completely released the recovered spectrum is not exactly same as original one before compression. Although the shape of the peaks are roughly the same, we note that the hydrous glass shows a better recovered shape. We also measured dry glass, and the result was almost identical with previous study (Durben and Wolf, 1991). Concerning the observations made by IR spectroscopy of OH stretching bands, we see the shape of the O-H band also change clearly at 6 GPa. The low frequency band (3000cm⁻¹) grows while the high frequency band becomes lower, suggesting increasing hydrogen bond strength of OH in the hydrous g-GeO₂ glass above 6 GPa.

It was shown thanks to X-ray and neutron diffraction study of dry glass, that from 0 to 6 GPa it has a tetrahedral (CN=4) structure. At 6 GPa and until 10 GPa the structure collapses (CN~5) and then gets a fully octahedral structure (CN=6) at 15 GPa (Guthrie et al, 2004). During the decompression the tetrahedral structure is recovered below 2 GPa. Our vibrational observations fit very well with these earlier works. Moreover we found that it is possible to see similar changes in hydrous glass. The hydrous glass seems to get back a better shape concerning the recovering of the main band. This suggests that hydrous glass, due to existence of non-bridging oxygen, may exhibit different structural change during compression. The present study demonstrated that O-H bonding can be used to get further information of structural behavior of glasses under pressure.

Synthesis and structural characterization of high-pressure AlPO_4 phases

Sindy Reibstein, TU Bergakademie Freiberg

supervised by Dr. Xianyu Xue and Dr. Masami Kanzaki

Because of its quartz like structural behavior at ambient conditions, AlPO_4 is seen as an appropriate analog for SiO_2 also at high temperature - high pressure conditions. The phase relation of AlPO_4 was target in several investigations at high temperatures (e.g. ⁽¹⁾Muraoka Y. & Kihara K. 1997) or high pressures (e.g. ⁽²⁾Sharma S.M. et al 2000). However, the phase relation of AlPO_4 in the middle temperature-pressure range is poorly known. There is only one study conducted by ⁽³⁾Seifert K.F. 1968 reporting the observation of two polymorphs of AlPO_4 at 6 GPa and 400-900°C with unsolved structures and one polymorph at 7-10GPa and 900-1000°C with a *Cmcm* structure containing one octahedrally coordinated aluminum site and one tetrahedrally coordinated phosphorous site. To obtain new information on the pressure-temperature phase relations in this system, this project was carried out.

An USSA-5000 Kawai-type multi-anvil press has been used for high-pressure synthesis. Two samples have been synthesized at 6 GPa and 1000°C, 1500°C respectively using a starting material of AlPO_4 chemical as received. A third sample produced at 6 GPa and 1500°C using a starting material of AlPO_4 chemical dried at 1000°C for 26 hours. The recovered samples have been characterized by a range of advanced NMR techniques, including ^1H , ^{27}Al and ^{31}P MAS NMR, ^{27}Al triple-quantum (3Q) MAS NMR, ^{31}P double-quantum (DQ) MAS NMR, $^1\text{H} \leftarrow \rightarrow ^{27}\text{Al}$, $^1\text{H} \leftarrow \rightarrow ^{31}\text{P}$ and $^{27}\text{Al} \leftarrow \rightarrow ^{31}\text{P}$ cross-polarization (CP) MAS NMR, and $^{27}\text{Al} \rightarrow ^{31}\text{P}$ 3QMAS/HETCOR (heteronuclear correlation) NMR, as well as micro-Raman and electron microprobe analyses.

For the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, two new crystalline AlPO_4 phases have been found to be stable at 6 GPa and 1500°C. Each of them contains multiple six (and five?) coordinated aluminum sites and multiple four coordinated phosphorous sites. For all three samples, minor hydrous phases were also detected. One of them has been confirmed to be trolleite $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$. Trolleite has been previously reported to be stable up to 2.3 GPa at 1000°C (⁽⁴⁾Bass and Sclar 1979). This study has confirmed that its stability field extends to at least 6 GPa.

⁽¹⁾ Muraoka Y. & Kihara K.; The temperature dependence of the crystal structure of berlinite, a quartz-type form of AlPO_4 ; *Physics and Chemistry of Minerals* 24 (1997) p.243-25

⁽²⁾ Sharma S.M. et al; High-pressure x-ray diffraction study of $\alpha\text{-AlPO}_4$; *Physical Review B* 62, 13 (2000) p.8824-8827

⁽³⁾ Seifert K.F.; Zur Druck-Kristallchemie der AX_2 -Verbindungen; *Fortschritte der Mineralogie* 45 (1968) p214-280

⁽⁴⁾ Bass J.D. & Sclar C.B.; The stability of trolleite and the $\text{Al}_2\text{O}_3\text{-AlPO}_4\text{-H}_2\text{O}$ phase diagram; *American Mineralogist* 64 (1979) p.1175-1183