

## Research of Helium Isotopes in Taiwan: The Legacy of Dr. Tsanyao Frank Yang

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Helium isotope systematics is a powerful proxy to distinguish fluid origins and conveys fruitful geological information. In the past several decades, this robust isotope systematics had offered pivotal knowledge on many key issues in Earth and planetary sciences. It revealed essential geological information of Taiwan as well. Taiwan is located on the junction of two subduction systems-Ryukyu Arc and Luzon Arc. The geotectonic setting is complex and intriguing.

Dr. Tsanyao Frank Yang was the pioneer of gas geochemistry studies in Taiwan. He established the first gas geochemistry laboratory in National Taiwan University in 1998 and started exploring all possible research topics on and around this tectonic-active island. In the past two decades, his research covered volcanic/hydrothermal gas studies, volcanic activity monitoring, gas hydrate exploration, soil gas as a tool to locate fault traces, soil gas flux measurement, earthquake precursory, mud volcanoes, low-temperature geochronology and many more. He died of pancreas cancer in March 2015. He was a warm and enthusiastic mentor, a prolific scientist and a great friend. He will always be remembered.

Here we present Dr. Yang's achievement on helium isotopes studies in Taiwan throughout his research career. We integrate all the research results from his team and summarize the observations. We will show the distribution of helium isotope ratios in Taiwan and its implications on tectonic settings.

Keywords: Tsanyao Frank Yang, Taiwan, Helium isotopes

## Volatile behaviors at an immature stage of subduction zone inferred from volcanic glasses in the Bonin fore-arc (IODP Expedition 352)

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IODP Expedition 352 was targeted to drill the entire magmatic sequence comprising the outer Bonin fore-arc to elucidate early subduction dynamics. During the expedition, a total of 1.22 km of igneous basement related to subduction initiation was cored from four sites (U1439, U1440, U1441, U1442). Two sites (U1440 and U1441) located nearer to the trench (stratigraphically lower and older sequence than U1439 and U1442), recovered igneous rocks at the basement that are mostly fore-arc basalts (FABs). From other two sites (U1439 and U1442) located ~15 km west from U1440 and U1441, boninites were recovered.

From all sites, we recovered fresh volcanic glasses manifest as chilled margins of pillow lavas, massive lavas, hyaloclastites and pyroclastic deposits. In order to constrain behaviors of volatiles at an immature stage of subduction zone, we analyzed volatile ( $H_2O$ ,  $CO_2$ , F, Cl, S) and  $P_2O_5$  concentrations of 100 volcanic glasses (31, 23, 1 and 45 samples from U1439, U1440, U1441 and U1442, respectively) using SIMS (CAMECA IMS 1280-HR) at JAMSTEC.

Glasses from the boninite sites (U1439 and U1442) are higher in  $H_2O$  (~1.9 wt%) at the lower parts of the holes and slightly lower in  $H_2O$  (~1.6 wt%) at the upper parts of the holes and are remarkably in low  $CO_2$  (< several ppm: below detection limit, DL) and S (7-130 ppm). Their F and Cl contents are 66-166 ppm and 357-981 ppm, respectively.

On the other hand, most glasses from the FAB sites (U1440 and U1441) have various  $H_2O$  contents (0.11-0.57 wt%) and measurable  $CO_2$  contents (67-151 ppm) with high S contents (776-1250 ppm). Their F and Cl contents are 62-111 ppm and 101-597 ppm, respectively. Three highly evolved glasses (MgO 3.3 wt%) probably from the same glassy layer from U1440 are high in  $H_2O$  (0.80 wt%), F (300 ppm) and Cl (2900 ppm). We also found a boninitic glass between FAB lavas from U1440, in terms of  $H_2O$  (1.95 wt%),  $CO_2$  (below DL) and S (301 ppm).

F/P ratios of glasses, which reflect their original source mantle, are  $0.49 \pm 0.03$  (1 standard deviation) for boninites and  $0.28 \pm 0.02$  for FABs. Since the F/P ratio of the depleted upper mantle (DM) is  $0.27 \pm 0.11$ , those of FABs have not been influenced by subducting materials. However, 10-50 times higher Cl/K (0.6-4) and 2-4 times higher  $H_2O/F$  (24-56) ratios of FABs than those of DM indicate influx of a small amount of Cl-rich fluid to the mantle wedge at the very beginning of subduction formation. Boninites are highly enriched in  $H_2O$  ( $H_2O/F$ : 110-298), but not in Cl (Cl/K: 0.1-0.4) relative to FABs, indicating that contribution and composition of subducting materials have changed with time.

Keywords: subduction zone, volatiles, IODP

## Noble gas and halogen subduction processes constrained by the analysis of olivines from Izu-Mariana arc lavas

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The presence of noble gases and halogens with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan [1,2], mantle-derived xenoliths from Kamchatka and Luzon arcs [3], and in seafloor and forearc serpentinites [4] along with seawater-like heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [5] strongly suggest the subduction of sedimentary-pore-fluid-like noble gases and halogens. The noble gas and halogen compositions of olivines in arc lavas of the Izu-Mariana subduction zone were determined to develop a better understanding of the processes that control the return of these volatile and highly incompatible elements into the mantle. Trace amounts of halogens (Cl, Br, and I) in the olivine samples were measured using a combination of neutron irradiation and noble gas mass spectrometry [6].

The  $^3\text{He}/^4\text{He}$  ratios of samples are in the range of the mid-ocean ridge basalt (MORB) value. This is consistent with helium isotope ratios of the subduction zone mantle xenolith [3], which indicates a considerably low contribution to the mantle wedge beneath the arc of radiogenic  $^4\text{He}$  in the subduction fluids observed in the Sanbagawa samples exhumed from depths in the range from 30 to 100 km [1,2]. In contrast, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for each volcano (299-620) are significantly lower than the MORB source (up to 32,000 [5]), which indicates significant involvement of atmospheric Ar ( $^{40}\text{Ar}/^{36}\text{Ar} = 296$ ) in the arc magmas. Systematically higher  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in the rear arc than in the volcanic front suggest that subduction of seawater-derived Ar has a significant effect on the noble gas composition of the magma-generation region. Although the halogen compositions of most of the olivines are close to that of MORB-source mantle, some samples from the rear-arc regions show a significant contribution from pore-fluid-derived halogens. Combined with the noble gas results, halogen-poor fluid associated with atmospheric noble gases may be dominantly released from the subducting slab beneath the arc, while halogen supply from the subducted slab is limited to the magma generation region beneath some volcanoes in the rear arc. This implies the relative persistence of halogens in the subducting slab compared with noble gases.

A simple mass balance calculation of subducted and mantle-derived Ar isotopes reveals that higher subduction flux than that of seawater-derived Ar in the pore fluids of the subducting sediment/crust is required. Although the serpentinitized lithosphere in the subducting slab has been regarded as the best candidate for the carrier of seawater-derived Ar with high subduction flux [4], the ratios of halogens and noble gases to water of slab-derived fluids preserved in the fluid inclusions of subduction zone mantle peridotites are inconsistent with the ratios in serpentinites collected from the Earth's surface. This requires strong coupling behavior of halogens and noble gases with their host water during hydration of the subducting materials, release of aqueous fluids from subducted slab, and upward migration of the fluids in the mantle wedge. It remains unclear whether noble gases and halogens in the subducting materials are completely released beneath the Izu-Mariana rear arc. However, the presence of seawater-like noble gases in the convecting mantle [3] implies that a small portion of seawater-dissolved atmospheric noble gases may be transported to greater depths in the deeper mantle, and then incorporated into the mantle convection.

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Keywords: halogen, noble gas, subduction, mantle, volatile recycling

## On the coexistence of high-Mg andesites and ultramafic volcanic rocks

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In order to understand the origin of magmas in the hydrous upper mantle, we have been investigating the phase relation and compositions of phases in the system peridotite-H<sub>2</sub>O. Using X-ray radiography technique together with Kawai-type multi-anvil high-pressure apparatus (SPEED-1500, SPring-8, Japan), the second critical endpoint in the peridotite-H<sub>2</sub>O system was determined to be at around 3.8 GPa and 1000 °C (corresponding to a depth of ~ 110 km) [1]. It is possible that two fluid phases (i.e., aqueous fluid and hydrous silicate melt) coexist up to 3.8 GPa. Above 3.8 GPa, however, hydrous silicate melt and aqueous fluid in upper mantle becomes indistinguishable from each other and the melting temperature of hydrous mantle peridotite can no longer be defined beyond this critical condition. Using the quenched recovered samples obtained by Mibe et al. [1], chemical compositions of aqueous fluid, silicate melt, and supercritical fluid magma in the vicinity of second critical endpoint were determined by the electron microprobe analyzer. In the run at 3.6 GPa, the composition of aqueous fluid was high-Mg andesitic, whereas the composition of hydrous silicate melt was komatiitic. Our experimental results indicate that high-Mg andesitic magma and komatiitic magma can be generated at the same time as the liquid-fluid immiscibility near the second critical endpoint in the peridotite-H<sub>2</sub>O system. Some natural examples on the coexistence of high-Mg andesites and ultramafic volcanic rocks from various tectonic settings and locations around the world will also be presented.

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Keywords: high pressure and high temperature

Redox dehydration melting of mantle transition zone deduced from the H<sub>2</sub>O storage capacity

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Knowledge of the H<sub>2</sub>O storage capacities of minerals forming mantle peridotite provides essential constraints on estimation of H<sub>2</sub>O content and the onset of hydrous partial melting in the mantle. In the mantle transition zone, wadsleyite can store significant amount of H<sub>2</sub>O in their crystal structures under extremely high oxygen fugacity. However, the H<sub>2</sub>O storage capacity has not been determined under the low oxygen fugacity predicted from the mantle transition zone<sup>7</sup>. Here we report that the H<sub>2</sub>O storage capacity of wadsleyite in equilibrium with the peridotite assemblage under lower oxygen fugacity is much smaller than that under higher one. Very low H<sub>2</sub>O storage capacity of wadsleyite can attribute to the low H<sub>2</sub>O activity in the melt. Considering the more reducing state in the deep mantle, dominant speciation of volatile phases is not H<sub>2</sub>O but H<sub>2</sub>. Low H<sub>2</sub>O activity in the reduced deep mantle requires that H<sub>2</sub>O storage capacity in the Earth's mantle is much smaller than that predicted from the maximum H<sub>2</sub>O concentration determined under the high oxygen fugacity. The hydrated and oxidised subducted slab will induce "redox dehydration melting" through decrease of oxygen fugacity by the surrounding reduced mantle transition zone. H<sub>2</sub>O in the generated melt will be reduced to hydrogen through the oxidation of iron-bearing minerals. Fe-H melt or FeH<sub>x</sub> trapping the released hydrogen would become the main carrier of hydrogen into the deep mantle.

Keywords: redox condition, water storage capacity, dehydration

## Noble gas incorporation into the deep Earth

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The present state of the Earth evolved from energetic events that were determined early in the history of the solar system. A key process in reconciling this state and the observable mantle composition with models of the original formation relies on understanding the planetary processing that has taken place over the past 4.5Ga and the range of most relevant P-T conditions governing primary segregation and mixing. Recent developments with the laser-heated diamond anvil cell have made possible extension of the conventional pressure limit for solubility and partitioning experiments as well as the direct study of volatile trace elements. In particular, selected results of liquid-liquid, metal-silicate (M-Sil) partitioning are presented for several noble gas and molecular elements in a synthetic chondritic mixture, spanning a wide range of atomic number - helium to iodine. The application of these methods is new and allows extension of geochemical studies performed in larger-volume apparatus. Not only is the attainment of uniform and equilibrium mixing important in this small-sample environment (perhaps 10-100 micrometers in linear dimension depending on the pressure), but also the microanalysis of quenched samples to determine the distribution of minor and trace elements. Systematic results on the solubility of He, Ne and Ar suggests that their incompatibility in solid silicate and metallic phases may not have been as great as previously thought -- and hence are candidates for storage in the deep Earth. Helium solubility in the metal phase relative to that of the silicate suggests the core should be considered a deep Earth reservoir for example. If the core is a reservoir, then the mechanisms for interaction with the lower mantle become important requiring examination of the processes of material exchange at the core-mantle boundary. The interpretation of the results depended on precise microanalysis of LHDAC samples, and the application of UV laser ablation, mass-spectrometric techniques that provided for the first time a spatially resolved depth profile in samples. Attention needs to be paid to the likely mode of solubility - entrapment versus bonded and non-bonded host environments for example - and we attempt to consider the real implications for the Earth in either case.

Keywords: Noble gases, Laser-heated diamond-anvil cell, core-mantle, element partitioning, solubility

## Hydrous bridgmanite: Water storage capacity in the lower mantle

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Recently hydrous ringwoodite was found in a natural diamond inclusion, which includes ~1.5 wt% H<sub>2</sub>O. In addition, the experimental studies show that wadsleyite and ringwoodite, which are the most abundant minerals in the mantle transition zone, can contain water up to 2.2-2.7 wt% [e.g. Inoue et al., 1995, 1998, Kohlstedt et al., 1996]. These results show that the mantle transition zone is a strong water reservoir in the Earth's interior, and at least locally, hydrous. On the other hand, the water storage capacity in the lower mantle is a matter of debate.

We have been conducting the study for the stability and water solubility of hydrous and nominally anhydrous minerals, and the recent target is the effect of Al. In this process, we found that Al-bearing bridgmanite (Mg-silicate perovskite) can contain significant amount of water. The possible H substitution mechanism can be proposed by means of chemical compositional relationship between Mg, Si, Al and H. In addition, we clarified the possible H position in the bridgmanite by means of the powder neutron diffraction analysis in J-PARC, together with the single crystal X-ray structural analysis in PF. This shows that the significant amount of H (water) can be stored in the Earth's lower mantle.

Because of the H in the bridgmanite, the physical properties of the bridgmanite can be changed. The information is very important to discuss the water content and the composition in the lower mantle. We have also conducted the equation of state and the ultrasonic wave velocity measurements of hydrous bridgmanite in BL04B1, SPring-8 to determine the elastic wave velocities and the elastic properties under high pressure and temperature condition. In this talk, I will introduce about our "hydrous bridgmanite" project.

Keywords: hydrous bridgmanite, lower mantle, Synchrotron X-ray in situ experiment, neutron diffraction, elastic property



## Formation of a hydration zone at the bottom of the lower mantle

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One of the major water carriers into the lower mantle is delta-AlOOH-phase H  $\text{MgSiO}_2(\text{OH})_2$  solid solution (aluminous phase H) [1]. Our experiments revealed that the solid solution containing water can be stable to the core-mantle boundary region, 120 GPa and 2500 K [2, 3], which is the condition along the normal mantle geotherm. The core-mantle boundary is the region with a large temperature gradient, thus dehydration or dehydration melting is inevitable at the core-mantle boundary. There are three possibilities on the roles of this hydrous phase at the core-mantle boundary region: First, the reaction of this hydrous phase with the metallic core to introduce hydrogen into the core. Second, dehydration melting at the core-mantle boundary which might create a partial molten low velocity zone at the core-mantle boundary. Third, formation of a hydrated zone at the base of the lower mantle by supplying fluid dehydrated at the hot core-mantle boundary. Here, we consider a possible role of this hydrous phase for formation of a hydration region at the base of the lower mantle, the third process listed above.

Ohira et al. [2] revealed that hydration of aluminous bridgmanite creates delta-AlOOH phase and  $\text{MgSiO}_3$  bridgmanite containing smaller amount of  $\text{Al}_2\text{O}_3$ . This hydration reaction can occur by supplying fluid dehydrated at the hot core-mantle boundary. Mashino et al. [4] measured the sound velocity of delta-AlOOH at high pressure and revealed that both  $V_p$  and  $V_s$  of this phase is greater than the major transition zone minerals such as ringwoodite and majorite, whereas the velocities are lower than bridgmanite at the bottom of the lower mantle. Drop of sound velocities can be expected by formation of delta-AlOOH phase by consuming  $\text{Al}_2\text{O}_3$  in bridgmanite at the base of the lower mantle. Decrease of the sound velocity can be accounted for the low velocity nature at the core-mantle boundary. Thus, the bottom of the lower mantle may be a second largest water reservoir next to the mantle transition zone.

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Keywords: Lower mantle, Core-mantle boundary, delta-AlOOH, Phase H, Hydration, Low velocity region

## Global water cycle constrained by the evolution of dynamic hypsometry

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The presence of liquid water on the surface is one of the important characteristics that make the Earth a unique planet, and it is usually considered to be critical for a planet to be habitable. Also, surface water is often believed to be essential for the operation of plate tectonics, which in turn enables the return of surface water to the planetary interior. The amount of surface water is thus a time-dependent variable that is controlled by the dynamics of Earth's interior. The Earth not only has surface water but also has just a right amount of it to allow the subaerial exposure of continental crust, which is important for the modulation of the atmospheric composition as well as various biogeochemical cycles. To better understand the role of water in the Earth history, therefore, we need to decipher how the distribution of water between the surface and the deep interior has changed with time and how it has affected the surface environment. In this contribution, we focus on reconstructing the history of surface water by assembling relevant observational constraints and theoretical considerations. It is now possible to derive a fairly robust constraint on the history of surface water, at least back to around 3 Ga, by examining the constancy of continental freeboard in light of the evolution of dynamic hypsometry. We also discuss its implications for the coevolution of Earth's interior and surface environment.

Keywords: oceans, mantle convection, plate tectonics

## Global fluxes of fluorine and sulfur efficiently released at mid-ocean ridges

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Fluorine and sulfur are major components of high temperature volcanic gases, and significantly affect surface environments due to high chemical activity. Therefore their fluxes between the mantle and surface environments are important to elucidate evolutionary histories of Earth's atmosphere and ocean. We estimated fluorine and sulfur fluxes at mid-ocean ridges (MOR) based on chemistry of submarine vent fluids and MORB vesicles which may reflect components efficiently released from magmas through upward propagation of film ruptures by bubble expansions during decompression[1]. Fluorine flux was constrained by two methods as follows:

1) Multiplication of fluorine concentrations in submarine hydrothermal fluids and the fluid flux at MOR may provide an estimate of fluorine flux at MOR. A worldwide vent chemistry research[2] suggested that vent fluids are depleted in fluorine ( $<0.74$  ppm F) relative to seawater (1.29 ppm F). The global flux of vent fluids of  $(8.0 \pm 2.1) \times 10^{15}$  g/y was calculated using a numerical Bayesian inversion procedure to explain the relationship between compositions of hydrothermal fluids and altered sheeted dikes[3]. This value is not consistent with the flux of  $(3.1 \pm 0.7) \times 10^{16}$  g/y obtained based on the  $^3\text{He}$  concentration of  $(1.7 \pm 0.2) \times 10^{-14}$  mol/g ( $1\sigma$ ) in 10 high temperature ( $>200^\circ\text{C}$ ) hydrothermal fluids at EPR and MAR[4], and the MOR  $^3\text{He}$  flux of  $(527 \pm 102)$  mol/y[5]. These two fluid fluxes, when multiplied by the maximum fluorine concentration of  $3.88 \times 10^{-8}$  mol/g, provides fluorine fluxes ranging from  $3.1 \times 10^8$  mol/y to  $1.2 \times 10^9$  mol/y with an average of  $(7.6 \pm 4.5) \times 10^8$  mol/y.

2) Multiplication of F/ $^3\text{He}$  ratios in MORB vesicles and  $^3\text{He}$  flux will provide another fluorine flux. We analysed eight MORB vesicles ( $13^\circ\text{N}, 17^\circ\text{S}$  on EPR;  $15^\circ\text{N}, 30^\circ\text{N}, 37^\circ\text{N}$  on MAR;  $24^\circ\text{S}-25^\circ\text{S}$  on CIR) with a crushing technique extracting fluorine and helium simultaneously[6]. Fluorine was extracted into alkaline solution and measured by an ion chromatography (ICS-2100; Thermo Fisher Scientific Inc.), while helium was measured by a noble gas MS (VG5400; Waters Corp.), both housed at AORI. F/ $^3\text{He}$  ratios in vesicles range from  $2.0 \times 10^5$  to  $<2.8 \times 10^7$  with an average of  $(1.2 \pm 0.5) \times 10^6$  ( $1\sigma$ ), providing a global fluorine flux of  $(6.4 \pm 3.1) \times 10^8$  mol/y by multiplying the MOR  $^3\text{He}$  flux.

One might calculate a weighted mean of two MOR fluorine fluxes to be  $(6.8 \pm 2.5) \times 10^8$  mol/y. However it should be noted that the actual MOR fluorine flux may be lower than this flux because the applied fluorine concentration in hydrothermal fluids is an upper limit, and seawater contamination was not deconvolved for MORB vesicles. We also note that this flux is much lower than flux ( $1.13 \times 10^{12}$  mol/y) estimated using the F/ $\text{CO}_2$  ratio in the MORB source and  $\text{CO}_2$  flux from the mantle[7], implying that the most part of fluorine resides in the melt and is not released immediately after the oceanic crust production.

Sulfur flux, together with carbon, will be estimated based on chemistry of vent fluids and MORB vesicles, which is similar approach as for fluorine. In addition, comparing MOR and arc fluxes, the global cycles of fluorine, sulfur, and carbon will be discussed in the presentation.

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Keywords: fluorine flux, sulfur flux, carbon flux, mid-ocean ridge basalt, hydrothermal fluid, volcanic gas



## Redistribution of noble gases during magma ocean crystallization

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Recent measurements of Xe isotopes place the formation of high  $^3\text{He}/^4\text{He}$  mantle to within the first 80 Ma of solar system history. This timeframe coincides with Earth's accretion, leading to the hypothesis that a magma ocean concentrated materials that now comprise the high  $^3\text{He}/^4\text{He}$  source. We have initiated an experimental study to better constrain the distribution of noble gases within the solid Earth during magma ocean crystallization and the petrogenesis of high  $^3\text{He}/^4\text{He}$  mantle. We report the Ar contents of minerals (bridgmanite, periclase) and liquids (silicate and Fe metallic melts) salient to magma ocean crystallization that were synthesized in the presence of Ar-rich fluids at high pressure. Our initial experiments are conducted with Ar because it is the middle noble gas, so its behavior is most representative of the bulk elemental group. Experiments were conducted using laser-heated diamond anvil cells (DAC) and multi-anvil (MA) apparatus and were analyzed by microprobe and laser ablation techniques.

The Ar contents of the large majority of bridgmanite and periclase analyses in the MA experiments were at or below the WDS detection limit. Detection limits are calculated from counting statistics and nominally approached 20 ppm Ar for longer duration analyses. Saturation of an Ar-rich fluid in the MA experiments was confirmed by high Ar concentration blebs throughout the recovered samples. Laser ablation analyses on a MA experiment yielded highly variable Ar concentrations in bridgmanite, ranging from 450 to 10 ppm. Given the observation of Ar-rich blebs in the MA experiments, we interpret the lower range in Ar concentration as our current best estimate of Ar solubility in bridgmanite. The Ar contents of samples from DAC experiments were more variable, but large areas of laser-heating spots on bridgmanite contain Ar contents at or below the detection limit by EDS microprobe (~100 ppm Ar). Bridgmanite disproportionated to (Mg,Fe)O and SiO<sub>2</sub> in some higher temperature heating spots. These phases also had undetectable Ar concentrations. In a parallel series of experiments, we have also quantified the concentration of Ar dissolved into silicate and Fe metallic liquids at 15 GPa using a DAC. Preliminary measurements by EDS yield Ar concentrations of 4000 ppm for the silicate liquid and Ar concentrations below detection in the Fe metallic liquid. This concentration is similar to previous determinations of Ar solubility in silicate liquids at transition zone pressures.

Our results imply that noble gases are strongly concentrated in silicate liquids over minerals and liquid Fe during magma ocean episodes. High  $^3\text{He}/^4\text{He}$  mantle is associated with unradiogenic noble gas signatures. Given this, we suggest that the petrogenesis of high  $^3\text{He}/^4\text{He}$  mantle is related to the fractionation of a silicate liquid during a magma ocean episode.

Keywords: noble gases, magma ocean, volatiles