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Aqueous Geochemistry at High Pressures and High Temperatures

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Project Goals

This project is aimed at experimental characterization of the sound velocities, equations of state (EOS), and derived physical and chemical properties of aqueous solutions and carbon dioxide at extreme pressure and temperature conditions relevant to processes occurring in the interior of the Earth. Chemical transport, phase changes (including melting), fluid-solid reactions, and formation of magmatic liquids at convergent plat boundaries are a key motivation for this project. Research in this area has long been limited by the extreme experimental challenges and lack of data under the appropriate pressure-temperature (P-T) conditions. The vast majority of studies of aqueous geochemistry relevant to terrestrial problems of fluid-rock interactions have been conducted at 0.3 GPa or less, and the widely used Helgeson-Kirkham-Flowers equation of state for aqueous species is

applicable only at ~ < 0.5 GPa. These limits are unfortunate because fluid flow and reactions plays a central role in many deeper environments. Recent efforts including our own, have resulted in new experimental techniques that now make it possible to investigate properties of homogeneous and heterogeneous equilibria involving aqueous species and minerals over a much broader range of pressure and temperature appropriate for deep crustal and upper mantle processes involving water-rich fluids. We carried out 1) Brillouin scattering measurements of the equations of state and molar volume of water and carbon dioxide to over 10 GPa and 870K using precise resistance heating of samples under pressure in the diamond anvil cell, and 2) the phase diagrams of the water and CO2, and 3) Exploring new experimental approaches, including CO2 laser heating of samples in a diamond cell, to measurements of sound velocities, EOS, and phase relations by Brillouin scattering to far greater pressures and temperatures.

Personnel Supported

1. Liqin Sang (Masters student, worked on phase diagram, velocities, and equation of water for the first 2 years of the project.)
2. Jin Zhang (PhD student, assisted Liqin Sang on all synchrotron work on H_2O, developed method for ultra-high P-T velocity and EOS measurements using laser heating of samples in the diamond cell ; worked on CO_2 phase diagram).
3. Carmen Sanchez-Valle (Post-doc and collaborator. No salary support but the project supported measurements in Bass lab.)
4. Jay Bass (PI, directed and assisted with all aspects of the work)

Progress Years 1-2.5

Design and Construction of new high-T DACS:

We have developed a new type of membrane diamond-anvil cells (MDAC) that allows us to easily adjust pressure and temperature in small increments without removing the diamond cell from the Brillouin scattering system. Design and construction of these MDAC's (Fig. 1) was one of the LLNL group's parts of the project. The UIUC group modified the Brillouin spectrometer at UIUC for use with the new MDAC, and designed adaptors for the Brillouin system at APS to accept the new MDAC. This MDAC was successfully used for studies at high pressures of Brillouin scattering at UIUC and combined X-ray diffraction and Brillouin scattering at the APS. For Brillouin scattering experiments there needs to be symmetric optical access to the sample, which is achieved through conical openings in the MDAC body and diamond seats. Our completed experiments utilized 60° conical openings, which allowed us to perform Brillouin experiments with a 50° scattering geometry. A new design to allow for 90° scattering was started but not completed. The vacuum housing for thermally isolating the MCAC was also modified so that it can be mounted on the omega-circle of the UIUC Brillouin system and it is now possible to quickly

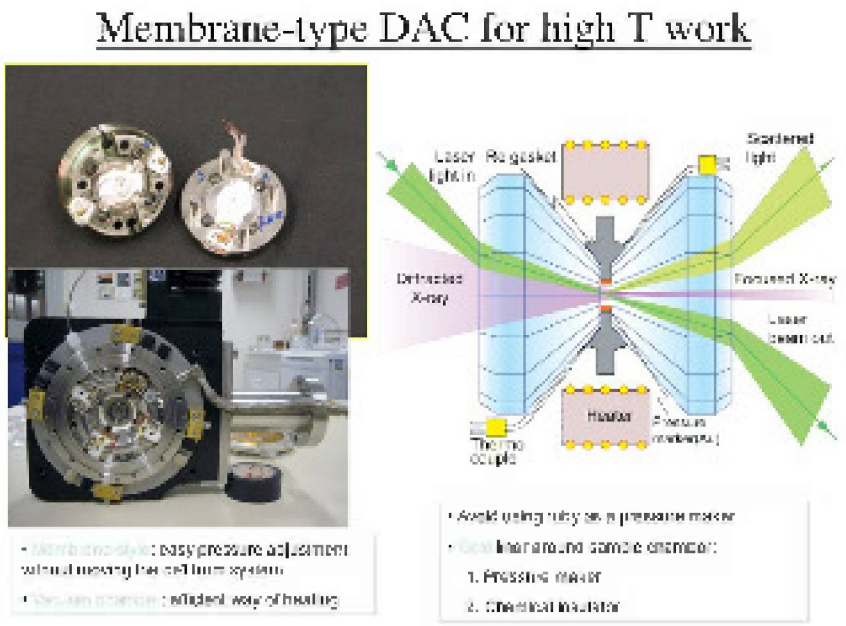

Figure 1: Membrane DAC's (left), and the experimental configuration used in Brillouin-synchrotron XRD experiments at GSECARS of the APS (right).

and efficiently switch the Brillouin system from its configuration for crystalline samples to the set up used for fluid high P-T studies with the MDAC. As part of our initial efforts, the LLNL group both provided the new MDAC's and training to the UICI group in how to run the system. Necessary vacuum systems, gas pressurization equipment, power supply and temperature stabilization systems were purchased and set up at UIUC. It was longer necessary to ship shared equipment (except for the MDACs) between LLNL and UIUC.

Brillouin Scattering

Extensive in-house experiments were carried out at UIUC on H_2O and CO_2. The quality of the Brillouin spectra was generally excellent. Initial experiments were carried out with the standard "two-hole" method (Fig. 2), in which the DAC is prepared with two circular sample chambers in the gasket. One chamber contained pure water, and the other hole contained the water plus a pressure marker, such as ruby or SrB_4O_7: Sm (Sm-doped). The problem that needs to be avoided, is contamination of the pure water or aqueous solution by the pressure marker, due to the extreme solubility of materials (including pressure markers) in supercritical water. Thus, by using two holes (sample chambers) in the gasket between the diamond anvils, one hole can contain a pure

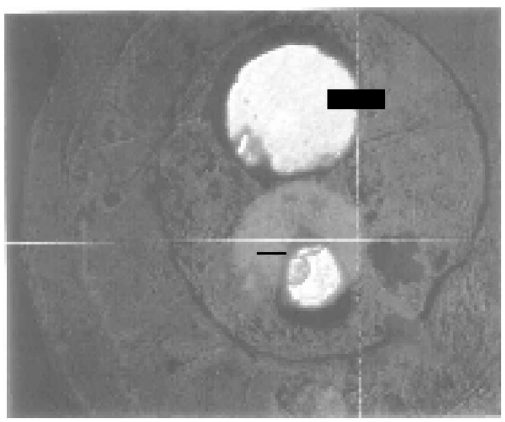

Fig.2. Photograph showing the compression chamber arrangement used for the study of highly reactive aqueous fluids. Two separated compression chambers are drilled in the Pt-liner isolating the samples from the stainless-steel gasket. Black scale bar = 60 microns.

sample (aqueous solution), and the other, contains a large amount of the pressure marker in a saturated solution. Pressure can then be measured using usual fluorescence techniques.
We found that the reproducibility of results using the two-hole method is much less than expected from the ruby or other fluorescence methods. The cause is simple: pressure is not always the same in the sample chamber and the pressure-measuring holes. We are in the process of quantifying this effect and worked towards improving high pressure and temperature DAC techniques to make the high temperature DAC a more reliable and accurate technique. We felt that it is essential to find an independent and less uncertain method of quantifying pressure in experiments on aqueous fluids and to this end, we believe we may have found a solution to the problem of measuring pressure by use of synchrotron X-ray diffraction (XRD) and simultaneous Brillouin scattering.

Integration of Brillouin Sound Velocity Measurements with Synchrotron X-ray diffraction:

Synchrotron XRD provides an accurate means of measuring pressure at high temperature in the resistively heated DAC. This method therefore circumvents the problems inherent in the two-hole method. The technique requires an inert (or mostly inert) pressure marker whose thermal equation of state is well known. For aqueous fluids the reactivity of the rhenium gasket at high temperature requires the use of an inert liner. In our work, we lined the sample chamber of the MDAC with Au, which is both chemically inert to the supercritical water sample, and which can also serves as a pressure standard. XRD from the Au liner (Fig. 3) can used to directly determine the pressure in the sample chamber, using the known equations of state of Au (e.g., Jamieson, Anderson).

During Years 1 and 2 of the project, we carried out a series of experiment at the 13BM-D beamline of GSECARS of the Advanced Photon Source (APS), Argonne National Laboratory to demonstrate the feasibility of this technique. This is a unique facility in the US, in that it has a Brillouin scattering system integrated with synchrotron XRD capabilities on a

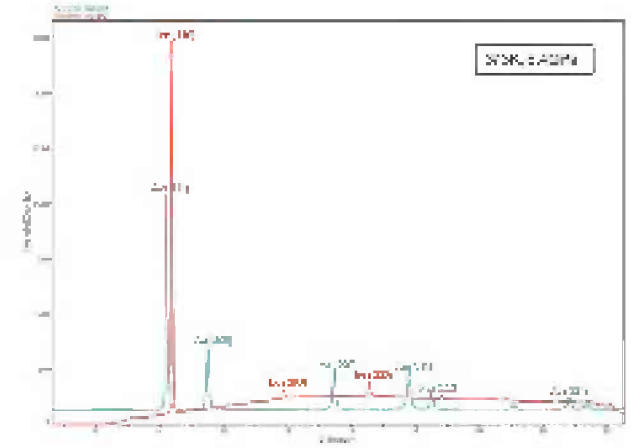

Figure 3: X-ray diffraction spectra showing ice VII and the gold liner pressure standard.

single beamline, allowing sound velocities (by Brillouin) and densities (by XRD) to be determined on a sample simultaneously. A figure showing the Brillouin-synchrotron system at the APS is shown in Fig. 4. The Brillouin portion of this facility was developed by Bass and coworkers (Sinogeikin et al., 2006) as part of a COMPRES Infrastructure Development project, and an Elasticity Grand Challenge grant from the NSF. Experiments were performed using a thin flake of Au within the sample chamber for comparison with the pressures obtained using diffraction from the edge of the Au liner. Our initial work shows that the pressures derived from the thin flake are identical in all cases to the pressure determined from the gasket edge when diffraction from both the sample and the gasket are present in the same spectra. The remarkably high level of consistency between pressures measured from the Au flake and the liner are likely due to the tightly focused X-ray beam (typically around 5 um at GSECARS), which allows us to isolate diffraction from the part of the Au liner immediately adjacent to the sample chamber where the stress state is close to hydrostatic and thus, records the pressure of the sample.

Two runs of 8 shifts each (about 2.5 days each) were made in Year 2 and another run was made during FY2011. The results obtained are shown in Fig. 5 and Fig. 7. Our most robust results obtained thus far are for the phase relations of water-ice VII at pressures to P~16 GPa and T=850C (Fig. 5). We performed phase identification using XRD, with crystalline ice VII giving clear Bragg diffraction peaks and water giving a diffuse diffraction spectrum (Fig 4). Phase identification was clear and unambiguous; only kinetic barriers to equilibrium conditions are not yet determined. The results obtained thus far clearly indicate that the melting curve of ice VII lies at substantially higher temperatures than obtained in the previous study of Datchi et al. (2000) (see also Lin et al., 2005). At the highest pressures of this study we find that ice VII melts at ~150C higher than found by Datchi et al. (2000). In-house experiments at UIUC will be done to reverse the water-ice VII reaction at a series of pressures (to demonstrate attainment of equilibrium) and to more tightly constrain the melting curve. These results will then be submitted for publication after the additional work (see future work below).

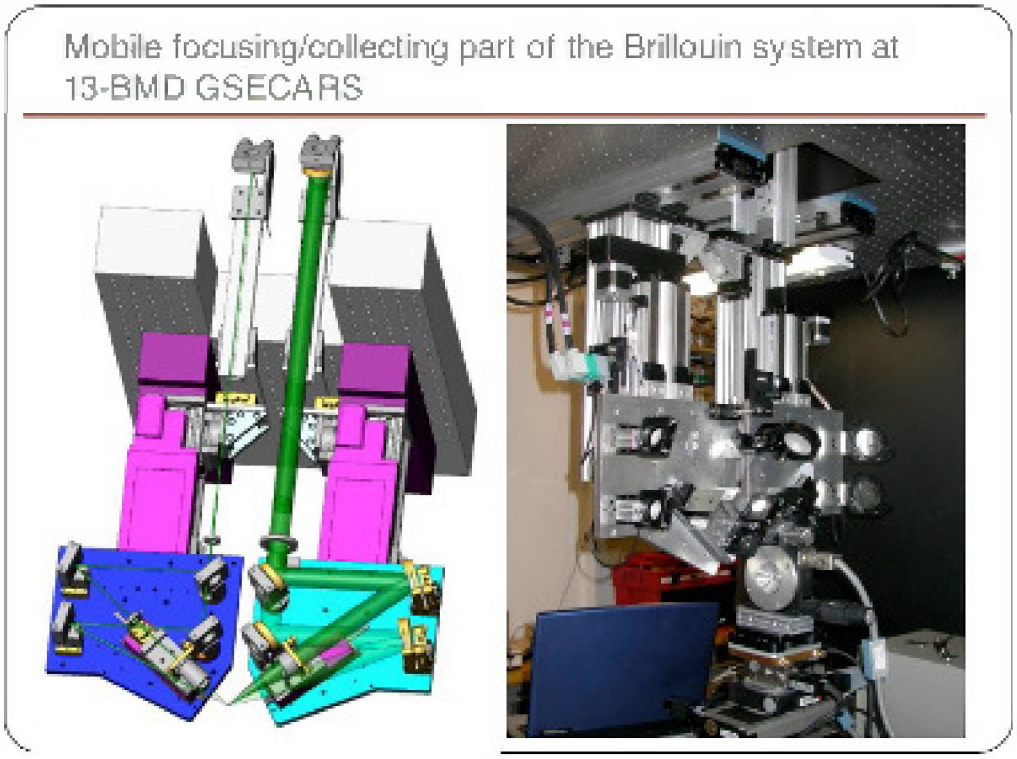

Fig. 4: Schematic (left) and photograph of the Brillouin scattering system at beamline 13BM-D (GSECARS, APS).

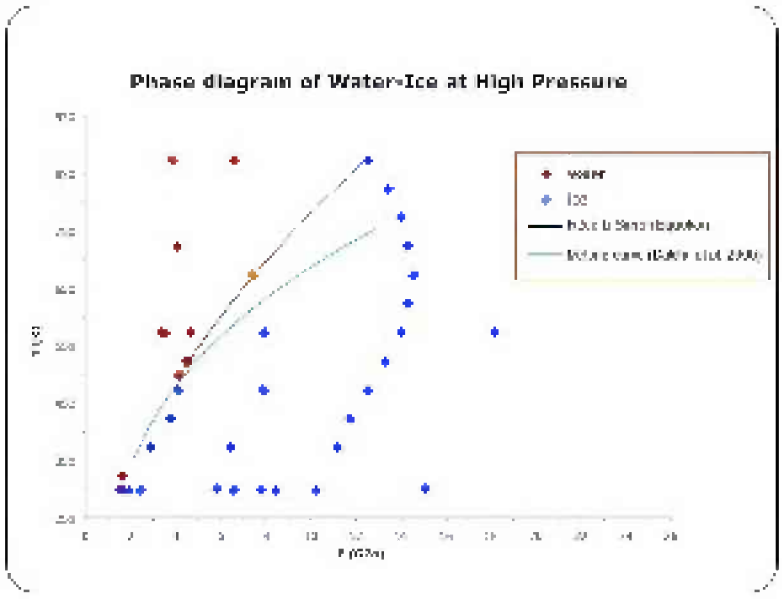

Figure 5: Phase diagram showing the phase boundary between liquid H2O and ice VII.

Our current thoughts on the reasons for the differences between our results and those of previous studies lies in the determination of pressures and temperatures in the DAC, and the purity of the sample. We contend that the LLNL design of DAC yields a very homogenous temperature environment and that our temperature measurements are accurate. To determine the validity of temperature measurements, we shifted some of our efforts to metrology, in order to accurately and precisely characterize the temperature and temperature gradients in our MDAC. For this purpose, we carried out a series of experiments using melting point standards (Fig. 6). Melting point standards were loaded into the MDAC using the same gasket and with thermocouples in the same position as would be used in a high- pressure experiment, but were not pressurized. We visually determined the onset of melting at 1 atmosphere pressure. Our data thus far shows that at temperatures up to 500C the error in our temperature measurements is approximately ±5°C at the extremes. The uncertainty in T increases at slightly higher temperatures to a maximum of ±20°C. At the highest temperatures we also varied the rate of temperature increase and varied the "wait time" between increasing temperature and making a observation of whether melting had occurred. We found that all these variables affect the inferred temperature and optimized our procedures for minimizing error in temperature determination. Moreover, melting is not uniform within the sample chamber, the first grains to melt are those in contact with the diamond anvils only, with sample material in contact with the gasket taking a much longer wait time to see melting.

We also note that our techniques allow us to make measurements on pure H_2O, In previous experiments of Datchi et al. (2000), as well as other studies, ruby, YAG, or SrB_4O_7: Sm^{+2} were contained in the sample chamber. As noted previously, due to the high solubility of these materials in supercritical water (especially SrB_4O_7: Sm), it is almost assured that the water is contaminated with appreciable solutes at higher pressures and temperatures. This likely explains, at least in part, why the results of this study deviate from those of Datchi et al. (2000) above P~3.5 GPa and T~475°C. We note that our results are consistent with what might be expected if the previous studies contained dissolved pressure marker in the sample chamber. In this case, the addition of components to the fluid should expand its phase field, thus reducing the melting temperature at fixed pressure. Another factor we believe contributes to the differences we observe is that virtually all other studies utilized the "two-hole" method of pressure measurement, which is known to require a pressure correction and can involve uncertainties of ~10% or more (Lin et al., 2005).

Sound velocities

We have measured the sound velocities in pure supercritical water and ice VII using the Brillouin scattering system at beamline 13BM-D (Fig. 8). These were among the first membrane diamond cell experiments carried out at that beamline. A 50° scattering geometry was employed. Our initial experiments were aimed at broadly exploring the full range of temperatures and pressures of interest. We have demonstrated that we can obtain high-quality data at all of the target pressures and temperatures of this project. Our results are in good agreement with the results of Abramson and Brown (2004) in the region where our data sets overlap (up to P=5.5 GPa and 400°C). Future efforts will concentrate upon obtaining a dense set of isotherms up to ~800°C in order to constrain the densities and equation of state of water (Abramson and Brown, 2004). Differences with previous results are likely to become apparent in the higher-temperature and higher-pressure regime since

ours is the first study not to use the “two-hole” method of determining pressure.

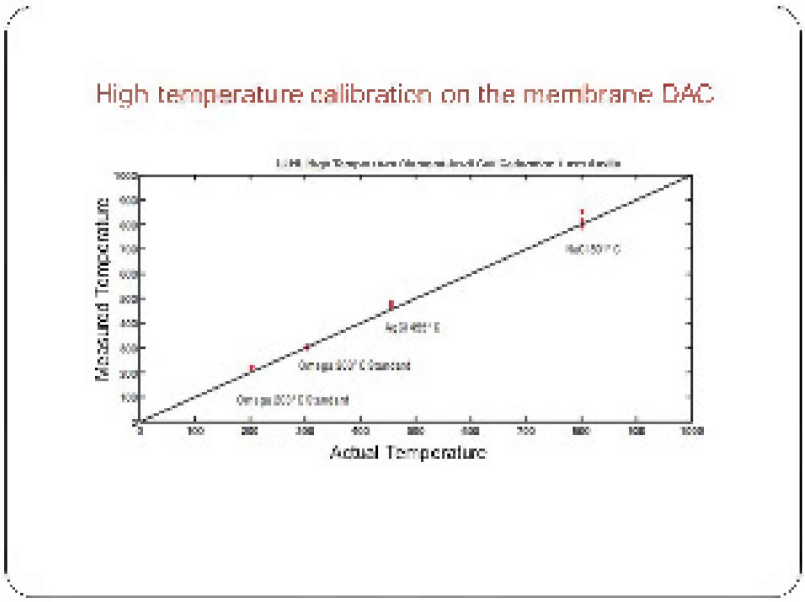

Figure 6: Calibration of sample temperatures in the membrane diamond anvil cell using melting point standards.

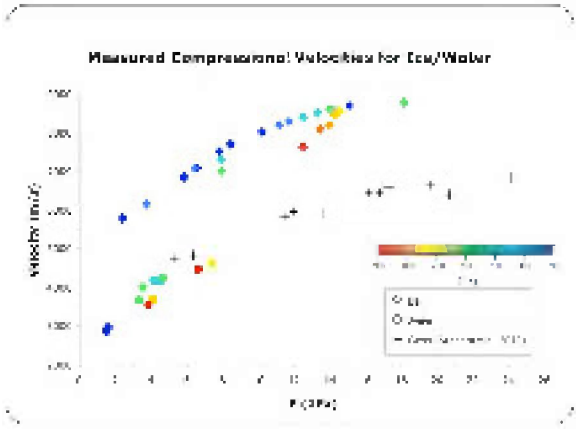

Figure 7: Speeds of sound for water and ice from measurements at beamline 13BM-D.
hole” method of pressure measurement, which is known to require a pressure correction and can involve uncertainties of ~10% or more (Lin et al., 2005).

Summary of Results Years 1-2.5

1. Design and fabrication of a new resistively-heated membrane diamond cell for Brillouin measurements.
2. Accurate characterization of temperature in the resistively heated membrane diamond cell using themocouple measurements.
3. Determination of the melting curve of ice VII to P=12.5 GPa and T=850°C.
4. Determination of the speed of sound of water to a maximum pressure of P=18GPa and T=850°K.

Progress & Activities From Year 3 to No-Cost Extension Years

During Year 3 of this project, several events significantly affected progress on this project and its direction. These were:

1. The Natural History Building, in which Bass' Brillouin and high-pressure labs were located, was condemned. It was necessary to dismantle Bass' labs and put them into storage while structural supports were installed for ceilings and floors. In 2011 Bass' labs started reconstruction.
2. The student who had been working on the project for her PhD, Ms Liqin Sang, decided to leave UIUC due to the time setbacks she foresaw from the disruption in Bass' lab operations. The work Ms Sang did on this project was a major portion of her Masters Thesis. Ms Sang is now at Texas A&M University.
3. Participation of the LLNL PI decreased steadily to zero by mid-to-late in Year 3. The UIUC group was left without any of the MDAC equipment that was needed to continue the synchrotron experiments started by Sang. The LLNL PI, Farber, is to my knowledge no longer employed by LLNL.

EOS of Water

We continued work with Dr. Carmen Sanchez-Valle (an unfunded collaborator), who had performed experiments on the sound velocities and EOS of H_2O at UIUC. These experiments, which were initiated while Dr. Sanchez-Valle was a post doc in Bass' lab, were performed with a commercial BETSA membrane DAC at UIUC with resistance heating up to 400C. The conventional two-hole method of measuring pressure was employed. These measurements form a baseline for comparison with all other work from our lab, and with prior results from other laboratories. The results of this work, which continued collaboratively after Dr. Sanchez-Valle moved to ETH Zurich, were published by Sanchez-Valle et al. (2013). This work is the first report of the refractive index and polarizability of supercritical H_2O at extreme PT conditions.

With the collaboration between UIUC and LLNL PI's discontinued by the latter part of Year 3 of this project, the UIUC PI modified his research plan and activities to continue moving the project toward its goals, but without input from the LLNL side. Our efforts included the following:

Equipment Development: Membrane Cells.

The design and construction of new gas pressure membrane diamond cells for fine and accurate control of pressure in experiments on fluids was needed. One thing that was learned during the initial

stages of this project is that membrane diamond cells offer great advantages over conventional screw-driven DAC's. We designed simple steel membranes and membrane containers to convert the conventional DAC's at UIUC into membrane driven cells. This effort was very successful and provided us the advantages of MDAC's at minimal cost. All parts were machined and constructed at UIUC. This effort helped compensate for the loss of MDAC's from our former collaborators. The new membrane cells would, however, require different types of resistance heaters and different strategies for insulating the heated samples and minimizing thermal gradients. Our membranes and membrane caps are shown in Fig. 8.

Figure 8: Photo of gas membrane, and membrane "caps" (containers) produced at UIUC for fine control of pressure with conventional diamond cells. The assembled adaptors with a DAC ready for use is shown at the top right.

Experiments on CO_2

We initiated experiments on CO_2, one of the volatile components of interest to this project. Our experiments extended into the pressure range of solid CO_2. We determined the elastic properties and EOS parameters of solid carbon dioxide by Brillouin scattering measurements at high pressure across the CO_2 I-III phase transition at ~10 GPa. These initial measurements were carried out at room temperature. Our results are in agreement with recent synchrotron X-ray diffraction measurements of the I-III transition, and Raman measurements of a high-pressure electronic transition in CO_2.

High P-T Elasticity and EOS Using Laser Heating

Our earlier work revealed that there are significant differences in the equation of state (EOS) and the phase diagrams of water, depending on the experimental details of resistance heating experiments using the diamond anvil cell. New experimental approaches are needed to accurately determine the EOS and phase relations of water and related substances at extreme pressure-temperature conditions. We decided to explore and develop the capability of performing high-pressure high-temperature

measurements of sound velocities and EOS using CO_2 laser heating of samples compressed in the diamond cell. Our hope was that we could access portions of P-T space at > 10 GPa and to 2000°C, which are inaccessible by resistance heating or other techniques. This would truly bridge the gap between current static measurements and the dynamic shock regime. This effort was high risk, but with a potentially high payoff. We were successful in developing a new apparatus for Brillouin scattering, sound velocity and EOS measurements at ultra-high pressure-temperature conditions. With this new system, heating of pressurized samples in the diamond cell is achieved via a carbon dioxide laser. Initial Brillouin scattering measurements were successfully made on liquid water to temperatures of ~2500K, greatly exceeding the P-T limits of previous measurements using resistance heating. The laser heating apparatus is shown in Fig. 9. This experimental advance will allow a new generation of measurements of the properties and phase relations of water and other materials under pressure-temperature conditions that were previously unattainable. This research formed part of the PhD dissertation of Dr. Jin S Zhang (PhD August, 2011). A paper describing our design was revised and resubmitted to Review of Scientific Instruments (Zhang, Bass & Zou, 2015) and is currently in review.

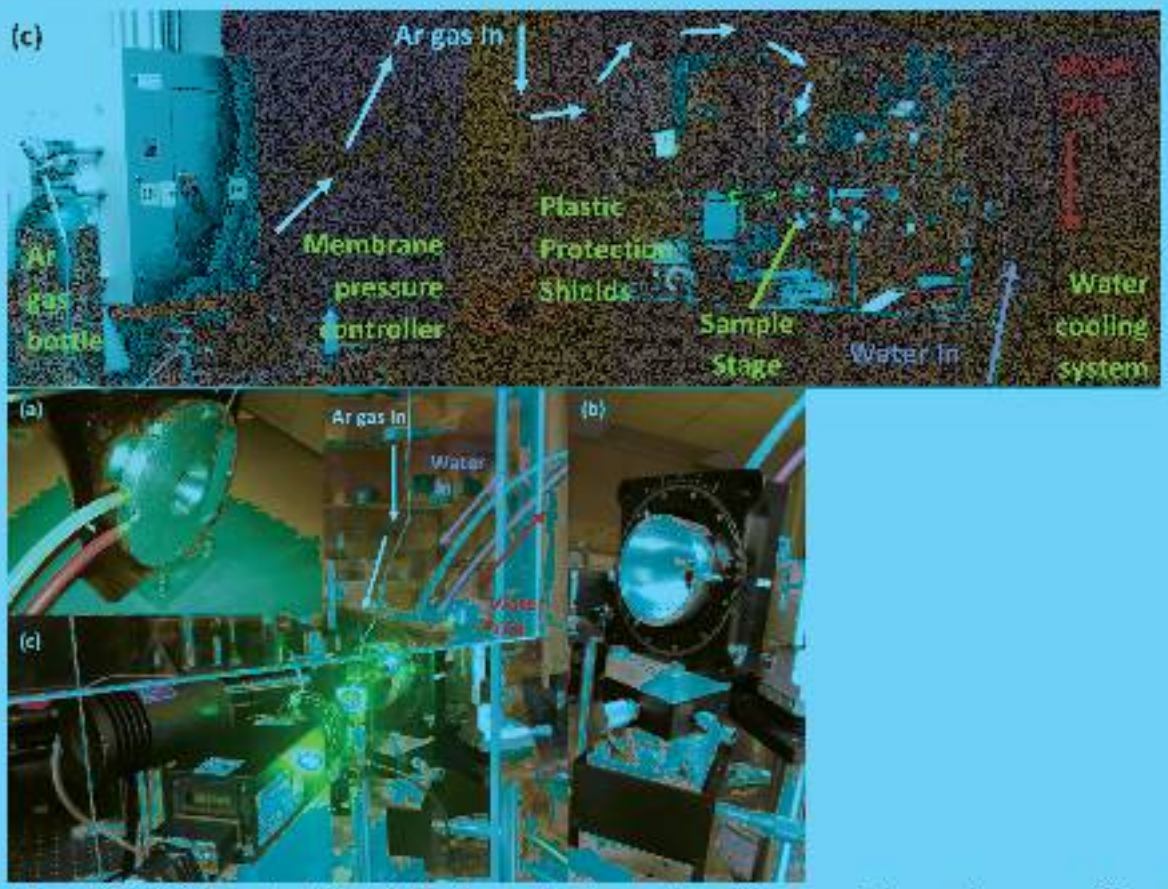

Figure 9: CO2 laser heating Brillouin scattering system. Top panel shows the system from the side, with pressure regulator for membrane cells, and clear plexiglass safety panels in place. Bottom panels show a) water-cooled diamond cell, b) 532nm laser light hitting sample during a Brillouin experiment, c) the DAC holder on a stack of translation and rotation stages for precise positioning.

Future Work

Although the grant period is over, we plan to finish up several aspects of this work that are not yet completed. These are:

1. Complete measurements on pressure uncertainties using the two-hole method of measuring pressure in diamond cell experiments on fluids.
2. Carry out a re-analysis of pressures obtained using the synchrotron X-ray diffraction of Au in the previous velocity-EOS-phase stability experiments. This is necessary before publishing this work, which we view as a very important contribution on the properties of water under extreme conditions.
3. Carry out a series of in-house experiments on the kinetics of ice formation at high PT conditions, for interpretation of the phase relations we have observed thus far in our APS synchrotron experiments.

Publications

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