Student questions: Kanani Lee colloquium on “Facilitating oxidation of the atmosphere through mantle convection”

8/22/18

Question 1: How does Bridgmanite influence the convection in the mantle?

Since Bm is expected to be the dominant mineral in the mantle (and Earth!), it’s physical properties (e.g., density, compressibility and viscosity) will largely influence convection in the mantle.

Question 2: When running the experiments in the diamond cell, how long are the samples exposed to the designated temperature/s and pressure/s before they are analyzed?

We typically heat the samples for ~10s of minutes while at pressure. This is typically long enough to at least assume local equilibrium. A sample can remain at high pressures indefinitely, but the samples I spoke about were at high pressures for a few days, up to a week.

Question 1: What analysis (if any) do you perform to ensure homogeneity of your initial glass sample. If it is not necessary why not?

We use electron probe microanalysis (EPMA) to determine composition and homogeneity of the glass samples.

Question 2: Is the levitation where the sample is reduced or oxidized conducted in a controlled atmosphere? Is atmospheric contamination of the sample a problem or is the levitating air stream isolating enough to prevent such problems.

The “atmosphere” is controlled in the sense that the levitated mass is completely surrounded by the gas of choice, however the whole setup is open to the air. We have found, however, that since the levitating gas pressure is far greater than the regular air pressure, that this is enough to influence to ferric iron content of the samples.

Question 1: What tectonic events (if any) would be necessary for the denser, reduced material at the bottom of the mantle to reach the surface of the Earth?

As long as the density contrast is not too large (>2+%), then more time will tend to mix the mantle up pretty well. Else, one might imagine a large flood basalt might help.

Question 2: What is the process for using mineral inclusions found in diamonds to determine the origin story of those diamonds?

First the mineral inclusions are identified and compositions measured. Often the kind of mineral and its composition can tell you a lot about what depths the diamond was formed at and from which fluids.
Question 1: How did geologists learn what the Earth's core, mantle, and crust were like 4.4 billion years ago?

Great question. There are very few samples that are this old, and so much is interpreted and assumed from those few samples, our understanding of the building blocks of Earth (e.g., meteorites) and how the Earth evolves.

Question 2: What is needed (for example, what sort of experiments, samples, etc) in order to perform these tests for the Martian mantle/atmosphere?

The same kinds of experiments can be performed at lower pressures/temperatures for Mars for any relevant compositions.

Question 1: Is it possible for the simulation to be run with more than just the two materials (densities) or would the addition of more not give any more insights into the mixing in the mantle?

That’s a great question. I don’t set the simulations up myself, thus this question is probably best be asked of Mingming Li (ASU). But I think that you can put as many materials as you would like.

Question 2: What is the actual makeup of the mantle in terms of “reduced” and “oxidized” materials? The simulation was run with a 50/50 split, does that match reality?

The actual makeup of the mantle is unknown. We used a 50/50 split, however that was just for convenience.

Question 1: Could this model be applied with a different gas to model mantles and the resulting atmospheres (possibly past atmospheres) of other planets or satellites?

Yes!

Question 2: What is the highest possible pressure/temperature that can be modeled using this experiment?

The pressures/temperatures of Earth’s mantle (up to ~150 GPa, 3000 K) are routinely attainable in the lab. Experiments become more difficult at higher pressures, especially when trying to do post-experiment chemical analyses. The simulations can be run at just about any P/T (I think—ask Mingming Li to be sure).
Question 1: What prevents the reduced iron Fe^0 in the lower mantle from dropping into the liquid outer core?

The low abundance of the metallic iron and the solid nature of the mantle. Certainly during a magma ocean, the metallic iron would readily sink to the core.

Question 2: Do other light elements (carbon, nitrogen, sulfur) effect the structure of the mantle minerals the same way heavy ones do?

These lighter elements, if in sufficient abundance can form their own phases outside of the usual bridgmanite and ferropericlase. For example, carbonates or carbides can form from an abundance of carbon depending on the oxygen fugacity. Likewise, nitrogen could form nitrates or nitrides (the latter if sufficiently reducing).

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Question 1: What is happening mechanically (or from a molecular/physical chemistry perspective) that produces larger volumes in more oxidized bridgmanite?

Larger ions such as iron and aluminum, which replace for smaller ions Mg and Si, will make for larger volumes than the MgSiO3 endmember. For the oxidized sample, all of the ferric iron and aluminum fit in to the MgSiO3 thereby expanding it so much that the Ca ion (which is by far the largest ion in the system) can be accommodated, further expanding the volume of Bm.

Question 2: How are the composition and properties of pyrolite determined if it doesn't “actually” exist?

Great question. “Pyrolite” is a fictitious rock that has had many different compositions (over literature time as our understanding of the Earth has evolved), but is basically supposed to represent the rock that when melted produces basalt. There are natural analogs to pyrolite. For example, a garnet lherzolite (a real rock), looks very similar to what has been proposed as pyrolite.

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Question 1: On the methods slide, in the first image, what is the tiny dot under the homogeneous bubble?

I think you’re referring to the scale bar under the SEM image of the glass bead, which is impossible to see but represent 100 micrometers.

Question 2: How do you know what the pressures are as you go further into the Earth since we cannot physically go there to measure?

It can be calculated by what we do know about the Earth’s mass and density distribution throughout the planet (its moment of inertia).
Question 1: How do we know the composition of the Earth's core?

The Earth’s core is an iron-nickel alloy with some light elements (up to ~10wt%). Some of the popular light elements include: Si, S, O, C and H, but it is conceivable that nearly the entire periodic table is in the core to some extent. We know this based on measurements of wave speed through seismology as compared to lab measurements of wavespeeds through materials at simultaneous high pressures and temperatures.

Question 2: How was the ratio of reduced/oxidized materials chosen for the models?

It was just a guess. We could have chosen any ratio as it is largely unconstrained.

Question 1: If a planet has an oxidized atmosphere, is there a direct way to infer the redox state of its mantle and is there a straightforward relationship between them?

It’s a complicated process. I don’t expect that the Earth’s atmosphere would be oxidized without photosynthesis, however, could it have occurred with a really reducing mantle? Probably not.

Question 2: Since volatility is related to oxygen fugacity for many elements, how does the bulk depletion of volatiles in the archaic model fit into this picture?

Indeed, volatility is related to oxygen fugacity for a lot of elements. Our model does not constrain or rely on other volatiles. We are merely looking at the effect of ferric iron content of the bulk properties of rock assemblages which then can affect mantle convection.

Question 1: What was it that made you pick your undergrad major?

I was fascinated with the TV show Macguyver growing up. When I asked my dad how Macguyver was so smart and could get out of any situation with some duct tape and a swiss army knife, rather than answering, “It’s Hollywood and isn’t real,” or something like that, he told me that Macguyver knew a lot of physics. I knew from then that I needed to study physics.

Question 2: What made you decide to go to grad school?

I knew when I started college that I wanted to become a professor. I didn’t exactly know in which field and I actually applied to both Earth science and condensed matter physics programs for graduate school. In the end, I chose geophysics!
Question 1: If the reduced material from the mantle were to ever be erupted to the surface, would we see evidence for that in the atmosphere's composition?

That’s a great question. Note that an oxidized mantle when erupted does NOT erupt oxygen. Our volcanoes erupt gases like water vapor, CO2, SO2 and so forth. We might imagine that a “reduced” mantle might instead erupt gases such as methane CH4.

Question 2: You mentioned the “Great Oxidation Event” at the beginning of your talk. Was there a change in the mantle that correlated with this event to help increase the O2 in the atmosphere so drastically?

While the timing in our mantle convection models are not precise, a more oxidized upper mantle early on could have helped (or buffered) any biological processes such as photosynthesis by adding more oxidized gases in to the atmosphere or hydrosphere (like water and CO2) that are necessary for photosynthesis.

Question 1: How are measurements of mantle temperature over depth and time attained in order to model the early internal structure of the Earth?

At present, near the surface, temperature at depth is measured and values of thermal conductivity of the rock is used to extrapolate to relatively shallow depths. This is because we think most of the Earth is convecting and well mixed and thus the T gradients follows more like an adiabat. We have some pretty good ideas on pinning down some of the temperatures based on experimentally determined melting temperatures of relevant materials that we think are present at depth (e.g., melting of a plausible core composition helps pin down CMB temperatures).

Since the Earth is cooling, we can expect early temperatures to have been hotter. We also expect that early on the Earth was likely fully molten (due to, say, a Moon-forming impact) and thus the melting curves of a relevant mantle compositions would be valid as starting guesses for temperature in the early Earth.

Question 2: Which assumption or approximation used in modeling the Earth's internal structure would you expect to have the most significant impact on your results?

Hmmmm… Composition. Composition affects the solidus and liquidus of the mantle strongly. It also affects density and viscosity thus a big player in terms of convection. Our study aims to investigate different compositions to see how this is affected. And we find that ferric iron abundance can play a large role.
Question 1: Is it possible to make the surface area on the diamond anvil smaller to get larger pressures, or do we use the 100 micron surface size to maximize sample processing area?

Yes. The smaller the surface area, the higher the pressures one can go. Some experimentalists use culets that of order 10 microns in diameter in order to go to hundreds of GPa in pressure!

Question 2: In the EDS maps, it looked like the reduced samples had better crystal form, does reduced versus oxidized have a control over nucleation sites for crystal grown?

It does appear that way. The scale bars aren’t the same, so it’s harder to compare. One way to know for sure, is to compare the raw XRD data to see how crystalline the sample is. I’d have to check.

Question 1: Looking back, what would you have done differently to improve the results from the research presented at the colloquium?

I would love to have been able to measure the Fe3+ abundance after the experiments. As it stands we only have been able to measure Fe3+ in samples before the experiments. Since it appears the Fe3+ abundance changed for the reduced sample (because we see Fe metal), it would be nice to be able to quantify how much. We can only give a guess using Monte Carlo methods.

Question 2: What are your next steps in furthering the research into the connection between the redox state of the Earth and the atmosphere?

I think there is a lot to be done on the convection model side of things: how to add changing redox with time. As it stands, the system is closed, however, in the real Earth there are subducting slabs that have been hydrated that penetrate deep in to the mantle. How does this change redox? On the experimental side, other compositions remain to be tested to see how well our findings hold up.

Question 1: What causes the major density difference between M1X & J95?

J95 is very dense because it has a lot of iron in comparision to MIX1G and pyrolite.

Question 2: How would mantle behave without any oxygen in our atmosphere?

The mantle would still convect if it is a silicate/oxide mixture. If the mantle composition were something like a carbide-dominated composition, convection may look very different if at all present…
Question 1: Has mantle convection help lead to the increased abundance of oxygen in the atmosphere over time?

_**I think it has helped.**_

Question 2: What does the difference in aluminum produced from the tests tell us about the mineral tested?

_Because Al is a 3+ ion, it can substitute for both the Mg and Si, 2+ and 4+, respectively. Iron is both divalent and trivalent. The interplay between Fe3+ and Al3+ in Bm appears to be the main player for the presence of free Al2O3. If there is enough Fe3+ to balance all of the Al3+ in Bm, then no free Al2O3 phase is necessary._

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Question 1: How does the oxidized rock affect the redox state of the atmosphere if it mostly comes to the surface and sits below an anoxic ocean?

_When the oxidized rock melts and erupts at the surface, indeed much of it may be under an anoxic ocean early on. But the dissolved gases can help to buffer the anoxic waters where eventually it’ll be enough to become oxic._

Question 2: Can seismic data be used to interpret the bulk composition of the different mineralogy?

_Yes, we can use our predicted seismic velocities of our different compositions to perhaps say something about regional differences in the mantle. At this point, we have only compared to 1D seismic models._

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Question 1: What would the mixing pattern look like if the time scale was increased from 5 billion to 10 billion years, or even further?

_**I think if we wait long enough, the signal of dense material at the CMB may go away.**_

Question 2: There is definite mixing in the mantle, as shown by your work - do we know if there is mixing the outer core for the same reasons (those reasons being oxidation and reduction)? Or is the movement there due to other geological processes?

_Perhaps. In separate experiments on core alloys, we have found immiscible liquids in the Fe-Si-O system where the O-rich iron melt is lighter than the Si-rich iron melt._
Question 1: What is the purpose of using the various powders to make the glass with Fe\(^{3+}\) and then crushing the glass to break it back down into a powder, and isn't that kind of repetitive?

**We make a glass to homogenize the composition, otherwise it isn't necessary that a mix of powders would be homogeneous.**

Question 2: With respect to the samples used in the various tests, the top two in the chart (J95 maybe?) showed fractions of 0.30 and 0.35 \(\pm 0.04\) for the reduced and oxidized samples respectively. Given that the error is almost the same as the difference between the two values, how is this confidently treated as being oxygen rich vs. oxygen reduced?

**The differences in Fe\(^3+\) are small, however, the effect is easily observed and reproduced in more than 10 sets of experiments that the volumes are different. That was another reason to try separate samples (MIX1G) that have very different Fe\(^3+\) abundance.**

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**Question 1:** Why did your model make the initial assumption that the primitive mantle contained 50% reduced and 50% oxidized material?

**It’s unconstrained so it’s just a ratio we picked. We could have started with any ratio.**

**Question 2:** What influence, if any, would the introduction of subducted plates containing modern oxidized material have on oxidizing the portions of reduced mantle in your model?

**This is something I’d love to test! My intuition says that it will oxidize the reduced stuff thereby making it more buoyant.**

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**Question 1:** Could the type of exsolution phenomena you observed (with Al\(_2\)O\(_3\)) have any effect on core or crustal chemistry?

**Seems like it should 😏.**

**Question 2:** Are you aware of any work being done to test for similar density-driven phenomena using more complex initial stoichiometry (e.g. radioisotopes or light elements suspected to comprise part of the core)?

**If I understand your question correctly, I’m not aware of any other similar work. Incidentally, our compositions are quite complex as compared to most studies which study a single phase or Mg-endmember compositions.**
Question 1: You showed the evolution of oxygen in one of your slides and mentioned the Great Oxidation Event. What are the physical evidences that point towards this hypothesis?

The changing redox state of Earth’s exosphere is most readily observed in banded-iron formations (e.g., https://en.wikipedia.org/wiki/Banded_iron_formation).

Question 2: How are the mantle samples obtained or chosen? What are the criteria for taking a particular composition of molecules/metals/minerals as a mantle sample?

We chose our two sets of samples based on some previous models in the literature on plausible lower mantle compositions: an enstatite chondrite lower mantle composition J95 (Javoy, 1995) and mixture of pyroxenites MIX1G (Hirschmann et al., 2003). There are many plausible mantle compositions, these are just two.

Question 1: What is the significance of the peak in the oxygen concentration jump at ~2 Gya?

This is the Great Oxidation Event (GOE) which signifies the point in which there is a good amount of oxygen (still order of magnitude lower than present) in the atmosphere that is stable over long periods of time.

Question 2: How can you tell what depth diamonds come from?

First the mineral inclusions in a diamond are identified and compositions measured. The kind of mineral and its composition can tell you a lot about what depths the diamond was formed at and from which fluids.

Question 1: In what ways could the simulation be misleading or inaccurate, and were these possibilities considered when creating it? For example, the simulation was presented in a rectangular shape where in actuality, the mantle is curved.

The Cartesian geometry is problematic, however it isn’t too bad. More expensive 3D spherical simulations are possible however were not done in our study. Other problems with the simulations include the lack being able to add changing compositions such as subducting hydrated slabs. Other assumptions on viscosity are also somewhat artificial.

Question 2: Could the mantle convection process have impacted not only the atmosphere, but also the hydro or other spheres? If so, in what ways?

Yes. Since most of the planet is covered in oceans and most of the magmatism occurs at the bottom of these oceans, it is very likely that there would have been/continues to be a big influence to the hydrosphere.
Question 1: Are there mechanisms other than volcanism that can transfer mantle gasses to the surface?

Other geothermal processes such as geysers are also useful in transferring mantle gases to the surface.

Question 2: Are there technologies and/or new information on the horizon that will reduce the 3000 possible outcomes produced the Monte Carlo simulation?

Lowering our experimental uncertainties or tightening up our assumptions will decrease the possible outcomes.

Question 1: How do you link diamond inclusions to a uniform layer of oxygen present at a certain depth rather than localized oxygen patterns?

Diamond formation is likely a local phenomenon.

Question 2: How would the results differ if you chose the end member minerologies from the 3,000 Monte Carlo results?

I’m not sure since we haven’t tried that. We have looked at the 1 standard deviation away from the average value and find that our conclusions are still robust.

Question 1: Does the geodynamic model you are using account for the “evolution” of the Earth? What parameters went into the convection model? By evolution I mean the gradual cooling down of the interior of the Earth since its formation. Does that even matter? If no, why? If yes, how?

Hmm… I will defer to Mingming Li. The parameters we used are described in our paper: T. Gu*, M. Li, C. McCammon and K. K. M. Lee, “Redox-induced lower mantle density contrast and effect on mantle structure and primitive oxygen,” Nature Geoscience, 9, doi:10.1038/ngeo2772 (2016).

Question 2: Why isn’t there a significant increase in temperature between the outer and inner cores? Both were listed as ~6000K on the slides. Also, why does the temperature gradient decrease with depth? (0GPa ~300K, 24GPa ~2000K; but 330GPa ~6000K and 364GPa ~6000K)

The outer core appears to convecting very vigorously and as such is likely well-mixed. The ~6000 K is the melting temperature of the iron alloy at the inner core boundary (ICB). At the ICB, the temperature should be just under the melting curve since it is solid there. The gradients are steepest at boundary layers where conduction is the mode of heat transport rather than convection (e.g., at the surface, at the CMB).
Question 1: Do you think there needs further modification in the laser-heated diamond anvil cell (LHDAC) experiment to have better results or understanding, apart from careful and accurate measures in the experiments or it’s adequate?

There are a lot of things that can be made better in the LHDAC. Experiments are often plagued with large temperature and pressure gradients. Additionally there are difficulties in measuring the temperature in the LHDAC (see my technical talk on 8/23/18). Even so, careful measurements can be made and thus make the LHDAC my tool of choice in simulating the conditions within planets.

Question 2: Your research talk was really amazing, in your opinion, what should be the next step in terms of research in Mineralogy in such fields?

Thank you. Investigating other compositions and Fe3+ abundances would be the next obvious step.

Question 1: When talking about the evolution of the atmosphere, you presented a slide that showed a period described as the “great oxidation” and a second period in more recent time when there was a small increase in the oxidation level. What causes the oxidation level in the atmosphere to increase quickly, settle, and then increase again during a later period?

Here’s a quick primer on the GOE and subsequent further oxygenation:
https://en.wikipedia.org/wiki/Great_Oxygenation_Event

Question 2: In your diamond cell experiments, how do you measure the pressure applied in a way that doesn’t interfere with the force applied to the diamond?

There are a number of ways to do this. One way is that the diamond anvils themselves have a Raman signal which has been calibrated, such that the shifts correspond to increasing pressure. There are also internal calibration standards that can be used with x-ray diffraction.

Question 1: What’s more important in to making a (diamond) composition pressure or temperature or both are equally and doest it differ the composition??

They are all important.

Question 2: Why the Monte Carlo MIX_RED compostion took a 3 million iteration and is it a really difficult mineralized?

I’m not really sure if I understand your answer correctly. We did 3 million iterations. We could have done more or less. Out of the 3 million, we found ~3000 solutions that fit the data.
Question 1: Which mineral inclusions in diamonds are the most useful for these studies?

Each inclusion tells us something about the conditions in which it was formed, so it depends on the question you’re trying to answer.

Question 2: What qualities make bridgmanite so obscure in spite of how common it is in the mantle?

It was only recently that a natural example of Bm was found in a shocked meteorite. We do not have a direct sample of Bm from the lower mantle, thus keeping it seemingly obscure.

Question 1: You mentioned on the methods page a model that assumed everything is equally abundant or homogeneous on Earth, why is that useful?

I’m not sure what you are referring to, maybe PREM? In any case, it’s good to have a baseline to compare to.

Question 2: Can your results lend any information to oxygen rates and abundances in the ocean over time, concerning adaptation of O2 in early microorganisms?

No, not precisely.

Question 1: I know the only difference between the two samples is oxygen fugacities (fO2) and their temperature and pressure are the same, however, is there any possible that different oxygen fugacities lead them to have slightly different temperature during the experiment?

Yes, this is possible since they have different absorption properties, thus what we measure and what is the actual temperature may be slightly off. Please see our paper for more details: J. Deng, Z. Du, L. R. Benedetti and K. K. M. Lee, “Wavelength-dependent absorption and temperature correction in the laser-heated diamond-anvil cell,” Journal of Applied Physics, 121(1), doi: 10.1063/1.4973344 (2017). But since the temperatures which we were investigating are rather low (~2000-2400 K), this effect would be rather small, perhaps 100-200 K different.

Question 2: Inspired by your interesting discoveries, I’m wondering if it also has some implications for explaining the formation of the Earth core?

Yes. There would be implications for core formation and evolution. Convection is the main mode of heat transport out of the planet.