Student questions: Penelope King colloquium on "Gas – Solid Reactions in Earth and Planetary Systems"

2/3/16

Question 1: When the magma dies off, causing the gas to die off and the water to flow in, where does the gas go? **There is no gas being produced any more as the magma crystallizes and stops degassing. An analogy might be stopping to blow into a straw in a cup of water.** Does it go back into the ground or escape out into the atmosphere or infuse in the meteoritic water? **Yes, in the waning stages of degassing, the gas would take the path of least resistance into all of these locations as it rises buoyantly.**
Question 2: How would you be able to verify your suspicions of this happening on Venus? Could you somehow do this from orbit, since surface analysis is currently somewhat prohibitive? **Yes, the mineral assemblage (collection of minerals) could be used to support this hypothesis in tandem with experiments using a Venusian composition gas. Schaefer & Fegley (2004) consider that these types of reactions occur on Venus.** Or maybe with a Venusian meteorite (whenever one is found)? **Yes, it would be nice if there was one to access, wouldn't it!?**

Question 1: What are some of the best benefits of studying volcanoes and volcanic eruptions when it comes to your specific research? **I think that it is important to study volcanoes in order to figure out the important variables in igneous systems (both volcanoes at the surface and magma chambers at depth). Once we make observations (e.g., sulfur degasses a lot at volcanoes), we can then make hypotheses (what might it do?), then we can better design experiments to replicate nature and igneous processes.**
Question 2: Other than volcanoes, what other natural processes do you look at? **I like most kinds of rocks! My research group looks at all kinds including biomineralized rocks, sedimentary, metamorphic and igneous rocks, plus meteorites and rocks discovered by the Mars rovers and asteroid missions.**

Question 1: Does your research on SO2 and its interaction with plagioclase provide some insights to SO2 role (if any) in theories of how Earth remained warm enough for liquid water in the earliest epochs when the Sun was 30% less luminous? **Yes, this research suggests that sulfate may be commonly produced through igneous processes. Addition of sulfate to water lowers its freezing point. We explored this concept relative to Mars, Europa, Ganymede and Callisto in King, P.L., Lescinsky, D.T. & Nesbitt, H.W., 2004. The composition and evolution of primordial solutions on Mars, with application to other planetary bodies. *Geochimica et Cosmochimica Acta,* 68, 4993-5008.**
Question 2: There is a great deal of discussion about SO2 role in keeping Mars warm in its earliest epoch. How might your line of research on anhydrite formation rates provide clues for future research of SO2 role in Mar's planetary history? **What a great question. Actually, we discussed that in our paper too!**

Question 1: Which steps are you anticipating to take in order to consistently predict the reactions of heterogeneous solutions? **You may find my answer strange, but I think that the first step will be to get some more students involved in this research so that we can move forward! (Are you interested?) I am expecting that we will need to employ some really careful sample preparation, then experiments followed by surface micro-analysis techniques. We are systematically going through different minerals to provide a predictive model.**
Question 2: Which courses have you taken that you use the most in your research? **Geochemistry, petrology and aqueous geochemistry, analytical techniques, thermodynamics.** What books or articles would you suggest reading to learn more about your area of research? **Basic chemistry and materials science text books.**

Question 1: Could further understandings of gas-solid interactions within the Earth help us better predict where valuable and useful mineral/resource deposits would be located, or would it be relatively unrelated? **Yes, for the types of deposits where the metal is transported in a gas phase, we should look for rock types where persistent degassing is known to occur. This is where there will be a strong concentration of sulfur.**
Question 2: Can more studies on these interactions provide insight into deeper Earth characteristics and processes such as plume formations and detailed mantle activity? **We are looking into this actually – good question!**

Question 1: What are the differences in chemical reactions between volcanic reactions on other planetary bodies vs our own? **I am not sure if I am interpreting this question correctly… As far as we know, there are no active volcanoes on Mercury, Mars or Venus. From meteorites, we think that magmas behave in a similar manner chemically on other planets relative to Earth, but there are differences in composition (e.g., in some cases, the meteorites we sample have less water, more Ti, less oxidized). We think that the physical processes might be quite different due to different gravity, lack of atmosphere, temperature, lack of plate tectonics etc. We see sulfur-rich eruptions on Io and those seem to be quite different from Earth.**
Question 2: Are gas-solid reactions on other planets the same as our own, or do they occur in different circumstances? **It is likely that the same chemical reactions occur on other planets (i.e. same laws of chemistry). However, I think that planetary scientists are still thinking about how processes or circumstances on other planets might differ from Earth. For example, if a planet has a lower pressure atmosphere that will likely affect the transport of gas.**

Question 1: In the cases where soluble anhydrite is still present, will future copper miners have to change their apprach in order to be able to safely extract their ore? **Yes, this could become an issue in deep mining when copper miners get into zones rich in anhydrite (where it hasn't been dissolved away). Some people have blamed some cave mine collapses on anhydrite.**
Question 2: Is the process you described today more prevelant in open-sytem degassing or closed-system decompression gassing zones, and why? **This is a good question and I would say that open-system degassing is likely to be the most prevalent mechanism. I should have explained that we look at closed systems as an "end member" but that they are really a theoretical idea and they are unlikely to occur in nature, particularly in active volcanoes where there is deformation and active processes.**

Question 1: Are you looking at any other solid-gas reactions which have a significant impact at the surface? **Yes… well, at least we think that we are!**
Question 2: Are humans responsible or in some way attributable to the abundances of gases in the crust? **Humans have a small impact on the scale of the crust. Our deepest drillhole is on the order of 13km which is small compared to the average crustal thickness. We have small scale gas-sequestration projects in some areas.**

Question 1: What exactly causes the reaction to turn into a chicken wire texture? **Generally textures form that minimize the energy at the surface under the conditions of formation. As far as I know, there have not been systematic tests in this system to examine all of the variables.**
Question 2: How do you plan on developing new approaches from the macro and micro levels for the constraint reactions? **See above.**

Question 1: What was the platinum wire used for when reactin the mineral chip with the rock. **The platinum wire is used to hang the mineral chip in the hot zone of the vertical furnace.**
Question 2: Where did the lunar volcanic gas come from, cometary impacts? **This is still a topic of debate and possibilities include initial accretion, cometary impacts, capture from Earth etc.**

Question 1: How would volcanic gas affect weathering on rocks as it escapes volcanos slowly? **The reaction of the plagioclase to anhydrite is a type of alteration (change of the rock) that would speed up any subsequent weathering (change of the rock in the near-surface).**
Question 2: Wouldn't these gasses require a significant amount of energy to pull the calcium up? **Yes, the energy is significant and we have calculated the energy balance at a range of P-T by tracing the ascent path as explained in the Supplement to: Henley, R.W.*, King, P.L.*, Wykes, J.L.*, <u>Renggli, C.J.</u>, Brink, F.J., Clark, D.A., <u>Troitzsch, U.</u>, 2015. Formation of porphyry copper deposits through sustained SO_2 flux and chemisorption. *Nature Geoscience*, 8, 210-15. doi: 10.1038/ngeo2367. **Equal contribution, King corresponding author.***

Question 1: You mentioned how some of the reactions can take place in a few minutes in the lab with anhydrite and others, like copper deposits in mines and volcanos takes place hundreds to thousands of times faster than most people had thought. **This is a little confusing. I talked about *rates* in terms of minutes for a reaction in the lab, and then I talked about *efficiency of H2S/SO2 production*. I didn't tell you the rates of reaction in the porphyry copper environment because we have not yet done sufficient experiments to calculate this.** Did you orginally expect the results of your research of gas-solid reactions to show such dramatically different figures than what had previously been thought? **We thought that gases would be more efficient, but didn't expect the values to be so high, so it was a big surprise.**
Question 2: With this new research that dismisses only a reaction between S and H2O and shows how these metals are deposited in such large amounts, can accurate estimates be made about the geological and chemical history of other places in the solar system? **Yes, we are applying this research to those problems. Good question**. Or is this research more applied to looking at the current amount Sulfide-metals present based on what chemicals we knew definitely were present befre the reaction? **We are doing both.**

Question 1: How does this information help further us in our understanding of how life originated on Earth? **These high temperature reactions may have been common in early Earth.**
Question 2: Has anhydrite been found on meteorites? Perhaps due to high temps from entering the atmosphere... **Yes and it appears to be extraterrestrial.**

Question 1: If more experiments are performed, and gas-solid reactions can be understood as well as any other gas related reactions, how much would that tell us about how earth and other planetary structures have formed over their lifetime? **We are trying to figure this out – good question.**
Question 2: Can the fact that gas-solid reactions are significantly fast be useful in practical applications? **Yes, potentially in removing SO2 from smelter stacks.**

Question 1: What can we do to take better experiments on gas-solid reactions to collect better data and have a greater knowledge of these reactions. **Yes, this is in progress.**
Question 2: Do you see any bad outcomes in the foreseeable future if we can learn to manipulate these gas-solid reactions to our own benefit? **I think that the worst outcome would be poisoning from SO2 and so I am making sure that all of these reactions are tested safely.**

Question 1: Does the shape and surface area of grains/particles have any effect on the reactivity of the gas/solid reactions? **Yes, this is in progress.**
Question 2: You spoke of reactions with plagioclase rich magmas and gases. Are there other compositions of magma that would have different reactions? **Yes.**

Question 1: Is it possible that similar reactions are taking place on a sublimatin comet? **Yes.**
Question 2: Does CO2 or NOx have similar reactions with solids? **Yes.**

Question 1: While understanding these fundamental geochemical processes in an abiotic, terrestrial context is important, I was wondering if enough progress had been made in this field to explore the relationship between Gas-Solid interactions and the existence of chemosynthesizing life at the bottom of our oceans? Specifically, ecosystem sizes and abundances in relation to reaction frequencies and/or their resultant chemical compositions.
This hasn't been done to my knowledge.
Question 2: Is the study of Gas-Solid reactions applicable to all celestial bodies or solely geologically active bodies? It seems that it would not hold much significance in the context of planetary bodies with static crustal activity. **These reactions are only relevant where gas is present. The geological activity might create gases, or might not. Also, gases may have been present in the past on some bodies, but not present now.**

Question 1: I understand qualitatively why you're getting SIMS profiles on your experiments, but are you trying to quantitatively derive Ca diffusion coefficients under SO2 to model natural systems? **Yes.**
Question 2: Can you explain the application to scrubbing of coal plants more? I heard the question, but don't understand the concept. **Coal may contain high levels of sulfur and therefore, when it is burned it gives off SO2 gas. The idea here is that SO2 reacts with something in its path that is reactive (e.g., plagioclase) and is consumed to be disposed of as CaSO4.**

Question 1: How does understanding the distribution of chemical elements with ~~heat~~ **gas** get us closer to understanding how life originated? **Gas reactions may provide redox or chemical potentials that microbes use as sources of energy. Gas reactions also increase porosity – creating microenvironments – and occur near the surface where microbes are most abundant.**
Question 2: Why are there so few experiments on gas-solid or gas-melt reactions? **Not sure – it seems like an obvious omission.**

Question 1: Does anhydrite occur with any calcium bearing mineral and SO2 reaction or is it only limited to plagioclase and calcite (the two minerals that you showed us)? **It is produced when SO2 reacts with other minerals.**
Question 2: You mentioned that having H2O in the chemisorption reaction cases it to reach equilibrium. **This must be a miscommunication. I mentioned H2O because it is the most common gas at volcanoes and so any reaction in nature needs to include it.** Have you ever tried to include water in one of your SO2 and plagioclase experiments and if not would it be possible? **Yes we have tried, but unsurprisingly H2SO4 (sulfuric acid) forms and this then corrodes the furnace and containers.**

Question 1: For your experiments, how far (deep) in the samples do the micro-fractures penetrate? **We are not sure – it seems to depend on the material, reaction time, etc.**
Question 2: How does the Ca depletion effect the structural integrity of the samples? Does this make a difference when occuring below the surface in nature? **The Ca depletion results in the formation of aluminosilicate minerals and silica and so does not really affect the structural integrity. The structural integrity is most affected by the fact that anhydrite can dissolve.**

Question 1: Is there any way to use the gas-solid reactions within the earth as a sustainable energy resource? **Wow- that would be great. I haven't thought of this before… perhaps?**
Question 2: How might gas-solid reactions affect seismic activity? **The volume change associated with these reactions might cause seismic activity.**

Question 1: In your talk you meantioned trying to dissolve marble with dry SO2, were the results on how quickly the SO2 reacted with marble faster or slower than non-dry SO2? **It is a bit hard to compare since wet reaction rates have been measured at much lower temperatures.**
Question 2: If Venus' atmosphere is made up of mainly SO2 gas, could we deduce then that there is likely very little marble at the surface because it was all dissolved? **Yes. See Fegley and Schaefer (2004).**

Question 1: How reliable is the data received from deeper within the Earth, being that the high temperatures could most definitely destort any tools and data received by volcanologists?
I am not quite sure which "data" you mean. For our calculations of H2S/SO2 at high P and T, we correct for temperature and pressure changes using thermodynamic data (enthalpy, entropy, molar volume, heat capacity etc.).
Question 2: Should the gas-solid reactions be expected to occur differently under different conditions than Earth? Such as the higher temperature and pressure of Venus or the lower temperature and pressure of Mars? (how do we make this data applicable to the rest of the solar system) **The answer is similar to the answer above – we use appropriate thermodynamic data to make these corrections.**

Question 1: At the beginning of your talk, you showed a photo of a piston cylinder apparatus you had built in 2001. Has the design of these changed since then or remained relatively the same?
The design has changed slightly over the years. I suggest going to see Christy Till's apparatus to find out more!
Question 2: Could you explain in a bit more detail what the chicken wire CaSO4 is? Where does it occur? **Chicken wire is the name given to the texture (crystal arrangement) of the anhydrite that we observed on the surface of calcite reacted with SO2. The name comes from the similarity of the crystal arrangement with chicken wire (used to hold chickens in a coop).**