Reading Guide to "Organic Molecules Formed in a 'Primordial Womb'"[1]

What questions do you have that we have not covered here? Bring 'em!

Please answer wherever possible with reference to specific figures, tables or sentences in the paper. Cite any outside source you use. Show your work where relevant.

When you draw a mechanism, be sure to include lone pairs on any atoms receiving or sharing electrons, mechanistic arrows, any intermediates, formal charges where needed, and representative resonance forms if applicable. When part of a mineral surface is needed in your mechanism, please draw out fully the exposed layer of atoms including any bonds which connect back into the bulk of the material. Show those bonds disappearing into the bulk substance and cut them off with a wavy line or something similar.

I am sending electronically three files for you to explore using VESTA. I could not find an acceptable data set for montmorillonite so the file vermiculte.cif will stand in (the key features are the same). For saponite we will use antigorite.cif; again, it's not the same mineral but it is close enough. I am also sending illite.cif which is, *wait for it*, illite.

Your suggested questions have been blended into the questions below!

1. What are clays? What are smectites? How do these terms relate, and how do terms like montmorillonite and phyllosilicate fit in?
2. Regarding the structure of montmorillonite: What is the interlayer? What's in it (generally)? What does T-O-T refer to?
3. What are the key differences between montmorillonite and illite? Why is the interlayer of montmorillonite expandable, but that of illite does not expand? Be as specific as possible about why illite does not expand.
4. Generally speaking, why does the face of the interlayer in montmorillonite have a negative charge? Why is the *net* charge variable?
5. Why was saponite used in this experiment? What role does it serve?
6. In the experiments the clays were "...K^+ exchanged to remove cations from the interlayer surfaces that were native to the natural environment of formation..." How would you do this? Be as specific as possible as if you were going to do it in lab (the authors neglect to tell us how they did it, so it's up to you!). What biochemical technique is analogous?
7. By my count, the authors took five different steps to establish a reproducible system with appropriate controls, though they didn't call each step a "control." What were these steps? What was the purpose of each step?
8. The experiments described here lead to some pretty large structures, for instance "alkyl benzenes" like toluene, $C_6H_5CH_3$. How did the authors figure out what was made in the clay (the identity) and how much was made?
9. What does Figure 2 tell us? Explain carefully, the figure is a disaster.
10. Suggest why montmorillonite stops producing hydrogen in Figure 3. Where is this hydrogen coming from? Follow the reference and find the equation!
11. In these experiments, the conditions are pretty rough: 300° and 100 MPa, so some of the rules we follow for mechanism might be stretched a bit, as might some other types of expectations. But first, exactly how much pressure is 100 MPa? Convert it to atmospheres. One atm is the pressure roughly at the surface of the earth, it's what you "feel" walking around, which effectively is nothing since it's "normal." For a better comparision, if you dive to the bottom of a swimming pool, say to a depth of 3 meters, what is the pressure there in atm? One definitely feels that on one's ears.
12. Dimethyl ether is the major product among the major products. A bit more is formed in the presence of *any* clay, but a lot is formed in the blank, so the formation of dimethyl ether doesn't depend upon clay as a catalyst. Draw a mechanism for the formation of dimethyl ether from methanol. Your mechanism should (automatically) balance the reaction. By the way, at normal temperatures and pressures, methanol will not form dimethyl ether.
13. The interlayer is the region where reactions are catalyzed. What other essential role does the interlayer play?

[1] Williams *et. al. Geology* vol. 33, no. 11, pgs 913-916 (2005).

Answers to the questions below due by 5 pm Saturday 24 February

14. Taking the structure of vermiculite (representing montmorillonite) at face value (i.e. the unit cell view I sent you):
    (a) What is the sum of the negative charges facing into interlayer?
    (b) Assume that the metal ion is Mg^{2+}. What is the net charge on this structure?

    In both cases explain carefully how you counted charges. You may want to print out a view of the structure and annotate it.

15. The authors state "...the interlayer contains the active sites for organic synthesis." Draw a picture of the surface of the interlayer after K^+ exchange. What species are present? Are they acidic, basic, neutral?

16. Imagine that the interlayer contains some protons, H^+, as well as aqueous ethanol (*eth- not meth-*).[2] Using just these three molecules, and $E1$, S_N1 and Ad_E mechanisms, show mechanisms leading to several functional groups and molecules with at least four carbons. Remember the conditions of the experiment – some of the intermediates you may draw would be considered unstable/undesirable at STP, but probably not here.

[2] Instead of protons, one might also imagine some Lewis-acidic metal ions.