Hi Julia,

As we have dicsussed, I have a number of serious issues with the analysis presented in the paper by de Vries and Costantini. In this little letter, I'll try to summarize my concerns coherently.

**The phase of the oscillations**   Here are the published $\chi(k)$ spectra from de Vries (left) and Zubavichus (right). The Zubavichus paper is the one that de Vries and Costantini cited as part of their justification for identifying high density amorphous (HDA) ice in the satellite observation.
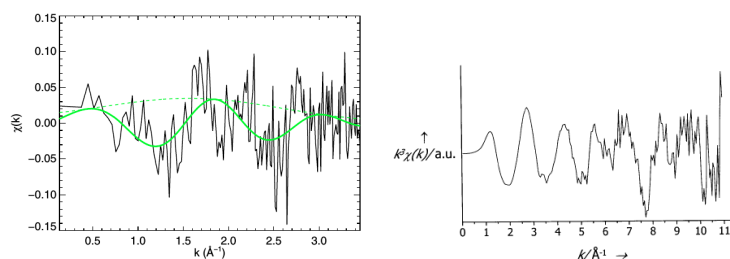


Note the difference in phase between these two plots. For example, near $2\,\text{Å}^{-1}$ the de Vries $\chi(k)$ is at a local maximum, while the Zubavichus $\chi(k)$ is at a local minimum. Similarly, around $2.5\,\text{Å}^{-1}$ de Vries is a minimum while Zubavichus is a maximum. This would appear to invalidate the claim that the astro data is due to ice II.

That the Fourier transform of the de Vries $\chi(k)$ has a peak – when plotted as the magnitude of the *complex* Fourier transform, see Fig. 2c in their paper – in about the same location as the peak in Fig. 3 of the Zubavichus paper does not contradict my statement in the last paragraph. By plotting the magnitude of the Fourier transform, de Vries and Costantini are obscuring the problem of phase in the $\chi(k)$ data.

Possible counter-argument: It is not clear what steps are taken between Fig. 2a and Fig.2b by de Vries and Costantini. Fig. 2a is plotted in the "astronomer way", not the "synchrotron way". That is, Fig. 2a is a plot of flux on the detector, not a plot of $\mu(E)$. So, it is possible that there is a parity problem in the comparison I made above. It is possible that Fig.2b is not a plot of $\chi(k)$, rather it may be a plot of $-1 \times \chi(k)$. If so, then de Vries and Costantini are guilty of confusing the XAS part of their audience, but not guilty of ignoring this phase problem.

**The likelihood of finding HDA ice**   HDA ice is metastable. It will spontaneously melt or crystallize into a solid phase under many conditions.

Creating HDA ice is not simple. Zubavichus describe growing it on gold substrate that had been modified by a hydrophilic, organic monolayer. That is, to get their sample to form in a high density phase, they had to grow it under highly controlled conditions. In their later paper in Langmuir, they mention that they cannot positively identify their sample as HDA ice. Rather, they say it is in one of the high density phases, which inlcudes the stable ice II.

In this paper presenting a neutron diffraction study of LDA and HDA ice, the ice is prepared by encapsolating a $H_2O/D_2O$ mixture in a piston and raising the presure to $1.6\,\text{GPa}$ at $77\,\text{K}$. This is a non-trivial sample preparation procedure.

Wikipedia shows a nice phase diagram for ice. A little material physics: the amorphous ice phases are formed by quenching (i.e. reducing the temperature too fast for crystallization to be initiated) from the

liquid part of the diagram. Thus LDA ice is formed by quenching below about 200 MPa. HDA ice is formed by quenching above 200 MPa. HDA ice will spontaneously reform into ice I, II, or V depending upon the temperature and pressure of the quench.

A bit of unit conversion: 1 atmosphere is about 100 kiloPascal, so HDA ice forms about 3 orders of magnitude in pressure above Earth's ambient pressure. The neutron study started by preparing the sample almost 5 orders above Earth ambient pressure.

The sample mesaured in the Zubavichus paper was prepared on a clean, oriented gold substrate. I don't know anything about the specifics of ice crystallization, but in general, the substrate has a lot to do with how materials crystallize. Controlling the crystallization conditions is likely essential to the formation of a specific phase of ice.

The notion that the majority of the oxygen (or at least the majority of the oxygen observable by XAS) in the universe is HDA ice seems extraordinarily unlikely from a thermodynamic perspective.

Weak counter-argument: Ice II exists all the way down to 0 K, according to the diagram at Wikipedia. Ice II and HDA ice are probably indistinguishable with noisy, broadened data. If Ice II somehow formed and remained unperturbed, it could exist at the temperature of interstellar space. Pressure is a problem....

**My processing of the satellite data**  Here's my best stab at representing the data you supplied in the form that we synchrotron folk typically plot $\mu(E)$ data.
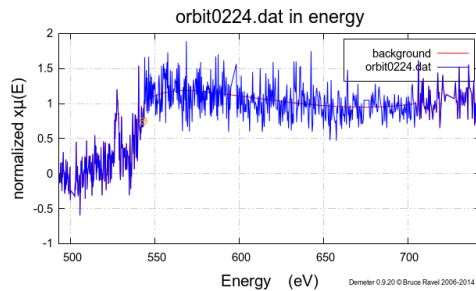


The blue shows the flux data, converted into $\mu(E)$, normalized to unit edge step. The red is the "background" function approximated by the algorithm used in my software.

The point of the background removal is to remove the step-like part of the data, leaving just the oscillatory portion. Here's the standard formula for this:

$$\mu(E) = \mu_0(E) \cdot \big(1 + \chi(E)\big)$$

The background algorithm, then, is an attempt to remove everything that isn't the oscillatory $\chi$.

de Vries and Costantini represented $\mu_0$ with a calculation of the neutral, atomic absorption for oxygen. That is, they had the revelation that occurs to every first year grad student in a group that does XAS. I had remember having that revelation way back when.

The revelation is that you can simply measure all the elements in their gaseous form and use that as the atomic background, $\mu_0$.

That revelation is usually followed by the revelation that the atomic background changes from sample to sample. That is, the atomic-like response of the absorber is altered by its surroundings. In the XAS

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literature, this is usually called the "embedded atom background". That is, the true $\mu_0$ function is due to the response of the atom in the potential environment of its surroundings, but without the effect of the scattering of the photoelectron from the neighbors. In practice, $\mu_0$ is different for different chemical species.

What's more, we in the synchrotron business use our $\mu_0$ determination algorithm to account for any low-frquency structure introduced by the response of the instrument or the properties (mostly inhomogeneity) of the sample.

Bottom line, it is not considered to be good practice in the XAS community to subtract a computed, neutral-atom background function and to call what remains $\chi$.

Carrying on....

Here is the result of applying the background removal algorithm from my software to the "orbit0224" data, plotted the same way de Vries and Costantini plotted Fig. 2a:
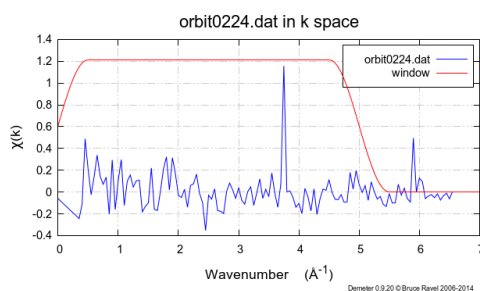


And here is the Fourier transform of that, using my best guess of the parameters of the Fourier transofrm that de Vries and Costantini used:
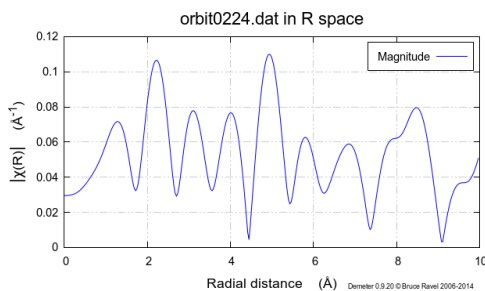


Your Fourier transofrm eyes did not fail you. The $\chi(k)$ plot *is* just noise.

Possible counter-argument: I misunderstood something major about how de Vries and Costantini did their data processing. While that might be true, I am pretty confident of how I did *my* data processing.

**Pre edge peak in the satellite data**  There appears to be some ambiguity in the data. Granted, I don't really understand what the differences are among the three files you sent me.

Here is a plot comparing the 'orbit0224' and 'orbit0592' files, which each presented as $\mu(E)$:

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0224_2
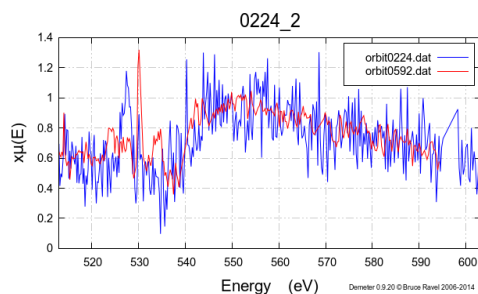
Compare this to Fig. 2a in de Vries and Costantini. The peaks that they label (cryptically) as "OI", "OII", and "OIII" are not obvious in the data, as you presented it to me. What's more, the peaks in the 525 eV to 535 eV range are not consistent in size, width, or location.

Although I am willing to believe that the main edge step is due to the drop in flux due to the O K edge, I am unsure how to intepret the features before the edge.

I should also point out that 'orbit0592' file does not contain data over a broad enough data range to took at the extended spectrum. Hence, the plots in the previous section were made using the 'orbit0224' file.

**Comparison with other O K edge spectra** Note: the ice data was given to me by Yan Zubavichas and appears to be the same spectrum published in the Chem. Phys. Chem. paper. The air and water data are from Adam Hitchcock's gas phase core excitation database. I believe that those spectra were measured by electron energy loss (EELS) in an electron microscope.

For starters, here are some standards:



standards
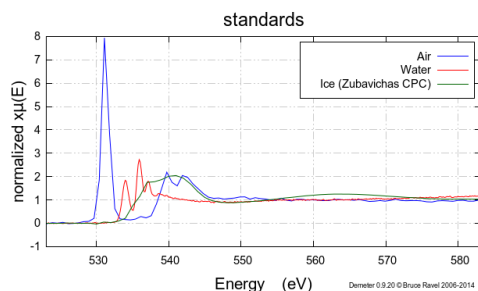
As is the nature of O K spectra, there is *a lot* of variability between compounds. Some things to notice:

1. The pre-edge, bound-state resonances change dramatically between $O_2$ and $H_2O$.

2. They disappear completely in the solid.

3. There is a significant – $\sim 2$ eV – shift in the main edge from sample to sample. (I am assuming, although I have no way of verifying, that the relative and absolute energy calibration is reasonable among these three spectra.)

This is another example of why I have always been more sanguine about using the XANES than the EXAFS to speciate the astronomical spectra. In many cases the XANES are wildly different from species to species, while the EXAFS can be hard to find in the level of noise of your data.

So, is the pre-edge feature in the astro data anindication of molecular $O_2$? Let's look. Here's 'orbit0224' compared to the air spectrum, along with broadened copy of the air spectrum:
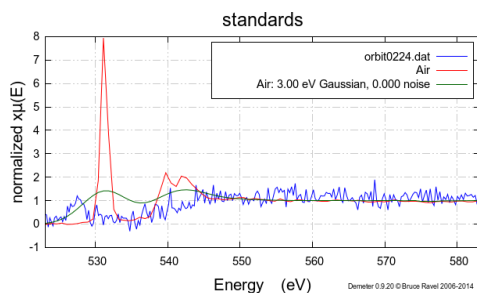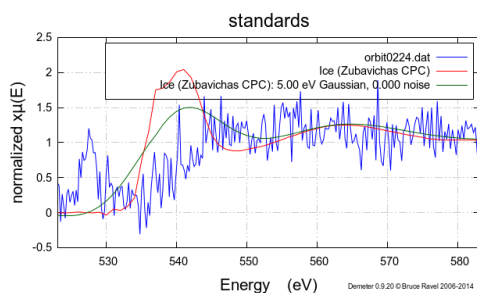


As you can see, the sepatarion between the edge and the pre-edge resonance is several volts larger in the 'orbit0224' data than in the air spectrum.
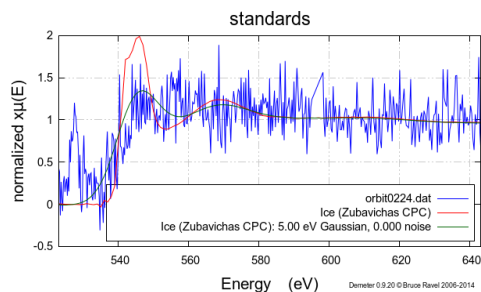
Here's the same plot with the 'orbit0592' data:
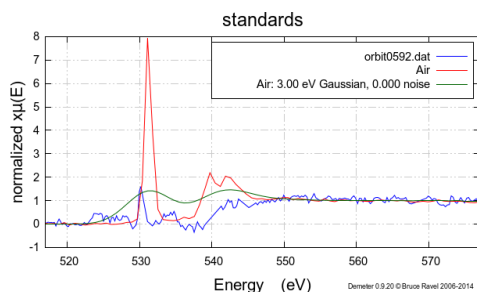


Here, the pre-edge resonance position is closer to the air spectrum, but something seems off to me. My memory is that the energy resolution of the satellite is quite a bit larger than what we measure at a synchortron or in an electron microscope. It is hard forme to understand why the feature near 530 eV is as sharp as in the EELS data.

Here is the 'orbit0224' data along with the Zubavichus' ice data (+ a copy with some broadening):



And here is the same, but with the ice spectrum shifted arbitrarily by 5 eV.

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**standards**

normalized xμ(E)

2

1.5

1

0.5

0

-0.5

540    560    580    600    620    640

Energy   (eV)    Demeter 0.9.20 © Bruce Ravel 2006-2014

orbit0224.dat ——
Ice (Zubavichas CPC) ——
Ice (Zubavichas CPC): 5.00 eV Gaussian, 0.000 noise ——

I think it's a bit of wishful thinking to see Zubavichus' data in the astro data. If anything, I see the same sort of phase problem I discussed above.

**So what are the astro data?**  Well, the easiest answer is: "not much".

But, there really does seem to be an edge step, so I kind of want them to be "something". Some thoughts:

1. As I said, I have no idea about absolute calibration of the terrestrial data. Suppose that they can be wrong by $\pm 5$ eV. Then, the astro data could be a combination of molecular oxygen and some form of solid-state oxygen.

2. In the terrestrial arena, oxygen is pretty reactive. Molecular oxygen eventually oxidizes things – metal, sulfur, carbon, hydrogen – pretty much everything. So we could be seeing a edge that is broadened by being a superposition of species with edge steps occuring over a range from about 538 eV to about 543 eV. That certainly happens in synchrotron data.

3. If the data are a superposition, it is practically impossible to do meaningful speciation at the O K edge. All you can say is that these data confirm that oxyegn exists in the universe (or at least the part in the line of sight to the X-ray source), probably in many forms. Not a very exciting result.