Response to Reviewers
Manuscript Number: acp-2014-34
Manuscript Title: Evolution of the complex refractive index in the UV spectral region in ageing secondary organic aerosol

We would like to thank the anonymous referee for having thoroughly read the paper and giving us useful comments. Following are the response to his/her comments.

Response to Reviewer #2 Comments:

1) Using a chamber presents a limitation on the number of trials possible which creates a scenario like a field campaign. So, while control of the initial conditions is possible in the chamber, I assume time limitations prevented repeat experiments. Ideally, repeat experiments would have been completed to allow statistical analysis. Were any repeat experiments performed or are any planned in the future?

The reviewer is correct that we had a 'field campaign scenario' with limited time to perform all of the experiments. We simplified the approach to the three cases of the α-pinene/limonene/p-xylene system to take advantage of the multi-methodological approach and long observation times of large chamber experiments; i.e., to learn from parallel long term measurements including a day/night cycle on the same system. The experiments at the SAPHIR chamber are resource and labor intensive and somewhat dependent on the weather conditions. Therefore we could not carry out more repetitions. However, Fig. 3a shows that our measurements are consistent with literature values.

The use of the chamber also may have contributed to the decision to operate in low/no NOx conditions. Have the authors considered how NOx would change their results? NOx was noted by Jacobson (1999 in JGR) as contributing to the UV light absorption of particles and thus would contribute to the imaginary part of the refractive index. The NOx concentrations could be important in considering anthropogenic cases so it is noted to be limited here and is perhaps not quite representative of anthropogenic cases.

The reviewer is correct NOx is important. For this study we decided to probe lower NOx conditions, which are not un-realistic if anthropogenic air masses containing BTX (benzene, ethylbenzene, toluene and p-xylene) mix with air masses from forests. We are now conducting experiments studying the reactions of NO_3 radicals with SOA at higher NOx conditions.
We added the following sentence to the conclusions: "The results from this study are representative of clean conditions due to the low NOx conditions used."

The last concern here has to do with wall interaction and this has probably been characterized but I am unfamiliar with SAPHIR literature so perhaps this warrants a comment.

Particle wall losses in the Saphir chamber were characterized in Salo et al. 2011. The losses of volatile species such as pinonealdhyde are only slightly faster than the replenishment rate. The SAPHIR chamber has a favorable surface to volume ratio < 1 m^{-1}. Wall interactions will influence the overall chemical system, but effects as strong as described by Matsunaga and Ziemann (2009) have not been observed.

On the other hand, the particles were characterized by several methods and the relations hold as given. We do not discuss yields where wall losses may be an issue. The chemical systems might have evolved slightly different in a wall free situation and this may affect the direct transfer of our results to the ambient (as for all chamber and lab experiments). However, Fig. 5 and Fig. 7 characterize where the studied SOA are compared to ambient observations: they are moderately aged particles with distinctive influence from semi-volatiles.

We modified the first paragraph of Section 2.1, the paragraph now reads (the highlighted phrases are the additions we made):

"The experiments took place in the outdoor atmospheric simulation chamber SAPHIR at the Forschungszentrum Jülich, in Jülich, Germany. The SAPHIR chamber has been previously described in detail (Bohn et al., 2005; Rohrer et al., 2005)==, and has been used for several SOA experiments (e.g. Donahue et al., 2012; Emanuelsson et al., 2013a; Salo et al., 2011; Rollins et al.,2009; Fry et al., 2011)==; only a short description is given here. SAPHIR is a double-walled Teflon chamber with a volume of 270 m3. It is operated with synthetic air (Linde Lipur, purity 99.9999%), and kept at a slight overpressure of about 50 Pa. To maintain the overpressure in the chamber and to compensate for the sampling by the instruments, a continuous flow of 7 – 9 m3 h-1 of synthetic air is maintained throughout the experiments. A fan is used to ensure mixing of the injected trace gases, and the chamber is equipped with a Louvre system to either open and expose it to natural sun light or close it to simulate night time processes.

2) With regard to the imaginary refractive index, most organic compounds do not have large absorption as recorded by UV/Vis spectroscopy above about 350 nm (and it could be said above 320 nm). Organic compounds have absorption to longer wavelengths with increased conjugation and with certain functional groups (see Jacobson reference above for example). Based on this, the low imaginary refractive index observed here for the wavelengths from 360-420 nm are to be expected. Are there any plans to extend the wavelength range?

We are currently modifying the instrument to extend the wavelength region covered.

Or alter the conditions?
Please see comments above

 As noted by Referee #1, perhaps the focus should be shifted to the real portion of the refractive index.

We respectfully disagree with the reviewer. Although the focus of the paper is the real part of the complex refractive index, it will be inaccurate to say that we only derived the real part. To obtain the retrievals we did not constrain the imaginary part to zero. We allowed the real part to vary for n > 1 and the imaginary part for k ≥ 0. We now added the errors of the retrieved imaginary components of the refractive indices.

Additional note: Referee #1 makes an important point about the use of the RI data at 420 nm to extend into the visible for calculations in RF. The authors and others have seen variable RI at these wavelengths (420 and nearby at 405 nm) and so this assumption may not be valid. There is much less change in RI beyond ~500 nm.

**The reviewers are correct and we removed this section**

Detailed comments:
page 4153, and also Table 1 and Figure 1 and 2 - Could the authors clearly list what time of day the experiments began?

**We added a column to Table 1. Please see below.**

Table 1. Description of the experiments performed in this study

Experiment	Description	VOC (ppb)	Initial [OH] ($\times 10^6$ molec. cm^{-3})	[NO$_x$] (ppbv)	Local time experiments began	Total duration
BVOCs	BVOCs mix only	α-pinene, limonene (48, 48)	7.4	< 0.25	11:30	~50 h.
Sequential	BVOCs mix & p-xylene-d$_{10}$ (p-xylene-d$_{10}$ added 5h after BVOCs mix)	α-pinene, limonene (39, 39) p-xylene-d$_{10}$ (51)	7.8	< 0.30	11:37	~ 29 h.
Mixture	BVOCs mix & p-xylene-d$_{10}$ (added together)	α-pinene, limonene (42, 42) p-xylene-d$_{10}$ (90)	8.0	< 0.25	11:33	~ 29.5 h.

For Figure 1 we changed the time shown to ~11:30 – 17:00 to indicate the time span of the experiments in general (for clarity reasons). We updated the caption: "Schematic of the experimental procedure and instrumentation used for measuring the evolution of secondary organic aerosol over a diurnal cycle. All experiments began around 11:30 hrs. local time." See the updated Figure below.
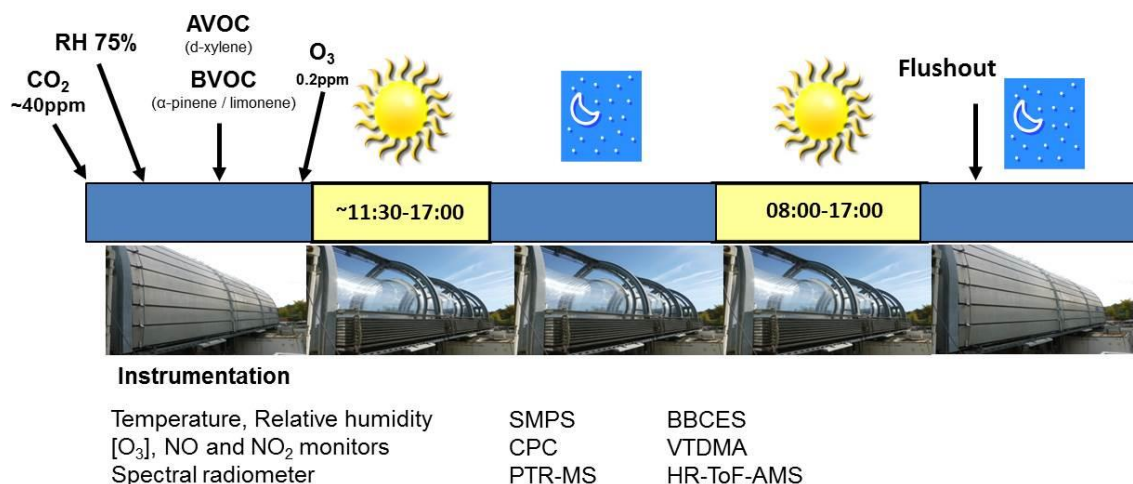
For Figure 2 we added the exact times at which each experiment began in the top panels of the figure. We also added at the end of the caption the phrase: "The local time at which each experiment began is shown in the top panels." See the updated figure below.
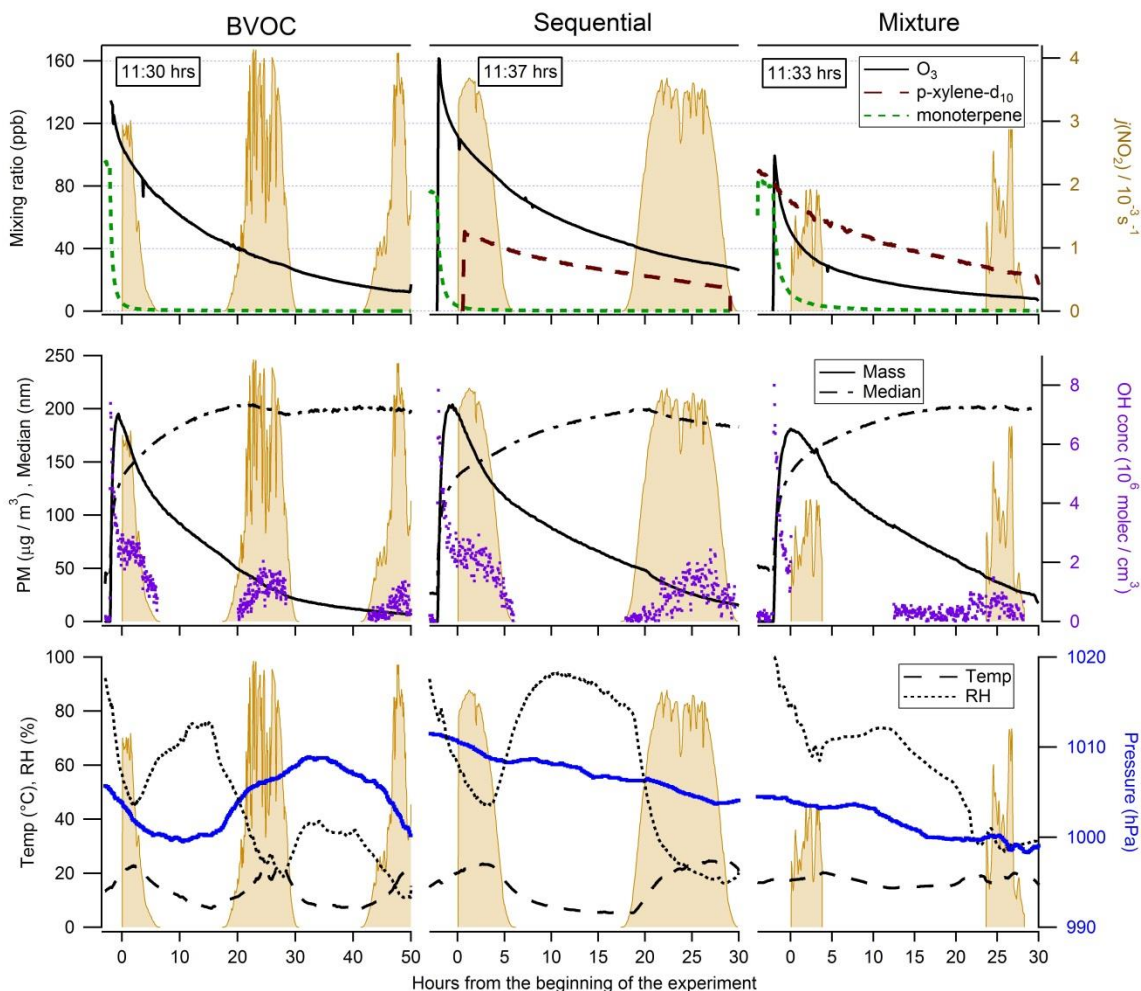
page 4155, lines 17-21 - Can the authors comment on the low particle concentrations beyond 15 hr. Is this due to wall losses? Dilution? How are the size selected optical property measurements made under these conditions?

The decrease in the particle concentration is due to the instruments pulling the aerosols out of the chamber and diluting the chamber with 7–9 m³h⁻¹ of (particles-free) air. Losses of particles (mass) are due to dilution flow and wall deposition, which is faster during day than during night as descript in detail in Salo et al. (2011). Regarding particle number, coagulation is also operative on the long time scales of observations. After 15 hrs we had more than 15,000 particles per cubic centimeter in the chamber, hence still high enough concentration to conduct size selected refractive index retrievals. Furthermore, the particles in the chamber grew with time (see Fig 2. middle panels). This allowed us to size select larger particles. In the size and wavelength range we are working, this enabled measurements with an acceptable signal to noise ratio.

page 4157, line 22 - The sizes selected for the refractive index retrievals is somewhat narrow (only D=175-300 nm) and some of these sizes were only used at the end of the experiment. Can the authors comment on how the narrow size range impacts retrievals, if at all? Do they obtain the same results at the end of the experiment if they use 175-230 versus 175-300 nm? Have

they done work where a wider range of size selected particles are possible (to 500 or 600 nm) and compared to results when size range limitations were placed?

We do not expect the narrow size range to affect the retrieval. Below is a figure showing an example of one of a retrievals with a narrow size range for a λ=365nm. In the figure one can see the best fit and the accepted range of refractive indices (RI). We also added curves of RIs that are outside the accepted range for comparison.
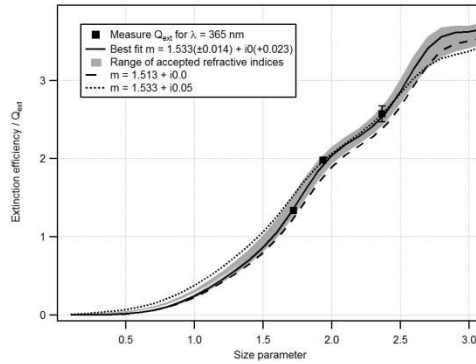
Furthermore, we took the data for the mixture experiment at 25.2 h and retrieved the RI for three different scenarios: 1) all the diameters from 200 – 300nm; 2) using only data from 200 – 250 nm; 3) using only data from 225 – 300nm. All are in 25 nm steps. As is can be seen in the figure below, there is no significant change of the retrieved RIs depending on the size range that was chosen.
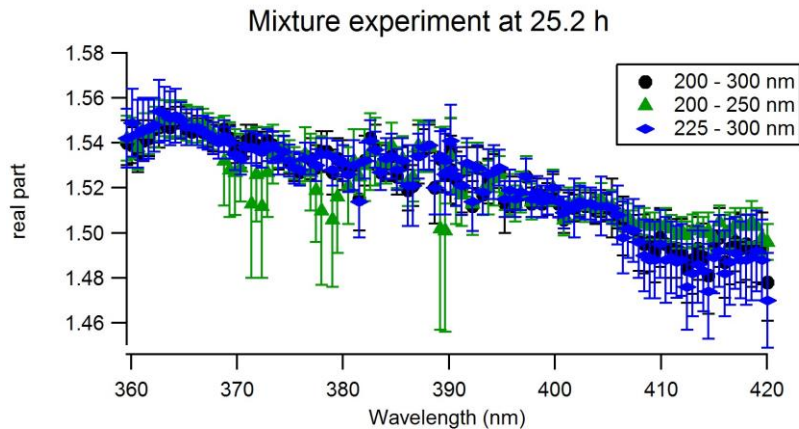
page 4157-4158 - How much fluctuation is seen in the light intensity of the particle free cavity over a retrieval experiment? Does this impact the retrieval results? If so, is a correction applied? Is the intensity monitored?

The retrievals are done by taking a particle-free measurement first, then a series of extinction measurements of size selected aerosols with varying diameters and finally another zero measurement is taken. For the analysis, the particle-free measurements are interpolated and the particle-free measurement is used to calculate the extinction coefficient of the selected diameter. The size-selection measurements took approximately 20 minutes. During this

period we did not observe fluctuations of more than 1% between the particle-free measurements.

page 4159, line 12 - Are the spectra smoothed before retrieval or are the RI averaged after retrieval? If the later, how much does noise across the spectrum impact the retrievals?

The spectra are averaged before retrievals. Each size selection measurement is an average of 150 spectra integrated for 0.3 s.

page 4159, line 17 - The BVOC data is limited because of the lack of data beyond 5 hours so the argument with regard to data trends seems weak.

We have changed the phrase: "From Fig. 3a we can see that the real part remains constant within the calculated error range up to 5 h after the experiment began, with n values varying from 1.51 (±0.01) at λ = 360nm to 1.49(±0.01) at λ = 420 nm." to "Fig. 3a shows that there is no distinguishable change in the RI, within the calculated error, from the two retrievals taken at 2.5 h and 5h after the experiment began. There is only a slight spectral dependence with *n* values varying from 1.51 (±0.01) at λ = 360nm to 1.49(±0.01) at λ = 420 nm. "

page 4160, literature comparisons -1) Could the authors give a bit more information for comparison to the literature? It would be useful to know how comparable this data is with their own with regard to oxidant concentration and exposure time. Perhaps such data could be included in Table 2? This is also relevant for the later comparison for oxidation level and RI on page 4162.

We've added initial VOC, O$_3$ and OH concentration and reaction time to Table 2. See the updated Table below.

In addition, the paragraph now reads (the highlighted phrases are the additions we made): "For example, for SOA generated from the ozonolysis of α-pinene, Liu et al. (2013) found values of the real part of *n*=1.517(±0.003) and *n*=1.509(±0.003) for λ=360 nm and λ=420 nm, respectively, using a variable angle spectroscopic ellipsometer with _initial ozone and α-pinene concentrations of 52.2 (±2.2) ppmv and 4.0(±1.4) ppmv, respectively_. The imaginary components they found in this range were below k<10^{-4}. Using cavity ring down spectroscopy (CRDS), Nakayama et al. (2012) retrieved values between *n*=1.463(±0.019) and *n*=1.475(±0.022) at λ=405 nm, and Nakayama et al. (2010) found values of *n*=1.458(±0.019) at λ=355nm. The imaginary parts for both studies were found to be below 0.003. _Both studies used initial concentrations of 0.1 ppmv of α-pinene, and 1.1 – 2.6 ppmv of ozone._ Wex et al. (2009) retrieved only the real part of the RI by using a white light optical particle spectrometer, and found a value of *n*=1.45 for the visible wavelengths. _They used O$_3$ concentrations of up 2.5 ppmv, and α-pinene concentrations in excess of that of O$_3$._ Similarly,

Schnaiter et al. (2003) determined a constant value of $n=1.44$ for $\lambda>350$ nm by measuring the wavelength dependence of the SOA scattering and extinction. *They generated the α-pinene SOA by admixing 470 ppb ozone, followed by the addition of 61 ppb α-pinene.* Using CRDS and a photo-acoustic sensor to measure RIs Lambe et al. (2013) found values between $n = 1.51(\pm 0.02)$ and $n=1.45(\pm 0.04)$ with imaginary part values of $k < 0.001$ at $\lambda=405$ nm for SOA formed by homogeneous nucleation and condensation following OH oxidation of α-pinene at different oxidation levels, using a potential aerosol mass flow tube reactor.

Table 2. Real parts of the RI for different O / C ratios in this study compared with literature values

Real part (n) of the RI	O/C atomic ratio	VOC (Initial conc. in ppmv)	SOA formation	Ini. [O₃] (ppmv)	Ini [OH] (×10¹⁰ mol cm⁻³)	Exposure time	Wavelength (nm)	Reference
1.50(±0.01) − 1.49(±0.01)	0.37 − 0.38	α-pinene + limonene (0.048 + 0.048)	ozonolysis and OH oxidation	0.2	0.00074	up to 50 h	405	This work
1.46(±0.01) − 1.50(±0.02)	0.39 − 0.44	α-pinene + limonene + p-xylene-d₁₀[a] (0.039 + 0.039 + 0.051)	ozonolysis and OH oxidation	0.2	0.00078	up to 29 h	405	This work
1.46(±0.01) − 1.51(±0.01)	0.35 − 0.42	α-pinene + limonene + p-xylene-d₁₀ (0.042 + 0.042 + 0.090)	ozonolysis and OH oxidation	0.2	0.00080	up to 29.5 h	405	This work
1.511 (±0.003)	< 0.3	α-pinene (4.0±1.4)[b]	ozonolysis	52.2±2.2[b]	Scavenger[c]	~38 sec	405	Liu et al. (2013)
1.514 (±0.003)	< 0.3	limonene (3.0)	ozonolysis	30±0.5			405	Liu et al. (2013)
1.51(±0.02) - 1.45(±0.04)	0.42 − 0.93	α-pinene (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.66(±0.04) − 1.58(±0.06)	0.52 − 1.29	naphthalene (NA)	OH oxidation	NA	22(±11) − 150(±20)	~100 sec.	405	Lambe et al. (2013)
1.55(±0.01) − 1.53(±0.01)	0.70 − 1.14	guaiacol (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.54(±0.01) − 1.48(±0.01)	0.37 − 0.89	tricycle[5.2.10²,⁶]decane (NA)	OH oxidation	NA			405	Lambe et al. (2013)
1.449(±0.030) − 1.567(±0.043)	0.64 − 0.73	toluene (4.0)	photooxidation	NA	~27	up to 4 h	405	Nakayama et al. (2013)
1.431(±0.026) − 1.498(±0.025)	0.64 − 0.73	toluene (4.0)	photooxidation	NA			532	Nakayama et al. (2013)
1.475(±0.022) − 1.498(±0.030)	0.43 − 0.47	α-pinene (0.1)	ozonolysis and photooxidation	1.1 and 2.6	~27	up to 4 h	405	Nakayama et al. (2012)
1.476(±0.021) − 1.458(±0.02)	0.43 − 0.47	α-pinene (0.1)	ozonolysis and photooxidation				532	Nakayama et al. (2012)
1.47(±0.02) − 1.52(±0.00)	0 − 0.35	squalene (NA)	OH oxidation	NA	0 − ~200	37 sec.	532	Cappa et al. (2011)
1.47(±0.02) − 1.54(±0.00)	0.45 − 0.75	azelaic acid (NA)	OH oxidation				532	Cappa et al. (2011)

[a]p-xylene-d₁₀ was added 5h after; [b]Average of four experiments; [c]Butanol was used as an OH scavenger; NA: not available

2) The trends noted in several of the cases presented are within the uncertainties making conclusions challenging.

page 4161 and Figure 4 - The lack of data between 7-22 hrs is concerning. Can the authors comment on this? Were particle concentrations too low?

Unfortunately we were unable to take more retrievals during this time due to problems with the reflectivity of the mirrors (see reply to Reviewer #1). We solved these issues only close to the end of that day's experiment when we were able to take the retrieval at 29.5 h.

Also, can some of the "rates" discussed be reinforced with fits so the slopes can be compared?

Due to the number of retrievals in the BVOC only and the sequential experiment, we believe that it is only appropriate to do fits to the data from the mixture experiment. We have calculated the slopes for each wavelength shown in Fig. 4C1. For the 390 – 420nm cavity we get an average slope of 0.6(±0.1) and for the 360 – 390nm cavity an average slope of 0.6(±0.1). This result only shows that the rate of change across the measured wavelengths is similar.

Finally, what are the uncertainties on the RI and O/C or H/C ratios? Are the trends within these values?

The uncertainties for the O/C and H/C ratios are 31% and 10%, respectively. They are stated in the caption of Fig. 4. We added in the text, Section 3.3 second paragraph, the error for each stated O/C and H/C value. The paragraph now reads (the highlighted numbers are the additions we made): "It can be seen that for the mixture experiment, the value of the RI increases with SOA ageing. This is correlated with the SOA increasing oxidation level (Fig. 4C1): the O/C values increase from ~0.34 (±0.10) at 1.5 h to ~0.42 (±0.13) at 29 h of ageing, the H/C ratio decreases (Fig. 4C2) from ~1.55 (±0.16) to 1.49 (±0.15), and the volatility (Fig. 4C3) decreases with $T_{VFR0.5}$ increasing from ~366 K (±2) up to ~388 K (±1). There is a similar trend for the sequential experiment. However, the magnitude of the increase in RI with respect to the O/C ratio is smaller, even though the O/C ratio increased more (~0.44) for approximately the same ageing time. Furthermore, the rate of change of the RI with respect to the H/C ratio is also smaller than for the mixture experiment: the H/C ratio decreased from around 1.50 (±0.15) to ~1.45 (±0.15). There is not a clear difference between the two experiments in the dependence of the real part of the RI on volatility. For the BVOCs experiment it is difficult to assess a relationship with only two retrievals within the first 5 h of the experiment. There is only evidence that the RI remained constant (as seen in Fig. 3) with a small increase in the O/C

ratio, and a slight decrease in volatility with $T_{VFR0.5}$ increasing from 365.5 K (±2.7) to 366.7 K (±2.6)."

The error for the RI is less than 0.03 for all retrievals. The average values for each set of retrievals made are stated in Fig.3's caption.

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