

Interactive comment on “Simultaneous stable isotope analysis of methane and nitrous oxide on ice core samples” by C. J. Sapart et al.

Anonymous Referee #2

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The manuscript by Sapart et al describes a system for the measurement of the long term changes in the stable isotopes of methane and nitrous using ice cores. These are important atmospheric gases, with significant roles in climate, atmospheric chemistry and stratospheric ozone. Their budgets and the causes of recent changes have significant uncertainty which might be reduced with measurements of changes in their concentrations and isotopes over the past. Air enclosed in ice cores offers the only way of doing this before the past several decades, but the air enclosed in ice is small in amount and difficult to extract and analyse. This manuscript addresses these technical challenges which are particularly relevant to isotopic measurements. The ms is well suited for AMT. The authors and their organisations are experienced in work of this nature and have good records of success. The general approach is sound- dry

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extraction (grating) of air from ice, using a development of a previously established technique, and continuous flow IRMS for the isotopic measurements (again, already described and published), which is particularly suited to the small air volumes and low trace gas concentrations. The authors have introduced some new developments such as special surface coatings for the extraction vessel. The description of the system and the tests that evaluate its performance is generally good. The ms reviews earlier work well and shows how their approach has learnt from it. The results are generally of good quality though there is a very large uncertainty in the methane isotope scales used by other groups, of the order of 25% of the $^{13}\text{CH}_4$ change over the industrial period. These differences must be resolved if the measurements are to be intercompared. More analysis of where these differences might originate, perhaps through the measurements of the air standards or ice core samples, would provide the reader with more confidence in the work. Some clarification is needed of the test procedures (eg. bubble free ice), of the issue of CH_4 production and how it was avoided and how air volumes were determined to evaluate the concentrations (see below). With these changes and clarifications made the ms would be suitable for publication.

Specific points P 4476 L24 delete “realized as” P 4477 L 18. A little more explanation about the metal-metal collisions is needed- what is colliding? How does a precise fit stop this? Was CH_4 contamination detected without this? Does the TiN coating address the problem? P 4478 L 10. T 3 presumably traps air including CH_4 ? L 13.flushed with He P 4479 L 21 delete “used” L 24 how was the 99.999% determined? How much of the remainder is removed by the GC column (next page)? P 4480 L1 CRYOFOCUS L 8 A description of how the NO^+ fragment determination leads to the position dependent isotopologues would help. L 12 The microtoming- why is this done, how much is removed? L 13...“is then” L 15,16 Confusing- 2 evacuation periods are given. L 19 Contamination from the system (not from the ice or from the ice grating process)? (presumably that is why the bubble free tests are done). L 21. What was the flow of the He flush used to determine the blank? If it is much faster than the true sample (ie. The residence time much shorter) then it may not reveal any modification of

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the sample. P 4481 L8 ..by listening, care is taken that the ice sample.... L 15 I wasn't sure what was being determined here. Since the extraction efficiency is unlikely to be 100%, given that there is probably air remaining in many of the 1-2 mm chips, it isn't possible to measure the total amount of air in the sample. Second, the volume (STP) of the air EXTRACTED from the sample is needed to calculate the concentrations of CH₄ and N₂O- is this what is found from the pressure of the released air? P 4482 L23 Is there evidence that knocking of the ice on the pot damages the oxide layer and leads to CH₄ production? Was it observed or just an expectation? There are several other similar dry extraction ice core techniques in use where ice impacts steel surfaces that apparently do not produce methane. Is it possible that methane produced in this system is due to other origins, such as movement of the grater, when high shake frequencies are used? L 9 How was the 97% efficiency determined? L 11 ...takes a long time... L 17 reproducible- in terms of amount adsorbed? P 4484 L6. How is it known that the BF ice contains no air? Does it also contain no traces of N₂O or CH₄? L7 ...they might not be L9 As mentioned above, how is the mixing ratio determined- is there a volume/pressure measurement and what is the uncertainty of the calculation? L13 no detectable difference- of CH₄ and N₂O mixing ratios? To what uncertainty? L26 N₂O isotope or mixing ratio measurements L22 trends might be a better word to patterns P 4487 L 5 This sentence needs a verb L16 A little information about the ice cores would help- approximate location, elevation.....Could the results for the cores be meaningfully compared with published records, perhaps shedding light on the calibration differences? P4488 L 9 ...systems are included P4489 L24 use a more precise word for signatures Figure 5 Caption Are the dashed lines best fits or 1:1 lines?

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