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Atmospheric Measurement Techniques Discussions

Interactive comment on "A sublimation technique for high-precision measurements of $\vec{\delta}^{13}CO_2$ and mixing ratios of CO_2 and N_2O from air trapped in ice cores" *by* J. Schmitt et al.

Anonymous Referee #1

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Review of Schmitt et al., A sublimation technique for high-precision measurements .. AMT. General comments This is a very detailed and comprehensive description of a technique that has important applications: the measurement of past atmospheric composition, notably 13C in CO2. The technique has some significant appeals as it can deal with ice that contains air as clathrates and that might also have organic drill fluid contamination. It therefore has most significance for deep, cold ice covering long time periods (typical of the deep Antarctic cores), which has presented problems for 13CO2 measurements til now. Its advantages for more recent (say Holocene) ice, which may be cleaner and contain only bubble-air, are less obvious. The manuscript describes the technique well. This is a very complex system (in most cases necessarily) and the at-

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tention to technical detail is impressive. There are several clarifications needed, listed below. A general point concerns the use of “Bubble free” ice. Is it known that this is also air free (ie. There are no dissolved or invisible gases inclusions)? Regarding the organic fluid effects. Are all cores drilled with organic fluid affected, or are some types of fluid less or not contaminating? Is it demonstrated that the system described here removes the vapour (for example, are the various organic fractions seen to emerge separate from the CO2 and N2O peaks)? Is it possible that the very low temperature of the water traps holds back the organics? VDPB-CO2 is often mentioned. I guess what is meant is VPDB. There are places in the ms where only a narrow selection of publications is cited, when there is actually a broader body of published work in this area with relevant results that should be mentioned. Finally, the goal of this system is to measure CO2, 13CO2 (and N2O?) with high precision and accuracy. What are the precisions and accuracies required to expose and explain past changes in the atmosphere that are relevant to the biochemistry, geochemistry and climatic issues? Has this work approached that goal? With these points and the changes and clarifications below addressed I would recommend that this work is suitable for publication. Assessment criteria (AMT) 1. Does the paper address relevant scientific questions within the scope of AMT? yes 2. Does the paper present novel concepts, ideas, tools, or data? yes 3. Are substantial conclusions reached? yes 4. Are the scientific methods and assumptions valid and clearly outlined? yes 5. Are the results sufficient to support the interpretations and conclusions? mostly 6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? mostly 7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Could be improved 8. Does the title clearly reflect the contents of the paper? yes 9. Does the abstract provide a concise and complete summary? yes 10. Is the overall presentation well structured and clear? mostly 11. Is the language fluent and precise? Some improvement needed- see below comments 12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? yes 13. Should any parts of the paper (text, formulae, figures,

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tables) be clarified, reduced, combined, or eliminated? no 14. Are the number and quality of references appropriate? Others could be cited 15. Is the amount and quality of supplementary material appropriate? None referred to

Detailed comments follow: Page 1854 Line 1 d13C of CO2 Line 16 and elsewhere: mechanical Line 26 knowing the causes of these changes is also relevant to the future behaviour of CO2 P 1855 Line 4 explain what is meant by fragmentary Line 8 in situ production of CO2 in the ice will affect all measurements of air extracted from bubbles. It seems that the melt extraction limitations are due to the effects in the following sentence, line 10 Line 14 Need to explain what is meant by pure bubble and clathrate ice Line 25 ..only extraction technique for CO2 ffor ice core samples... Page 1856 Line 1 date for Siegenthaler reference Line 10 to create a highly resolved record in deep ice cores with thin annual layers Line 11 please provide a reference for the drill fluid observation Line 21 to take advantage Line 24 changes over time? Explain a little Line 28 ...are discussed Page 1857 Line 8 What about the impurities eg. Drill fluid vapour? Line 14 Sharp peak or pulse of gas? Line 18 Does the reference device introduce only air or air from ice- the latter more closely mimics the actual ice sample analysis. Line 25 Why choose all metal components when only 2 lines previously it is said that these (and glass) surfaces most notably degass CO2? Page 1859 Line 13 becomes unstable Page 1861 Line 22 are permanently heated Page 1862 Line 13 Except for the possibility of impurities, mentioned above. Page 1863 line 24. The sample process rate is an important feature of the system and could be mentioned earlier. Page 1864 The recent 2000 years of the Holocene is covered in detail in the Law Dome ice records (MacFarling Meure et al, Etheridge et al). P1865 line 13...is organic... Line 20 Francey et al did not report this. In fact they say they found no difference between ice drilled with or without fluids P1866 line 12 (and elsewhere) I think Figure 3 is meant Line 24 Explain what is meant by “Alternatively....” Page 1870 line 11 More detail of the CO2 absorption issue would be nice Page 1871 line 5 Were any extractions done to 100% completion to demonstrate this? line 12 Does this fractionation occur only to clathrated ice? Line 23 ...section on data...? Page 1876 line 24 “Talos Dome ice core is more

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reliable than from other cores" which other cores? Has the inorganic impurity content be measured and compared with others? Is the N2O in situ production observed for all other cores? Are the processes behind that expected to be the same for CO2? More detail is needed in this section, and on line 12 of the next page. Page 1877 line 9 the 3 references given cover only some of the well known ice core measurement techniques Line 17 as for CO2, there are other N2O measurement techniques not mentioned Page 1878 line 23 Several Law Dome cores were measured by Francey et al and subsequent studies. Lines 25 and 28. What are the uncertainties of the matches with the overlapping periods of the various ice, firn and atmospheric measurements? This is important as it is one of the only ways that the ice core technique can be verified (although only for recent ice and therefore not clathrate ice).

Figure 7 caption. This cracker system is different from the tube cracker presented in this paper- it should be called "ice air extraction cracker" or similar to avoid confusion. Also, "pure bubble ice" presumably refers to ice with no clathrates as compared to ice with no impurities.

End of review

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1853, 2011.