Atmos. Meas. Tech. Discuss., 4, C1610–C1614, 2011
www.atmos-meas-tech-discuss.net/4/C1610/2011/

Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #1

Received and published: 15 September 2011

General comments:

This paper presents a dry extraction system for combined CH4 and N2O stable isotope analysis from ice core air, using an ice grating device. This is a new analytical method for simultaneous measurements of both CH4 and N2O stable isotopes in ice air based on only 600-700 g ice samples. This paper is thus within the scope of Atmospheric Measurement Techniques. The CH4 and N2O stable isotope provides insightful information on the past CH4 and N2O budget and enhance understanding their biogeochemical cycles. In general the paper is well written and organized. Most parts of the design of the new analytical system and diagnostic tests are pretty straightforward. However, there are still some points about the test design which should be clarified or

corrected. The paper can be significantly improved with these corrections. Please refer to the specific comments below. I thus recommend major revisions before publication on AMT.

Specific comments:

Page 4477, line 3-6: What is the normal ice weight required for CH4 and N2O stable isotope analysis for ice core air? What is the rough temporal resolution for 200-800 g ice?

Page 4478, line 6-8: What is the shape of T1, T2, and T3? Coil trap or U-tube trap? Are they stainless steel or glass? What is diameter and length? It is better to mention them here.

Page 4478, line 17: The reference "Brass and Rockmann, 2010" should be the final revised AMT paper instead of the discussion paper.

Page 4478, line 20-21: What is the carrier gas used? UHP helium?

Page 4478, line 23: What kind of cold bath is used to keep -132°C?

Page 4478, line 24-25: "the cooling is stopped" to "the cold bath is removed and the cooling is stopped".

Page 4478, line 25: What is the temperature for warming up? Room temperature?

Page 4479, line 2: "focussed" to "focused"

Page 4479, line 15: Does this mean the ice sample size will double for simultaneous analysis of both δD and δ13C of CH4?

Page 4479, line 21: Rockmann et al., 2003b presented N2O isotope measurements based on >125mL air sample with ambient N2O concentration. The analytical uncertainty is $\pm$0.1‰ and $\pm$0.2‰ for δ15N and δ18O, respectively. But 200-800 g ice core provides much less amount of N2O. What is the analytical uncertainty for your auto-

AMTD
4, C1610–C1614, 2011

mated system based on similar amount of N2O as that from 200-800 g ice sample?

Page 4479, line 23: How pure is your helium? Page 4480, line 12: How much ice is removed by microtome? 1-2 mm thickness?

Page 4480, line 16-17: What is the final pressure after pumping for 90 min?

Page 4480, line 21: "blank is also carried out" to "blank measurement is also carried out". How pure if your helium?

Page 4480, line 22: Why do you use different procedure for blank run from real ice core sample run? When you run blank measurement, you should mimic the same procedure as real ice core sample, e.g. keep T2 and T3 cold first and then remove cold baths and warm them up. One important issue here is that for a real blank run, a bubble free (BF) ice should be placed in the grating cylinder inside the SS pot. After evacuation, UHP helium is loaded in and the same procedure described in section 3.3 should be followed.

Page 4481, line 8: How to prevent the ice from knocking against the walls?

Page 4481, line 10: Ethanol-liquid nitrogen mixture cannot hold -80°C for a long time. If you want a cold bath to remove water vapor, you can use ethanol-dry ice mixture.

Page 4481, line 13-16: How accurate is the MKS Baratron pressure gauge? Could you clarify how you exactly calculate the amount of air in the ice and the gas mixing ratio?

Page 4483, line 9: how do you determine how much air is extracted from ice?

Page 4483, line 16: Does the mesh size of the Hayesep D affect the trapping efficiency? How do you determine the optimal mesh size of 80/100?

Page 4484, line 4: Is the container sealed when you make BF ice? How do you take BF ice out from the plastic tube? Is the BF ice clear?

Page 4484, line 5: Before the BF ice is grated, do you also first cut with band saw and

AMTD

4, C1610–C1614, 2011

then clean with microtome?

Page 4484, line 6-7: Why is BF ice softer than deep ice core ice? Are you sure about this?

Page 4484, line 9: Why didn't you run BF ice with reference with IRMS instead of GC-FID? To ascertain your system is working for isotope analysis, you should run BF ice with different reference gases in IRMS (the same procedure for real ice core sample, use one piece of BF ice for each run) and obtain the isotopic ratios and find out the accuracy and precision of isotope analysis from these tests (not mixing ratio only). The consistent mixing ratio does not guarantee consistent isotopic ratios. Your design of tests with BF ice is way too simplistic. Section 3.3 should be a very important part in this paper.

Page 4484, line 18: Can you clarify how you run the reproducibility tests with leftover grated ice samples? Is the leftover grated ice the ice left in the SS pot after a real ice core sample run? Do you mean you mix the reference gas with the leftover grated ice? Shouldn't the reproducibility tests be based on BF ice instead of the leftover grated ice? Because you can mimic the process of real ice core run with BF ice and reference gas including the cutting, microtoming, and grating. A BF ice sample should be used only once and then discarded. Multiple BF ice samples are needed to get precisions. Please refer to the above comment.

Page 4484, line 26-27: How do you determine 200-350 g ice is enough for high precision for CH4 isotope analysis? And how do you get the precision? Do you run leftover grated ice with reference gas to get the standard deviations? This "high precision" is an arbitrary word. Have you done some calculation and figured out the required precision for providing useful information on the methane budget in the paleoatmosphere based on existing methane ice core records?

Page 4485, line 3: Similar as the above comment, how do you determine 600 g ice is enough for N2O isotope analysis? And how do you get the precision? Do you run

AMTD

4, C1610–C1614, 2011

leftover grated ice with reference gas to get the standard deviations? Have you done some calculation and figured out the required precision for providing useful information on the N2O budget in the paleoatmosphere based on existing N2O ice core records?

Page 4486, line 7-8: Why do you need a better precision at zone B? What is the precision you really need for the ice core samples? Please refer to the above comment.

Page 4486, line 13: "the reproducibility remains good" is an arbitrary statement. How do you define "good"? How do you know the reproducibility in zone A is large enough to provide useful information on the methane budget in the paleoatmosphere based on existing methane ice core records?

Page 4488, line 5: Can you give the numbers of the differences and the combined error?

Page 4497, Table 2: Why is the ice weight and gas amount rough numbers? Didn't you weight the ice before you grated ice? And you mention you calculate the amount of air in the ice. So the gas amount should be a certain number. It is better to show numbers with errors instead of rough numbers.

Page 4498, Table 3: Can you provide the exact number of measurements for each sample type?

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 4473, 2011.