

Comment on “Record of $\delta^{18}\text{O}$ and ^{17}O -excess in ice from Vostok Antarctica during the last 150,000 years” by Amaelle Landais et al.

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1. Introduction

[1] On the basis that oxygen triple-isotope fractionation resulting from water vapor diffusion in air should differ in magnitude from that associated with equilibrium evaporation and condensation, and with very low sensitivity to temperature, *Angert et al.* [2004] postulated that the regression line of $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$ for meteoric waters may be displaced by very small, positive shifts from the corresponding data points for oceanic waters. In turn, the magnitude of this ‘ ^{17}O -excess’ in meteoric waters should be controlled primarily by the relative humidity of the vapor source region. *Barkan and Luz* [2007] discussed this concept further and defined the magnitude of the offset as:

$$^{17}\text{O-excess} = \ln(1 + \delta^{17}\text{O}) - 0.528 \ln(1 + \delta^{18}\text{O})$$

This is based on an appropriate approximation of the definition proposed by *Miller* [2002] for quantifying the magnitude of a ^{17}O anomaly. Because of the very small magnitude of the ^{17}O -excess, its values are given in per meg (per 10^6). *Landais et al.* [2008] assert that, in a previous study [*Landais et al.*, 2006], it was found that meteoric waters have an excess of ^{17}O with respect to ocean water. It is noted here that this claim has not been validated because VSMOW (an artificially prepared reference material) may not be representative of the oxygen triple-isotope composition of ocean water, at the scale of measurement precision reported by *Landais et al.* [2008].

[2] Samples of surface snow collected in eastern Antarctica along a transect from Terra Nova Bay (74.7°S, 159.7°E) to Dome C (75.1°S, 123.4°E) all exhibit ^{17}O -excess, according to *Landais et al.* [2008], who note that there is no trend in the value of this parameter with respect to temperature, $\delta^{18}\text{O}$, or distance from the coast. Attention is drawn here to additional conclusions that may be drawn from the oxygen triple isotope data of the eastern Antarctic transect samples.

[3] The ^{17}O -excess concept was also applied by *Landais et al.* [2008] to ice core samples (depths of 137 to 2,065 m) from Vostok, Antarctica. Calculated ^{17}O -excess values

appear to show significant shifts between glacial and inter-glacial times, from which it was inferred that normalized relative humidity and/or wind speeds were higher over the (oceanic) vapor source region in glacial times. This interpretation does require, however, that ^{17}O -excess remains independent of temperature even at the very low temperatures experienced at Vostok during glacial periods. Without such validation, palaeoclimate inferences based on ^{17}O -excess measurements of the Vostok core samples may be misleading.

2. Oxygen Isotopic Composition of VSMOW

[4] VSMOW, which was first distributed as an isotopic reference material by the IAEA in 1968, was prepared by R. Weiss and H. Craig at the Scripps Institution of Oceanography, La Jolla, USA. It was obtained by mixing distilled Pacific Ocean water fractions (sampled at latitude 0° and longitude 180°) with small amounts of other water [*Gonfiantini*, 1978; *Gröning*, 2004; *Wise and Watters*, 2005; H. Craig, Message to ‘ISOGEOCHEM’, 1995, available at <http://www.eeb.cornell.edu/isogeochem/>] in order to adjust the $\delta^{18}\text{O}$ and δD composition to that of the SMOW reference [*Craig*, 1961]. SMOW itself was prepared by distillation and mixing of ocean water samples from several locations and was calibrated for $\delta^{18}\text{O}$ and δD against the NBS 1 standard (distilled Potomac River water). The salient point is that VSMOW is not a sample of naturally occurring water. Until a comparison of the oxygen triple isotope composition of VSMOW is made with the corresponding values of ‘real’ ocean waters, at the levels of accuracy and precision reported by *Landais et al.* [2008], the assertion that the concept of ^{17}O -excess has been validated [*Barkan and Luz*, 2007; *Landais et al.*, 2008] is not justified and the magnitudes of the reported ^{17}O -excess values are therefore open to question.

3. Spatial Variations in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of Precipitation Over Eastern Antarctica

[5] The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurements reported by *Landais et al.* [2008] of surface snow collected in eastern Antarctica represent a comprehensive and precise confirmation of the *Li and Meijer* [1998] findings for the oxygen triple-isotope relationship in meteoric waters. From Table S1 of *Landais et al.* [2008], it is evident that slope λ of the $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$ plot is 0.5281 ± 0.0004 (all precision values reported herein refer to the 95% confidence level). A new result is that the corresponding ordinate axis intercept is 47 ± 15 per meg.

[6] Confirmation that VSMOW is indeed slightly offset from the fractionation line formed by natural waters is

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provided by data from *Barkan and Luz* [2005]. Their replicate, high precision measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in VSMOW, GISP and SLAP, reported relative to atmospheric O_2 , give a fractionation line of $\lambda = 0.5279 \pm 0.0001$, as stated by the authors. Further inspection, however, reveals that the inclusion of VSMOW in the $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$ regression is responsible for a small but distinct reduction in the slope, compared to that obtained if this sample is excluded. For the reference line formed from 20 replicate measurements of SLAP and 19 of GISP (one outlier measurement of GISP is excluded), $\lambda = 0.5282 \pm 0.0003$. With the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data reported relative to VSMOW, the attendant ordinate axis intercept is 15 ± 11 per meg. For the line obtained from the GISP data and the 30 reported measurements of VSMOW, $\lambda = 0.5275 \pm 0.0002$. The λ values are independent of the reference material relative to which the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data are reported [Miller, 2002], although the corresponding ordinate axis intercept values clearly are not.

[7] The precision of oxygen triple-isotope measurements on waters reported by *Landais et al.* [2008] is undoubtedly better than has been obtained by any other laboratory hitherto. ^{17}O -excess measurements of the 29 samples from the eastern Antarctic transect were duplicated to within <1 to 13 per meg, with mean value 8 per meg. Furthermore, all the data lie within ± 20 per meg of the $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$ regression line. However, SLAP and GISP data from *Barkan and Luz* [2005], reported relative to VSMOW, lie below that regression line, with respective offsets of -39 ± 30 and -35 ± 16 per meg. The reason for this discrepancy is not clear.

[8] The finding that all surface snow samples collected along the transect from Terra Nova Bay to Dome C fit, to within ± 20 per meg, a single regression line on the oxygen triple-isotope plot, has two important consequences not referred to by *Landais et al.* [2008]. Firstly, *Angert et al.* [2004] predicted that, at temperatures below $\sim -20^\circ\text{C}$, kinetic fractionation associated with ice formation from water vapor would result in a negative ^{17}O -excess, the magnitude of which would increase as a (non-linear) function of the lowering of the temperature at which the precipitation forms. Using the *Jouzel and Merlivat* [1984] model for kinetic fractionation, Figure 5 of *Angert et al.* [2004] predicts a ^{17}O -excess of ~ -50 per meg in precipitation forming at -40°C ; the value increases to ~ -130 per meg at -50°C . Those data are with respect to a meteoric waters reference line with λ assigned to be 0.525; the values will be slightly less negative for $\lambda = 0.528$, and significantly less negative if a low S function is used in the *Jouzel and Merlivat* [1984] model.

[9] In contrast, if substantial descent of the tropopause occurs during the polar winter, perhaps even to the land surface at high elevations on the Antarctic plateau [Roscoe, 2004], surface snow at Dome C might be expected contain a component derived from stratospheric water. Theoretical considerations show that such a component would be characterized by an excess of ^{17}O , relative to tropospheric waters [Lyons, 2001, 2003; Franz and Röckmann, 2005; Zahn et al., 2006], although predictions of the magnitude of the anomaly vary widely. Measurements by *Franz and Röckmann* [2005] of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in water vapor from the lower stratosphere at high southern latitudes showed that

the magnitude of any associated anomaly was ≤ 2 ‰ and that a value of zero could not be excluded.

4. Relationship Between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in Vostok Ice Core Samples

[10] *Landais et al.* [2008] applied the concept of ^{17}O -excess to 359 duplicated measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in Vostok ice core samples to investigate the variation of ^{17}O -excess values over a timescale from $\sim 5,000$ to 150,000 years before present. For the following analysis, one pair of isotope measurements (ice core depth 579 m) from Table S2 of *Landais et al.* [2008] has been excluded, because the duplicate values are very different from each other.

[11] From the 358 other samples for which duplicate ^{17}O -excess measurements were reported, the reproducibility ranges from <1 to 30 per meg, with a mean of 8 per meg. However, regression of the $\ln(1 + \delta^{17}\text{O})$ data versus $\ln(1 + \delta^{18}\text{O})$ gives a slope of 0.5310 ± 0.0003 , with a corresponding ordinate axis intercept value of 201 ± 18 per meg (see Figure S1 of the auxiliary materials).¹ Deviation from this regression line ranges from -26 to $+31$ per meg, although plotting the residuals against ice core depth or age (Figure S2) shows that the scatter is not random. From plotting the ice core ^{17}O -excess values against corresponding $\ln(1 + \delta^{18}\text{O})$ data, which are a proxy for temperature, it is evident that ^{17}O -excess is linked to temperature (Figure S3), whereas this is clearly not the case for the surface snow transect samples. Although the empirical observations are consistent with the ^{17}O -excess model of *Landais et al.* [2008], a temperature-related fractionation effect cannot be excluded. It is noteworthy that the respective $\ln(1 + \delta^{18}\text{O})$ ranges for the ice core and surface snow transect samples are different and barely overlap. The greater the extent of ^{18}O -depletion in the precipitation (i.e., the lower the temperature), the greater the potential for kinetic fractionation, leading to an apparent lowering of ^{17}O -excess values [Angert et al., 2004]. Although the data reported by *Landais et al.* [2008] show no indication of this occurring at Dome C, the possibility of it being of significance at the lower temperatures associated with precipitation at Vostok (notably in glacial times) cannot be dismissed.

5. Conclusions

[12] The high precision oxygen triple isotope measurements of Antarctic surface snow samples and Vostok ice cores reported by *Landais et al.* [2008] are an important contribution to the literature. The authors' claim, however, that their results validate the concept of ^{17}O -excess in meteoric waters relative to ocean water cannot be substantiated until comparable measurements have been conducted on samples of ocean waters. What the authors have demonstrated is that the VSMOW reference material is slightly depleted in ^{17}O relative to the oxygen triple-isotope relationship that describes meteoric waters. The lack of any spatial variation in the very small degree of scatter from the regression line shown in Figure 1 of *Landais et al.* [2008]

¹Auxiliary materials are available in the HTML. doi:10.1029/2008GL034505.

tends to refute the suggestion by *Angert et al.* [2004] that kinetic fractionation during ice formation from the vapor phase, at the temperatures associated with precipitation on the Antarctic transect sampling sites (1287 to 3219 m elevation above sea level), results in the formation of a (negative) ^{17}O anomaly. Furthermore, the same data also show that, if there is a stratospheric water component in surface snow at any of the sites sampled along the transect, any associated (positive) ^{17}O anomaly is so small that it is beyond detection, even at the very high levels of precision reported by *Landais et al.* [2008].

[13] Regardless of whether or not the concept of ^{17}O -excess is validated in the future, the empirical finding that Vostok ice core samples are characterized by a $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$ slope and ordinate axis intercept that are significantly different from the corresponding values associated with present-day meteoric precipitation, regardless of locality, cannot unequivocally be attributed to higher normalized relative humidity and/or wind speeds over the source oceanic regions in glacial times.

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