SOLAR WIND ^{15}N/^{14}N FROM GENESIS – A TALE OF TWO VALUES. R. H. Becker, School of Physics and Astronomy, University of Minnesota, 401 Shepherd Laboratories, Minneapolis, MN 55455, USA. rhbecker@tc.umn.edu

Introduction: Values for solar wind nitrogen of -385‰ [1] and +320‰ [2] have been reported from Genesis samples in the past year. These values represent a factor of two difference in ^{15}N/^{14}N. Clearly, both cannot be valid. Possible explanations for the discrepancy between them are considered here.

Minnesota Samples: Since the result reported by the Nancy group [1] is within error equivalent to the δ^{15}N values observed for the Jupiter atmosphere and other reservoirs expected to be representative of the original solar nebula (Fig. 7 in [1]), and since the Minnesota samples all show low nitrogen yields relative to the expected amount of solar N (maximum yield of 50%, minimum as low as 10%) [2], it would not be surprising if the Minnesota result were the one considered suspect. However, there is no obvious source of a factor of two error in ^{15}N/^{14}N in the Minnesota analytical procedure.

There are currently 4 samples in the Minnesota data set, all within 1σ of an average value of +310‰. Nitrogen is released as N_2 from gold films on sapphire (AuOS) by room temperature amalgamation, which discriminates against N-containing organic contaminants. As a result, solar N makes up about 15-80% of total measured N_2. Over-estimates of blank contributions would shift positive δ^{15}N to higher values while resulting in low observed yields, but would not convert a truly negative δ^{15}N to a positive one, and in any case the effects here are too small. Incomplete recovery of N could result in mass fractionation, but the sample with the largest yield (50%) would require loss of half the ^{14}N atoms with no loss of ^{15}N atoms, not something expected for typical mass fractionation processes.

Masses measured in the analyses are 28, 29, 30, and 14.5. Hydrocarbons are sufficiently separated that they do not contribute to measured 29 and 30. (In some cases, these masses were scanned across during the analyses, to ensure hydrocarbons were not being included.) Contributions of CO would result in high δ^{15}N values, but CO amounts were determined and corrected for by two independent methods, one involving 29/28 and 30/28 mass ratios and the other the ratio of mass 29 to 14.5. If the explanation is another interfering species, it must double the 29 mass (in samples of varying sizes) without appearing in the other masses being measured or altering spectrometer peak shapes.

Samples were analyzed in a system which had at times seen ^{15}N-enriched nitrogen, so one might invoke

memory effects as a possibility. However, flight samples were interspersed with samples of unflown AuOS and with calibration standards, and the only samples to show large positive δ^{15}N values were the flight samples. Finally, excess N_2H^+ due to solar H_2 in the spectrometer might be suggested as a contributor to mass 29 in flight samples but not unflown ones. N_2 is however frozen on a metal surface at -196ºC at one stage in the analytical procedure, which should separate it from most if not all of any solar H_2 released from the AuOS.

Nancy Samples: Samples analyzed by the Nancy group came from gold deposited on the framework of the Concentrator apparatus flown by Genesis, rather than from wafers directly exposed to the solar wind, and were extracted by laser ablation. An advantage of using material from the Concentrator was that the solar N amounts expected were much larger than in the AuOS. As a result of the heating involved in nitrogen extraction, however, even with the enhanced solar N content measured N_2 samples contain only 0.5% to 3.5% solar wind N. The usual process of subtraction of measured blank amounts from individual sample amounts could not be done.

Instead, it was assumed that the samples analyzed could be treated as two component mixtures of solar wind and terrestrial contamination, with solar Ne amounts in individual samples acting as proxies for solar nitrogen in those samples. In essence, the terrestrial end-member of a two-component mixing line is assumed to have a δ^{15}N value determined at a ^{20}Ne/^{14}N ratio of 0, and the solar wind end-member to have a δ^{15}N value determined at the ^{20}Ne/^{14}N ratio of the solar wind, or in solar-normalized terms at a value of 1.

There are two explicit assumptions in this analysis, namely that the solar wind ^{20}Ne and ^{14}N are retained in the gold in their implanted ratio, and that there are in fact only two nitrogen components in the gold. While the Minnesota group is looking into the (admittedly counter-intuitive) possibility that implanted N can be lost from gold at relatively low temperatures as a potential explanation for the low yields from AuOS, partial loss of N from the Concentrator gold would change the numerical value of δ^{15}N derived from the Nancy samples but not the fact that it would still be negative.

Possible 3-component mixing. Total ^{14}N amounts for the areas analyzed by the Nancy group (Table 2 of [1]), normalized for surface area, are 30 to more than 100 times the ^{20}Ne amounts. Since the solar ^{20}Ne/^{14}N

ratio is ~1 (see section 3.3 in [1]), implanted solar ^{14}N is at best a minor contributor to the ^{14}N totals, which should be determined in each individual sample by the thickness of gold ablated and the concentration of terrestrial N within it. A plot of ^{14}N vs. [20]Ne should show no relationship between these two parameters unless the data were precise enough to allow the solar [20]Ne/^{14}N ratio of about 1 to show through. However, what is observed in such a plot (Fig. 1) is an apparent correlation with a slope of ~13 ± 5 and r^2 =0.34. For a 16 point data set, this r^2 value represents a better than 96% probability that a relationship between total ^{14}N and implanted [20]Ne exists in the Nancy gold samples.
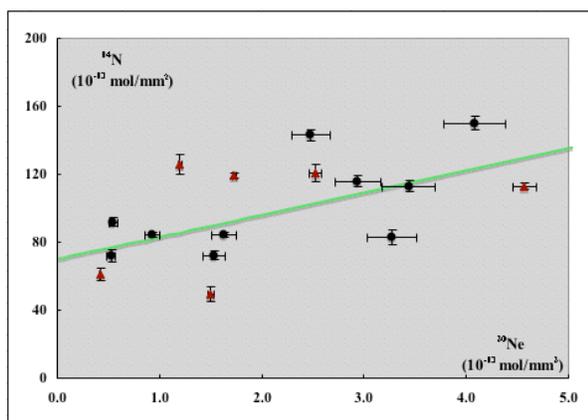

Fig. 1. Total ^{14}N vs. total [20]Ne (both in units of 10^{-13} mol/mm^2) from Genesis Concentrator gold samples (from Table 2 of [1]). Data in red from GCA-1, black from GCA-2. Line shown is from the model discussed below, with slope = 13, intercept = 70x10^{-13} mol/mm^2.

If the correlation between ^{14}N and [20]Ne is indeed real and not a statistical anomaly, the extra 12 or so ^{14}N atoms per [20]Ne atom relative to the solar wind ratio are implicitly not the same component as the inherent nitrogen whose $\delta^{15}N$ value was determined on reference gold [1]. These extra N atoms represent a 3rd nitrogen component whose $\delta^{15}N$ value is essentially unknown. The extrapolation as a two-component mixture to the solar wind [20]Ne/^{14}N value [1] is then inappropriate.

It is possible to model a three component system to attempt to fit the isotopic data in [1], while reflecting the apparent elemental correlation in Fig. 1. Figure 2 shows the result of one such model, assuming one solar ^{14}N and 12 contaminant ^{14}N atoms are added to the terrestrial nitrogen already present in the gold for each [20]Ne atom added, with the total added nitrogen having a $\delta^{15}N$ value of -12‰. Variations within the uncertainty of the slope in Fig. 1 and the uncertainty in the $\delta^{15}N$ of the nitrogen in the gold (+14 ± 9‰ [1]) allow a range of possible values for the total added nitrogen

between about -8 and -20‰, while fitting all or nearly all of the data points in Fig. 2. The curve derived is asymptotic to the $\delta^{15}N$ value chosen in the model for total added nitrogen (-12‰ in this case), and thus does not extrapolate to extremely negative values.
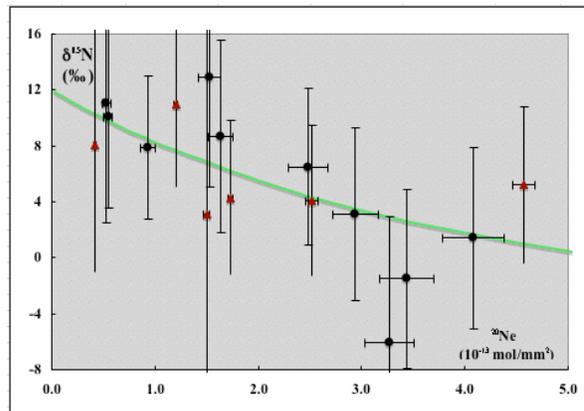

Fig. 2. $\delta^{15}N$ vs. [20]Ne from Genesis Concentrator gold samples (from Table 2 of [1]). Data colors as in Fig. 1. Curve shown assumes 70x10^{-13} mol/mm^2 terrestrial N in the Au with $\delta^{15}N$ of +12‰ and $\delta^{15}N$ for the N added in conjunction with Ne (13:1 atom ratio) of -12‰.

The possibility of a 3rd component of N in the Concentrator gold is not completely without a foundation. Many surfaces within the sample canister on its return were coated with a variable thickness (typically 3-5 nm) layer of polymerized material, presumably produced by photodissociation of organic films that originated somewhere within the canister, which contain on the order of 0.1% to 1% or so N [3]. Continued release of the organic species that produced the films, or remobilization of N from the films by sputtering or some other process, would thus provide a source of N for the extra component. A mechanism for getting it into the Concentrator gold in conjunction with the [20]Ne is not however currently known.

Conclusion: Although the $\delta^{15}N$ value reported in [1] may be preferred as the solar wind value given the context of other $\delta^{15}N$ values representative of the solar nebula, there is a reasonably high probability that an underlying assumption used to derive the value may be flawed. In contrast, there are no obvious flaws in the derivation of the value reported in [2] that would yield such a value if the solar wind were truly that reported in [1]. It is too soon to say with any certainty that the solar wind $\delta^{15}N$ is in the neighborhood of -400‰.

References: [1] Marty B. et al. (2010) *Geochim. Cosmochim. Acta, 74,* 340-355. [2] Pepin R. O. et al. (2009) *LPS XL,* Abstract #2103. [3] Burnett D. S. (2010) personal communication.