Measuring $\delta^{15}N$ of N-poor rocks: In-tube combustion meets continuous flow Andrew J. Schauer, Eva E. Stüeken, Roger Buick Δ *IsoLab, Department of Earth and Space Sciences, University of Washington, Seattle, WA, 98195

-Abstract

We have developed an in-tube combustion / continuous flow hybrid approach for the $\delta^{15}N$ analysis of hundred nanomolar quantities of nitrogen in ancient sedimentary rock samples. Nitrogen concentrations are as low as 5 ppm. This quantity precludes the use of traditional elemental analysis isotope ratio mass spectrometry (EA-IRMS) because flash-combustion of large quantities of rock powder may not quantitatively oxidize all silicate- and organic-bound nitrogen phases. We assembled a vacuum preparation line to prepare these low N samples for in-tube combustion. This approach has the advantage that larger powder aliquots (400 mg or more) can be combusted efficiently. Such in-tube combustion preparations have traditionally been analyzed by dual-inlet IRMS which can be extended down to about 220 nmole through the use of a cryogenic microvolume. To achieve better sensitivity, we developed a front-end continuous flow line with a tube-cracker so samples could be released into a helium stream, collected on a molecular sieve cryogenic trap, purified away from any CO with a molecular sieve GC column and analyzed as a nitrogen pulse, much like traditional EA-IRMS. Our current blank is 11 nmole nitrogen (vacuum line plus continuous flow line). Typical sample reproducibility (1 σ) is 0.5 %. Blank corrected USGS41 δ^{15} N relative to our reference gas is +47.5 (σ = 0.05 ‰, n = 2). Our average δ^{15} N for SGR-1 is +17.8 ‰ (σ = 0.48 ‰, n = 5). This in-tube combustion / continuous flow IRMS approach will allow us to measure δ^{15} N from sedimentary and possibly igneous rock samples with compa-

rable precision and accuracy.





Method Development

Total system blanks with method developmental steps for combustion tubes with reagents only (\bigcirc) and for reagents and sand (\blacklozenge) . Step 1 is one combustion tube, using pre-baked Cu (turned out to be contaminated). tubes with molecular sieve. Step 3 is fresh Cu, Step 2 is fresh Cu and secondary combustion different lengths of evacuation from a few hours to overnight, but made no difference. In step 4 we started pre-combusting the reagents prior to sample addition. Step 5 is the installation of a turbomolecular pump, but only used for a few hours. Step 6 uses the turbo pump overnight (current state, see Sample Preparation Method).



Blanks Current blank level mean ($\pm 1 \sigma$): $1.17 (\pm 0.36) \text{ Vs} = 11.10 (\pm 3.41) \text{ nmol N}$ δ^{15} N = -4.04 (± 2.21) ‰

This histogram shows the distribution of 30-minute tube cracker line blanks (n=85). After installing a sample tube, the cracker line is purged with scrubbed helium for 30 minutes to remove the introduced atmospheric air (see Sample Analysis Method). The sample trap is then frozen for 30 minutes and then thawed and its contents released for N quantity measurement. If the line blank is larger than 5 nmol of N, a leak is assumed, the convoluted tubing is adjusted, and the process is repeated. These blanks are simply used to ensure proper installation of the sample tube and purging of atmospheric air prior to cracking the sample tube. The total system blanks (below) are used to blank correct the sample data.

This histogram shows the distribution of total system blanks (combustion plus tubecracker line) for two treatments in two time periods. Prior to the installation of a turbomolecular vacuum pump on the Sample Preparation line, blanks were tested with combustion reagents only $(\square, n=22)$ and with combustion reagents plus sand as a blank sample placeholder (\Box , n=5). These data are also shown above in Method Development as stages 1-5. Smaller blanks are observed after the installation of a turbomolecular vacuum pump on the Sample Preparation line (stage 6 above in Method Development) for both combustion reagents only $(\square, n=6)$ and combustion reagents plus sand (**■**, n=5).

ncy	0.25 ·	
iduei	0.20 -	
e ire	0.15	
lauv	0.10	
Ke	0.05	

	1.2	
ICY	1.0	
Ianh	0.8	
	0.6	
auve	0.4	
Kel	0.2	

