

Determination of D/H in atmospheric H₂ at nano-molar quantities. T. Rahn and J. Eiler, California Institute of Technology (Geological and Planetary Sciences, mail code 150-21, Pasadena, CA 91125, trahn@gps.caltech.edu and eiler@gps.caltech.edu).

Introduction: Molecular hydrogen is the second most abundant reduced gas in the Earth's atmosphere (after methane) with a mixing ratio of ~500 ppbv. Variations in its isotopic composition have the potential to constrain problems in atmospheric chemistry, pollution, and atmosphere-biosphere-lithosphere interactions, however, these variations are not well characterized largely because of the difficulties of established methods. Previous measurements involve liquification of air using mechanical pumps, oxidation of residual, non-condensable molecular hydrogen to water, reduction of that water over a metal catalyst, and conventional mass spectrometry of the evolved H₂ [1-4]. These methods require thousands of liters of air and involve significant corrections for blanks and fractionations associated with sample processing. Studies using this technique in association with investigations of bomb produced tritium established that atmospheric H₂ is enriched in D relative to Standard Mean Ocean Water (SMOW) by ~60-180 ‰ and that urban and industrial pollution shifts this ratio to values significantly depleted in D relative to SMOW [1-4]. Gerst and Quay [5] refined these methods and found an average δD value for H₂ in unpolluted air from widely dispersed locations of 126 ± 20 ‰ (n=36); they also suggest that δD differs between the northern and southern hemispheres and varies with time in any one location. However, the rate at which samples can be processed by even this refined method precludes highly resolved time-series or spatial coverage in a reasonable time frame.

We describe here a method of cryogenically separating H₂ from air followed by introduction to a mass spectrometer in a continuous flow of helium; this method requires ~10² cc's of air, takes ~1 hour per sample for purification and analysis (i.e., 10-15 samples can be analyzed per day) and corrections for blank and analytical fractionation are negligible. We have applied this method to several suites of natural air samples and laboratory experimental products; data for variably polluted air in the Los Angeles basin will be presented.

Method: Whole air flask samples (~0.5 liters) are exposed to a cold trap (Janis Research Co.) held at 30 K by a two-stage, closed-cycle, compressed He refrigeration unit (CTI-Cryogenics, model 8200). Temperature in the trap is controlled by a digital temperature controller (Neocera Inc., model LTC-11) with a precision and stability of 0.005 K. Nominally all of the N₂, O₂, Ar, and other condensable trace constituents are

frozen in the trap within minutes of exposure, after which an isolation valve is closed, leaving residual H₂, He, Ne and a non-zero but minor equilibrium vapor pressure of N₂ in the ~500 cc initial sample flask. These gases are then quantitatively transferred to a small (~5 cc) volume with an external sample port using a pre-evacuated Toepler pump. The sample is then exposed for 30 minutes to 5A molecular sieve held at liquid nitrogen temperatures in a pre-evacuated ~1.5 cc finger with stopcock. The finger is then removed from the vacuum line and connected to a helium stream feeding the inlet system of a continuous-flow isotope ratio mass spectrometer (Finnigan Delta plus-XL). After purging room air from the sample stem, flow is diverted to the mass spectrometer source through fused silica tubing that has in line a 0.8 mm i.d. pyrex focus loop filled with 5A molecular sieve. With the focus loop immersed in liquid N₂, the sample finger is opened and the sample gases are collected on the focus loop; the liquid N₂ dewar is then replaced with a dry-ice-ethanol slurry and the rapidly de-sorbed H₂ is swept into the mass spectrometer source. Comparison of the sample peak to a concurrently analyzed reference gas yields the δD of sample H₂ with accuracy and precision of ± 3 ‰. Peak area provides a measure of sample size with ± 5 % precision, although frequent calibration with standard gases is required.

Results: We used the above method to study in detail (58 samples) variations in δD and concentration of H₂ in air from the Los Angeles Basin and adjacent San Gabriel Mountains. Urban air varies in H₂ concentration from near ambient (~550 ppb) to strongly enriched (~2000 ppb). Variations in concentration are correlated with δD , extrapolating to an average local source component with δD of ~-260 ‰ and to unpolluted air of ~+60 ‰. Samples collected in the San Gabriel mountains indicate the regional clean air maximum to be on the order of 75 ‰ although there is observable diel variability, some of which is attributable to convective mixing of polluted air but some which we speculate could be related to unexpectedly rapid production and loss processes. Measurements of nighttime air collected at Haleakala Observatory in Hawaii record a clean air value of 54.0 ± 3.4 ‰ (n=4).

[1]°Bainbridge A. E. et al. (1961) *Nature*, 192, 648-649. [2]°Ehhalt D. H. (1966) *Tellus*, XVIII, 249-255. [3]°Gonsior B. et al. (1966) *Tellus*, XVIII, 256-261. [4]°Friedman I. and Scholz T. G. (1974) *JGR*, 79, 785-788. [5]°Gerst S. and Quay P. (2001) *JGR*, 105, 26433-26445.