



Cryogenic separation of oxygen-argon mixture in natural air samples for isotopic and molecular ratios

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The discovery of mass independent isotope fractionation in oxygen during the formation of ozone in the stratosphere has initiated a wide application in isotope geochemistry field. Separation of oxygen-argon mixture has become the foundation of high precision analysis of $\Delta 17O$ and $\delta(O_2/Ar)$ for geochemical applications. Here we present precise and simplified cryogenic separation of argon oxygen mixture from the atmospheric and dissolved air using 30/60 mesh 5A molecular sieve zeolite. A pioneer study of this method was conducted by Thiemens and Meagher in 1984. The column which is made of glass tube contains about 1.1 grams of molecular sieve zeolite and both ends of column was filled with glass wools. The experimental set up was tested for different combination of molecular sieves and slurry temperatures. We found the most efficient condition for the separation was at a column temperature of $-103^\circ C$. For complete transfer of O_2 and Ar mixture usually takes in 15-20 minutes time. The isotopic ratios of oxygen were analyzed using mass spectrometer (Thermo Fischer Delta Plus) relative to reference oxygen-argon mixture at 3V of m/z 32 for both sample and reference side. The signals of m/z 28, 32, and 40 were measured by dynamically to determine oxygen –argon ratio and to check nitrogen contamination. Repeated measurements of atmospheric air yielded a reproducibility (SE n=80) of 0.006, 0.004 and 0.19‰ for $\delta 17O$, $\delta 18O$ and $\delta O_2/Ar$ respectively. The isotopic and molecular fractionation of argon- oxygen mixture during gas adsorption and desorption while using molecular sieve under liquid nitrogen temperature was studied. We have established a linear relationship governing the effect of 13X and 5A molecular sieves on molecular fractionation. And suggested the use of single 1/8" pellet 13X molecular sieve provided a negligible fractionation.