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An On-Line Technique for the Determination of the $\delta^{18}O$ and $\delta^{17}O$ of Gaseous and Dissolved Oxygen

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Few studies have used the stable isotopic composition of O_2 as a tracer of gas transport or biogeochemical processes in environmental research. Here we demonstrate field sampling techniques for gaseous and dissolved O_2 and describe an analytical method for measuring $\delta^{18}O$ and $\delta^{17}O$ values of O_2 in air, soil gas, and water samples using continuous-flow isotope-ratio mass spectrometry (CF-IRMS). A Micromass CF−IRMS was altered to accommodate a sample gas injection port prior to a CO_2 and H_2O trap and GC column. The GC column was a 1-m, 5-Å molecular sieve column held at 35 °C. The resolved sample O_2 was introduced to the IRMS via an open split. $\delta^{18}O$ and $\delta^{17}O$ values were determined by measurement of O_2 isotopes at m/z 34/32 and 33/32 and comparison to a reference pulse of O_2. Repeated injections of atmospheric oxygen yielded a repeatability (±SD) of ±0.17‰ for $\delta^{18}O$ and ±0.5‰ for $\delta^{17}O$. IRMS source linearity was excellent for O_2 over a sample size range of 60−400 μL. The smallest sample for routine $\delta^{18}O$ and $\delta^{17}O$ determinations was ∼80 μL of O_2, with a sample analysis time of 180 s. Preliminary results from a riverine and soil gas study illustrate natural oxygen isotope fractionation processes.

Molecular oxygen is a key component of the biosphere and hydrosphere and is essential to many life forms that live and reproduce in these environments. Numerous biogeochemical processes in soil, rivers, lakes, and groundwater consume oxygen, and human impacts such as effluent discharges on these systems can have detrimental impacts. Despite the importance of gaseous molecular (O_2) or dissolved oxygen (DO) in many environments, there are relatively few studies that use the isotopic composition of oxygen as a tracer of transport or biogeochemical processes in terrestrial and aquatic systems.[1−6] The isotopic composition of molecular O_2 may, in fact, be particularly suitable as a tracer as it does not readily undergo isotopic exchange with water or other gases,[1,7] and so isotopic fractionation should mainly result from diffusive transport, biogeochemical consumption, oxidation−reduction processes, or photosynthesis.[1,3]

Part of the reason for the lack of O_2 isotopic research is that conventional off-line techniques of extracting O_2 from air (20.9% O_2), soil, or water and conversion of O_2 gas to CO_2 for isotopic analysis are time-consuming and potentially fractionating, and considerable sample may be required for low oxygen content gas and dissolved oxygen samples. Previous off-line dual-inlet IRMS-based preparation techniques for DO involve two basic techniques. The first involves extraction and concentration of O_2, Ar, and N_2 in liquid He, with the subsequent analysis of O_2 against reference gas O_2 in the presence of Ar and N_2.[4] The second involves He or CO_2 stripping of O_2, cryogenic removal of CO_2, and quantitative conversion of the remaining O_2 over hot graphite to CO_2 with subsequent analysis of the carbon dioxide for $\delta^{18}O$.[1,6,7]

The advent of continuous-flow isotope-ratio mass spectrometry (CF−IRMS) has reduced the large sample requirements of conventional dual-inlet analysis by orders of magnitudes with only a slight loss in precision over dual-inlet analysis. CF−IRMS is especially suited to chromatographic gas separations and subsequent on-line stable isotopic analysis. In fact, recent work has shown that CF−IRMS is also suitable for measurements of small amounts of mineral oxygen derived from geologic minerals by laser ablation techniques.[8] The goal of this paper is to (1) demonstrate a field sampling protocol for gaseous and dissolved oxygen suitable for isotopic preparation and (2) to outline a rapid, on-line CF−IRMS analytical procedure to measure the $\delta^{18}O$ and $\delta^{17}O$ of O_2 from environmental samples. Preliminary data from field sites are presented to demonstrate the potential utility of oxygen gas isotope analysis as a tracer and show a range of $\delta^{18}O$ values encountered in aquatic and terrestrial environments.

METHODOLOGY

Field Sampling Techniques. Soil gas, air, and DO sample collection and preparation was a modification of the procedures outlined by Kampbell et al.,[9] modified to include soil and atmospheric O_2 samples, and improved to eliminate potential microbial respiration. Sample collection vessels were clean sterilized 250-mL serum bottles (Wheaton 2725), to which 100 μL of saturated HgCl was added as a bactericide. The serum bottles were crimp sealed with butyl blue septa (Bellco Biological

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Glassware, Vineland, NJ) that had been prewashed (0.1 NaOH then distilled H_2O), dried, and sterilized. The sealed serum bottles were evacuated using a rotary vacuum pump to <0.001 atm by inserting a 21-gauge needle coupled to a vacuum manifold. Testing showed that serum bottles sealed and evacuated in this way retained full vacuum for at least 2 months.

For soil O_2 sampling, a three-way valve and needle system similar to that described by Kampbell et al.[9] was connected to field soil gas sampling probes. The three-way valve was initially positioned to enable flushing of the soil probe and sampling needle (21 gauge) with sample gas in order to eliminate atmospheric contamination. While the needle was flushed with the soil gas, it was pushed through the septum into the evacuated sampling bottle. Gas in the sample bottle was permitted to completely fill (~1 min) with soil gas before the needle was withdrawn. Soil samples were measured for O_2 concentration in the field using a Gastech GT series gas meter (0−30 vol % O_2 model). Atmospheric O_2 samples were taken by puncturing the septum with a needle and allowing the serum bottle to fill with air or by collection in glass gastight syringes.

For DO sampling, a 21-gauge disposable sampling needle was used to penetrate the septum while the evacuated sample bottle was submerged under water. The needle was previously purged under water to eliminate residual air bubbles. Water was drawn into the serum bottle by suction and required ~3 min to fill. Due to degassing of the water sample, a small headspace remained in the serum bottle. After filling, the sampling needle was withdrawn and the sample bottle was labeled. DO samples were stored in a cooler in the field and upon returning to the laboratory were stored in a refrigerator. DO concentration and percentage O_2 saturation was measured in the field using a Hydrolab DataSonde system. HgCl-fixed DO samples were analyzed as soon as possible, but testing with local river water showed that samples could be stored for 2 weeks before isotopic analysis with no apparent sample degradation. A new disposable needle was used for each septum puncture, as 21-gauge needles became blunted with repeated use.

For the preparation of collected samples for oxygen isotope analysis, the three-way valve and needle system described above was used to dynamically flush the needle with helium to avoid introduction of atmospheric O_2 contamination. While flushing with He, the needle was partially inserted into the butyl stopper. The three-way valve was then switched to a He-filled gastight syringe attached to one of the three-way ports. The septum was penetrated and the syringe was used to overpressure the sample vessel containing soil gas with 5 mL of 99.99% He. For DO samples, the same 3-way valve and syringe system was used, but instead 5−10 mL of water was displaced with 99.99% He as described in ref 9. The serum bottle containing water samples and He was then shaken using an orbital wrist shaker for 30 min to partition O_2 into the He headspace. Between 500 and 3000 μL of the headspace gas, depending on the O_2 concentration in soil and water samples, was drawn into a 5-mL gastight syringe. The headspace sampling syringe was also equipped with a similar 3-way valve and needle fitting that allowed purging of the needle with He prior to sample withdrawal and again before sample injection into the CF−IRMS system, described below.

IRMS Analytical Procedures. The $\delta^{18}O$ values of molecular oxygen in air, soil gas, and water samples were measured by CF−IRMS using a Micromass Optima-EA instrument. Pure O_2 was used as the analysis gas and the isotopic reference gas. The UHP He carrier gas used was purified of trace O_2 and other contaminants using a Supelco carrier gas scrubber.

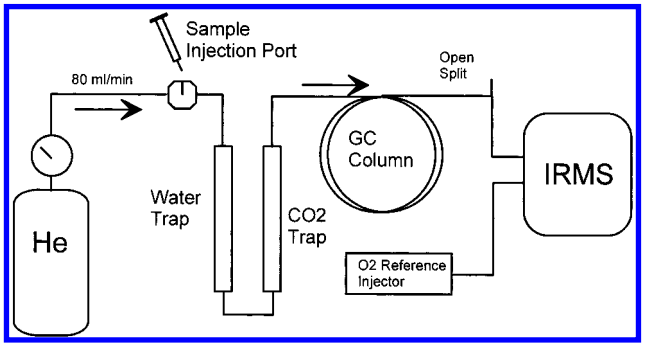

Figure 1. Schematic diagram of the CF−IRMS system used for O_2 stable isotopic measurements. See text for detailed description.

An existing Carlo Erba NA1500 elemental analyzer was modified to accommodate an inexpensive custom in-line sample gas injection port. The injection port was a standard Swagelock $^1/_4$-in. UltraTorr union tee, connected to the existing NA1500 $^1/_{16}$-in. stainless steel sample flow line with Swagelock adapters. The third fitting on the $^1/_4$-in. UltraTorr tee fitting comprised the sample injection port. The nut and ferrule were removed from the third fitting, a Supelco Thermogreen 12.5-mm LB-2 septum was inserted, and the nut and ferrule were replaced and tightened. This sample gas injection port fitting was attached in-line following the NA 1500 combustion columns and prior to a 10 cm long by 1 cm o.d. CO_2 trap (ascarite granules), a 20 cm long by 1 cm o.d. water trap (50/50 mixture Magnesium perchlorate granules and quartz chips), and the EA-GC column (Figure 1). The EA-GC column used to resolve the remaining sample O_2 from N_2 was a Carlo Erba 1-m 5-Å molecular sieve oxygen separation column held at 35 °C. The resolved O_2 sample pulse was then introduced to the mass spectrometer via an open split capillary. For measurement of O_2 gas, the TCD detector on the NA1500 elemental analyzer was turned off to prevent oxidation of the TCD filament. A schematic diagram of the gas introduction and handling system is shown in Figure 1.

The $\delta^{18}O$ and $\delta^{17}O$ values of sample oxygen were calculated by measurement of O_2 isotopes at m/z 34/32 and 33/32 and comparison to a reference pulse of UHP (99.99%) O_2 supplied by Praxair. As previously observed by Young et al.,[8] the relative proportion of ^{17}O to ^{18}O in the compressed UHP reference O_2 did not coincide with that normally found in terrestrial systems.[10] Trace amounts of natural argon (m/z 40) present in the samples could not be resolved chromatographically from O_2 by the GC column. However, Ar was separated from O_2 in the isotope-ratio mass spectrometer and did not have an effect on the oxygen isotope analysis. A typical 32/33/34 sample injection and reference ratio trace is shown in Figure 2. The IRMS source was empirically tuned and tested for maximum linearity for O_2 using a trap current of 400 μA. Instrument source linearity was excellent for O_2 over a sample size range of 85−400 μL (peak area, 55) of O_2; however, below 85 μL of O_2 (peak area, 8) degradation of precision by an increase in variability was evident (Figure 3). The smallest sample

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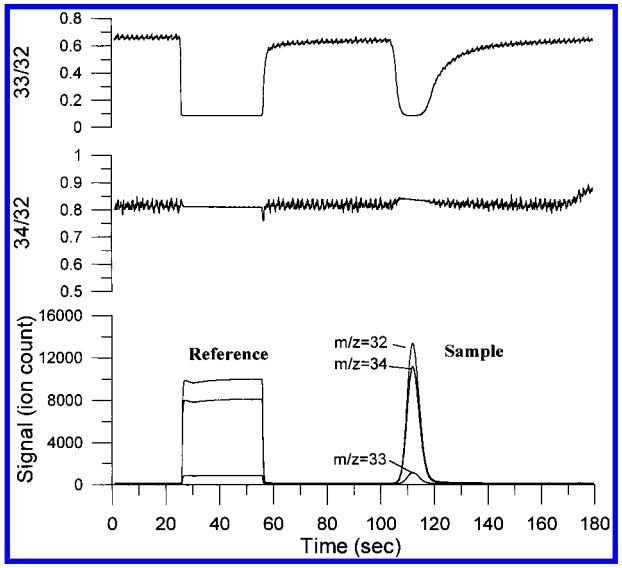

Figure 2. Typical CF−IRMS sample and reference signal chromatogram and ion current ratios (34/32 and 33/32) for O_2. The reference gas used was UHP tank O_2.

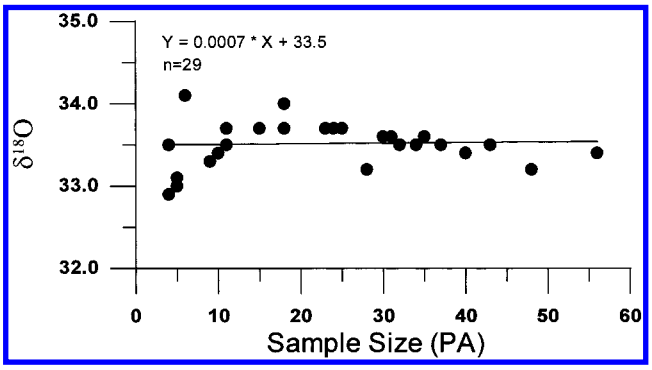

Figure 3. Relationship between measured $\delta^{18}O$ values and sample size (e.g., linearity) over a range (shown as peak area of *m*/*z* 32) of ~60−~400 μL of O_2 gas. A peak area of 8 is equivalent to ~85 μL of O_2.

size for routine $\delta^{18}O$ determinations using these source-tuning parameters was therefore ~3 μmol of O_2, suitable for most environmental applications. The reference O_2 pulse was automatically introduced using the dual-inlet bellows or the Micromass reference gas injection box. The sample was manually injected ~40 s after initiation of the analysis, with the sample peak appearing at ~115 s. Total analysis run time per sample is ~180 s (Figure 2).

RESULTS

Repeated injections of air samples collected from across Saskatchewan and Alberta, Canada, over a 2-month period yielded a repeatability (±SD) of ±0.17‰ for $\delta^{18}O$ and ±0.5‰ for $\delta^{17}O$ (n = 35). Atmospheric oxygen was assumed to have $\delta^{18}O$ and $\delta^{17}O$ values of +23.5 and + 12.0‰, respectively with respect to standard mean ocean water (SMOW) according to ref 7 and was subsequently used to correct sample and reference gas values, assuming mass-dependent fractionation between oxygen isotopes. The contribution of ^{17}O to mass 34 was assumed negligible.

Laboratory and Field Investigations. Here we present some preliminary oxygen isotopic data from some ongoing research to illustrate a wide range of gaseous and dissolved oxygen $\delta^{18}O$ values we found in nature, all measured using the methods described above.

A series of laboratory tests using this technique on air-saturated tap and distilled water confirmed the $\delta^{18}O$ isotopic fractionation of +0.7 ± 0.2‰ between air and water at ~20 °C (n = 8), in accordance with the results of Kroopnick and Craig.[7]

A series of soil O_2 gas samples (n = 50) taken through 30-m-thick mining waste rock showed that combined biochemical consumption and gas transport processes in the subsurface can significantly fractionate oxygen isotopes.[1] Overall, $\delta^{18}O$ values ranged from air values of +23.5‰ (20.9% O_2) a few centimeters below ground surface to as high as +45.5‰ (1.4% O_2) at depth. A

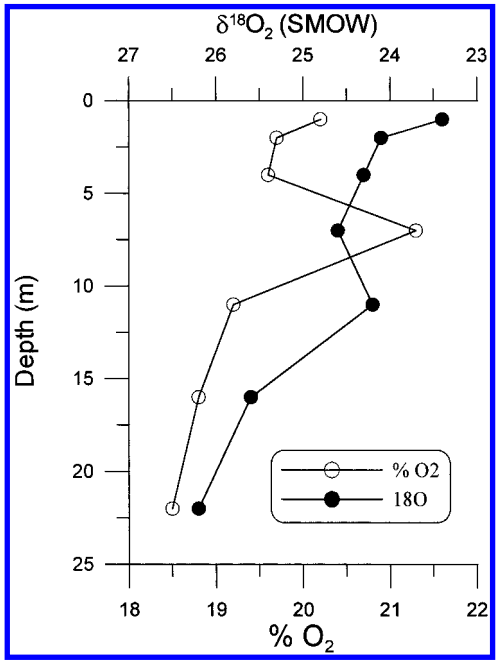

Figure 4. $\delta^{18}O$ and O_2 concentration profile through a 22-m-thick deposit of unsaturated mining waste rock, Key Lake Uranium Mine, Saskatchewan, Canada.

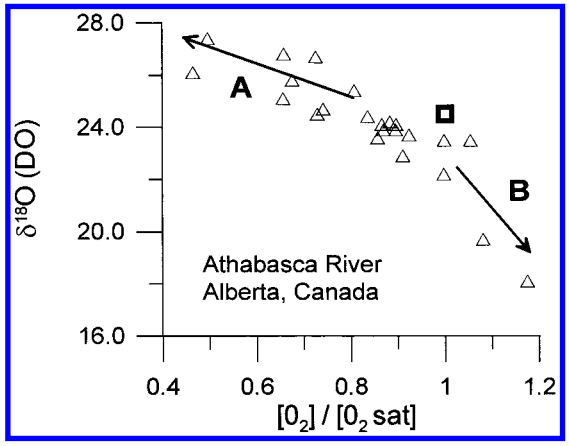

Figure 5. $\delta^{18}O$ of under-ice dissolved oxygen (reported as percent O_2 saturation) along a 1000-km transect of the Athabasca River, Alberta, Canada, in March 1999. Average river water temperature was −0.1 °C. Solid square indicates experimentally determined oxygen isotopic composition of O_2 in air-saturated water at +0.1 °C. Trend line A indicates direction of isotopic fractionation expected for aquatic respiration (DO consumption) and trend line B indicates input of isotopically light photosynthetic oxygen, leading to oxygen-supersaturated conditions.

typical vertical soil O_2 profile is shown in Figure 4, showing the preferential biological consumption of ^{16}O with depth.

Preliminary data on under-ice riverine DO along a 1000-km transect of the boreal Athabasca River in Alberta, Canada, in March 1999 show a trend of systematic ^{18}O enrichment with decreasing DO saturation downstream, indicating ^{16}O is preferentially consumed under the ice by aquatic respiration (trend line A). Conversely, under-ice photosynthesis leading to oxygen supersaturation imparts a strongly ^{18}O depleted signature to dissolved oxygen in the upper reaches of the Athabasca River (trend line B; Figure 5). Photosynthetic O_2 produced under ice in the river should have an isotopic composition similar to water oxygen,[3] which ranged between −19 and −21‰ (SMOW) along the entire Athabasca River. That all results are away from air-saturated $\delta^{18}O$ values suggests DO in the Athabasca River is a complex balance of mixtures of O_2 derived from air and photosynthesis and DO fractionated by under-ice respiration. These results and processes are remarkably similar to the only riverine dissolved oxygen isotope study conducted to date in the Amazon River in South America[2] and indicate that similar biochemical and physical processes may affect O_2 in both rivers, despite their vastly different geographical and climatic setting.

CONCLUSIONS

There are several significant advantages of the CF−IRMS technique over conventional methods for gaseous and dissolved O_2 isotopic measurements. First, the technique does not require cryogenic preconcentration of O_2 or conversion to CO_2 for the analysis, thereby significantly reducing the possibilities of isotopic fractionation during sample preparation, which is particularly problematic with small samples. Second, samples are processed directly and rapidly in contrast to the laborious and costly requirements of off-line methods. Third, measurement of the $\delta^{18}O$ values of oxygen in the atmosphere, soil, and water using O_2 as the analysis gas instead of CO_2 permits measurement of $\delta^{17}O$ values. Finally, the field collection and extraction technique described is simple and inexpensive and does not require the construction and use of costly vacuum manifolds for sample processing.

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