Isotopic Composition of Atmospheric Oxygen During the Geological Past

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Ablation products of iron meteorites recovered from Tertiary and Devonian sediments have preserved the $^{18}O/^{16}O$ ratio of atmospheric oxygen from the respective time periods. While the Tertiary atmosphere was characterized by a rather modern $\delta^{18}O$ value (~23.3‰ vs. SMOW), the δ-value of the Devonian free oxygen reservoir was markedly lower (~17.3‰) which can be explained in terms of a reduced ^{18}O release by contemporary land photosynthesis.

Atmospheric oxygen is not in isotopic equilibrium with oceanic water ("Dole effect"). The most recent measurements by Kroopnick and Craig [1] show an ^{18}O enrichment of atmospheric oxygen of 23.5‰ relative to SMOW (Standard Mean Ocean Water). This enrichment in ^{18}O can be explained as resulting from isotope effects during both continental photosynthesis [2] and global oxygen consumption, notably by respiratory processes [3, 4].

If determined for certain periods of the geological past, the $\delta^{18}O$ value of atmospheric oxygen would probably provide an important parameter reflecting the evolutionary stage of contemporary life. Although not yet completely understood in its quantitative aspects, the "Dole effect" should furnish at least qualitative information, monitoring, in particular, major discontinuities and ecological changes in the terrestrial biosphere after the advent of free oxygen in the environment.

There is reason to believe that the $^{18}O/^{16}O$ ratio of atmospheric oxygen from the geological past is being preserved by the oxide phases (mainly magnetite) of cosmic spherules [5–7], i.e., ablation droplets of iron meteorites oxidized in the atmosphere at high temperatures. Fossil spherules as well as fragments of primary fusion crusts of iron meteorites ("flakes") have been reported from various geological environments [8, 9], the oldest occurrences hitherto known being of Lower Cambrian age [10, 11]. There is strong indication that the oxygen isotope composition of these magnetite particles remained substantially unchanged over the geological time period under consideration.

We were successful in obtaining both spherules and flakes from Tertiary and Devonian sediments in sufficient quantities (0.4 – 1.0 mg) to enable an oxygen isotope analysis to be carried out. For the recovery of the particles standard procedures of sedimentary petrography have been applied [12]. The bulk of the particles has been recovered from limestones which were dissolved in monochloroacetic acid, the insoluble residue being subsequently washed through a set of sieves down to 50 μm mesh size. Since magnetic separation usually failed to yield clean magnetite concentrates, handpicking under the binocular had to be applied in the final stage. With about one magnetic particle $>50\ \mu$m present in one kg of rock, the separation procedure as such was very time-consuming.

The magnetite concentrates obtained were reduced with graphite, the resulting mixture of CO and CO_2 being quantitatively converted to CO_2 by glow discharge between platinum sheets. The $^{18}O/^{16}O$ ratio of this CO_2 was measured relative to a standard with an Atlas M 86 mass spectrometer. Details of the experimental procedure have been described in a previous paper [13]. With a sample size of 0.5 mg of magnetite the overall reproducibility of the measurements is better than ±1‰.

The separation factor α relating the $^{18}O/^{16}O$ ratio of airborne magnetite to the respective ratio of atmospheric oxygen has been determined from the fusion crust of iron meteorites fallen during the last hundred years. With a δ-value for these meteorite crusts of 17.6 ± 0.4‰ [SMOW] [13] and the present "Dole" value of 23.5 ± 0.3‰ [SMOW] [1], this separation factor would be

$$\alpha_{M-O_2} = \frac{(^{18}O/^{16}O)\ \text{airborne magnetite}}{(^{18}O/^{16}O)\ \text{atmospheric oxygen}} = 0.9942 \pm 0.0005\,.$$

The results of our measurements are shown on Table 1.

The isotopic composition of the Tertiary spherules indicates that there is no difference in the "Dole" value between today and some 30 million years ago. This is not unexpected since the global processes of O_2-production and O_2-consumption are unlikely to have changed during this time period. The situation was obviously different during the Devonian. At this time (about 350 million years ago) the oldest continental flora characterized by largely leafless psilophytes had just made its appearance, to be followed by "higher" pteridophytes ("Cyclostigma-Archaeopteris flora") towards the close of the system [14]. The initial stages in the morphogenesis of the leaf (in the widest sense) must have been passed during this period [15]. It would not surprise, therefore, that the contribution of continental photosynthesis towards an ^{18}O enrichment in the atmospheric reservoir was considerably smaller than today where

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Table 1. $\delta^{18}O$ values [‰, SMOW] of fusion crusts (Recent) and fossil ablation products (Tertiary and Devonian) of iron meteorites. The isotopic composition of ancient atmospheric oxygen has been calculated using the separation factor $\alpha_{M-O_2} = 0.9942 \pm 0.0005$ which relates the $^{18}O/^{16}O$ ratio of meteoritic fusion crusts [13] to the respective ratio of contemporary atmospheric oxygen [1].

Sample, age	$\delta^{18}O$ (magnetite)	$\delta^{18}O$ of atmospheric oxygen	Remarks
Recent Fusion crusts of iron meteorites	17.6 ± 0.4	23.5 ± 0.3	δ-value for crusts represents average of 4 falls (Braunau, N'Goureyma, Treysa, Sikhote Alin) [13]. δ-value for atmospheric O_2 from Ref. 1
Tertiary Magnetite spherules (aver. 300 μm)	17.4	23.3	Oligocene of Niederrhein Basin ($26-38 \times 10^6$ yrs ago); value based on 2 aliquots (17.1 and 17.6)
Devonian Magnetite flakes (>50 μm)	11.4	17.3	Nehden Stage of Upper Devonian, Kellerwald Mts. ($345-360 \times 10^6$ yrs ago); value based on 2 aliquots (10.7 and 12.1)

photosynthetic activity of angiosperms – notably deciduous trees – accounts for an estimated 10 permil shift in the δ-value of atmospheric oxygen [2]. With angiosperms (and also gymnosperms) absent from the contemporary flora, a reduction of the "Dole" value by some 6‰ during Upper Devonian times could be explained in terms of a reduced ^{18}O release by land photosynthesis.

It should be noted that fossil magnetite lapilli as products of ancient volcanism [16] might provide an additional source of information on the oxygen isotope composition of former atmospheres. Investigations on lapilli from the latest Precambrian are in progress.

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