

Isotopic Composition of Atmospheric Oxygen During the Geological Past

K. Heinzinger, M. Schidlowski, and C. Junge

Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz

(Z. Naturforsch. **29 a**, 964–965 [1974];

received April 19th, 1974)

Ablation products of iron meteorites recovered from Tertiary and Devonian sediments have preserved the $^{18}\text{O}/^{16}\text{O}$ ratio of atmospheric oxygen from the respective time periods. While the Tertiary atmosphere was characterized by a rather modern $\delta^{18}\text{O}$ value ($\sim 23.3\text{‰}$ vs. SMOW), the δ -value of the Devonian free oxygen reservoir was markedly lower ($\sim 17.3\text{‰}$) 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 Craig¹ 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 photosynthesis² and global oxygen consumption, notably by respiratory processes^{3,4}.

If determined for certain periods of the geological past, the $\delta^{18}\text{O}$ 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 $^{18}\text{O}/^{16}\text{O}$ 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 applied¹². 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 $50\text{ }\mu\text{m}$ 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 $>50\text{ }\mu\text{m}$ 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 $^{18}\text{O}/^{16}\text{O}$ 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 paper¹³. With a sample size of 0.5 mg of magnetite the overall reproducibility of the measurements is better than $\pm 1\text{‰}$.

The separation factor α relating the $^{18}\text{O}/^{16}\text{O}$ 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 $17.6 \pm 0.4\text{‰}$ [SMOW]¹³ and the present "Dole" value of $23.5 \pm 0.3\text{‰}$ [SMOW]¹, this separation factor would be

$$\alpha_{\text{M-O}_2} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{airborne magnetite}}}{(^{18}\text{O}/^{16}\text{O})_{\text{atmospheric oxygen}}} = 0.9942 \pm 0.0005.$$

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 system¹⁴. The initial stages in the morphogenesis of the leaf (in the widest sense) must have been passed during this period¹⁵. 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

Reprint requests to Dr. K. Heinzinger, Max-Planck-Institut für Chemie, D-6500 Mainz, Saarstraße 23.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

Table 1. $\delta^{18}\text{O}$ 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 $\alpha_{\text{M-O}_2} = 0.9942 \pm 0.0005$ which relates the $^{18}\text{O}/^{16}\text{O}$ ratio of meteoritic fusion crusts¹³ to the respective ratio of contemporary atmospheric oxygen¹.

Sample, age	$\delta^{18}\text{O}$ (magnetite)	$\delta^{18}\text{O}$ of atmospheric oxygen	Remarks
<i>Recent</i>			
Fusion crusts of iron meteorites	17.6 ± 0.4	23.5 ± 0.3	δ -value for crusts represents average of 4 falls (Braunau, N'Goureyima, Treysa, Sikhote Alin) ¹³ . δ -value for atmospheric O_2 from Ref. 1
<i>Tertiary</i>			
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)
<i>Devonian</i>			
Magnetite flakes ($>50 \mu\text{m}$)	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 oxygen². 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 volcanism¹⁶ 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.

Our thanks are due to Dr. J. Indans, Geologisches Landesamt Krefeld, for providing the Tertiary sample. Laboratory investigations have benefited from our cooperation with G. Josten, D. Götz, and U. Kuhning. Financial support by the Deutsche Forschungsgemeinschaft (SFB 73) is gratefully acknowledged.

¹ P. M. Kroopnick and H. Craig, *Science* **175**, 54 [1972].

² G. Dongmann, H. Förstel, and K. Wagener, *Nature (New Biology)* **240**, 127 [1972].

³ G. A. Lane and M. Dole, *Science* **123**, 574 [1956].

⁴ P. M. Kroopnick and H. Craig, *Trans. Amer. Geophys. Union* **52**, 255 [1971].

⁵ W. D. Crozier, *J. Geophys. Res.* **71**, 603 [1966].

⁶ J. Rosinski, *J. Atm. Terr. Phys.* **32**, 805 [1970].

⁷ K. P. Florenski, A. V. Ivanov, N. P. Ilyin, M. N. Petrikova, and L. J. Loseva, *Geochem. Intern.* **5**, 967 [1968].

⁸ K. Leuteritz, H. Pietzner, and J. Vahl, *Fortschr. Geol. Rhld. Westf.* **17**, 1 [1969].

⁹ M. Schidlowski and S. Ritzkowski, *Neues Jahrb. Geol. Pal., Mh.* **1972**, 170 [1972].

¹⁰ H. A. Viiding, *Meteoritika* **26**, 132 [1965].

¹¹ K. Utech, *Neues Jahrb. Geol. Pal., Mh.* **1967**, 128 [1967].

¹² G. Müller, *Methoden der Sedimentuntersuchung*, Schweizerbart, Stuttgart 1964, p. 303.

¹³ K. Heinzinger, C. Junge, and M. Schidlowski, *Z. Naturforsch.* **26 a**, 1485 [1971].

¹⁴ W. Gothan and H. Weyland, *Lehrbuch der Paläobotanik*, Akademie-Verlag, Berlin 1954, p. 535.

¹⁵ *Ibid.*, p. 509.

¹⁶ H. Förster and H. Borumandi, *Naturwiss.* **58**, 524 [1971].