# Oxygen Isotope Ratios in the Crust of Iron Meteorites

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(Z. Naturforsch. **26 a**, 1485—1490 [1971]; eingegangen am 3. Juni 1971)

The separation factor, $\alpha_{M\text{-}O} = (^{18}O/^{16}O)$ magnetite/$(^{18}O/^{16}O)$ atmospheric oxygen, between the magnetite crust of iron meteorites and atmospheric oxygen has been determined to be $0.9946 \pm 0.0005$. It is concluded that this fractionation of the oxygen isotopes is the consequence of an equilibrium isotope effect at high temperatures. It can be assumed that this is also valid for cosmic spherules, which are mainly ablation products of iron meteorites. As these spherules are found in sediments of different geological ages, their oxygen isotope ratio can give information on the development of atmospheric oxygen.

The difference of the oxygen isotope ratios between magnetite from the lithosphere and airborne magnetite can be used to distinguish between terrestrial and extraterrestrial material.

## 1. Introduction

The $^{18}O/^{16}O$ ratio of the molecular oxygen of the atmosphere is not in equilibrium with the oxygen isotope ratio of the ocean water. This deviation from equilibrium is called the Dole-effect and has not been understood completely up to now. There is general agreement that a steady state situation exists with respect to the $^{18}O$ abundance in atmospheric oxygen. The oxygen production by photosynthesis alone cannot explain the Dole-effect, for this oxygen has an isotopic composition very nearly the same as the water consumed in this process. The main contribution to the Dole-effect must occur during oxygen consumption. Fractionation factors for various consumption processes have been reported [1], but the main difficulty is the lack of knowledge about the rates through the different production and consumption channels. Although there is still need for further studies for a complete quantitative explanation of the Dole-effect, it is obvious that variations of the Dole-effect through the geological ages may provide useful information on the development of the atmospheric oxygen.

Cosmic spherules, which consist mainly of airborne magnetite, have been preserved in sediments of the last 400 million years. It can be expected that the oxygen isotope ratio of this magnetite is representative for the oxygen isotope ratio of the atmosphere of the geological age, determined by the geological layer, in which the spherules are found. If it is assumed that the $^{18}O/^{16}O$ ratio of the ocean water has not changed during this time, the spherules can be a useful tool to study the Dole-effect.

The cosmic spherules are mainly ablation products of ion meteorites. They are produced during the time between melting and retardation. The melting temperature will be reached at the surface of the meteorite at a height of about 90 km for income velocities of about 30 km/sec. It will be slightly lower at lower velocities, 80 km at 15 km/sec [2]. It can be roughly estimated that the oxidation will start at a height of about 80 km. The height of retardation of iron meteorites is as low as 4.4 km for Sikhote Alin [3]. This means that we have to take into consideration for the oxidation processes the whole atmosphere up to a height of 80 km. It is generally accepted that the atmosphere is well mixed up to a height of 100—120 km. Special investigations by DOLE [4] prove this for the oxygen isotope ratio. He showed by ballon flights that up to a height of 26 km the oxygen isotope ratio is the same as on the surface within the experimental error of $\pm 0.5‰$. From his rocket sampling experiments up to heights of 51 km he again concludes that the $^{18}O$ abundance does not change up to this height. These last results are not convincing. He has to apply quite high corrections which make the results too uncertain to

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[1] G. A. LANE and M. DOLE, Science **123**, 574 [1956]. — P. M. KROOPNICK and H. CRAIG, Trans. Amer. Geophys. Union **52**, 225 [1971].

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rely on. There is other indirect information on this problem. BIERI et al.[5] showed that there is up to heights of 63 km no change of the isotope ratios of noble gases within the limits of error of $\pm 1‰$. This proves that there is also for oxygen no diffusive isotope separation up to this height. A shift of the oxygen isotope ratio at this height would only be possible by molecular exchange processes. But this is highly improbable as the amount of all other oxygen containing molecules in the atmosphere is too small to have an influence on the oxygen isotope ratio. In addition DOLE[4] and VINOGRADOV[6] could show that the $^{18}O$ abundance in the molecular oxygen of the atmosphere is the same over the whole surface of the earth.

The formation of magnetite can be connected with an isotope effect. In order to relate the oxygen isotope ratios of the spherules to the ratios of atmospheric oxygen, a separation factor $\alpha_{M-O}$ defined by

$$\alpha_{M-O} = \frac{(^{18}O/^{16}O)_{\text{magnetite}}}{(^{18}O/^{16}O)_{\text{atmospheric oxygen}}}$$

has to be determined. A possible way to measure $\alpha_{M-O}$ in the laboratory would be to reproduce the kinetics of the meteorite in the air by an air-jet similar to the experiments by BLANCHARD[7]. Considering all aspects of the problem it seemed to be much easier and at least as reliable to determine $\alpha_{M-O}$ by measuring the oxygen isotope ratio in the crust of iron meteorites fallen in the last hundred years. It is reasonable to assume that the magnitude of the Dole-effect did not change during this time period. As it is known in addition from the discussion above that the oxygen isotope ratio is the same in the whole atmosphere at least up to a height of 80 km, a scattering of results for $\alpha_{M-O}$ for different meteorites can only be caused by varying isotope effects in the oxidation processes.

## 2. Experimental Procedure

The main features of the experimental set-up are shown in Fig. 1. The basic parts have already been used successfully by different authors[8,9]. They are combined here to solve the limited aim, the reduction of magnetite, in the easiest way.

The ground magnetite sample is mixed with graphite 1 : 1 in weight and pressed into a cylindric form of 1 mm diameter and a length of 5 mm. The reduction

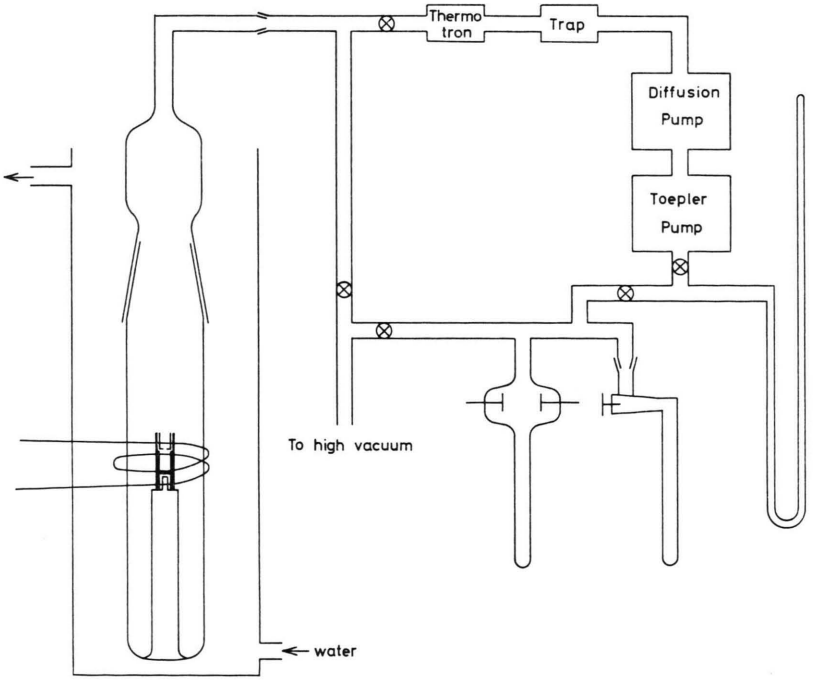


Fig. 1. Experimental arrangement.

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[6] A. P. VINOGRADOV, V. M. KUTYUMI, and I. K. ZAKOROZHOGI, Geokhimiya **3**, 195 [1959].
[7] M. B. BLANCHARD, Meteoritics **5**, 181 [1970].
[8] R. N. CLAYTON and S. EPSTEIN, J. Geol. **66**, 352 [1958].
[9] H. CRAIG and A. LONGINELLI, Science **156**, 56 [1967].

takes place in a graphite crucible, which has a length of 3 cm and 1 cm diameter. The upper part can be taken off for filling. It has a hole through which the formed gases can escape. The crucible is resting on the top of a rod. The rod as well as the tube is made out of quartz. The crucible is heated by an induction furnace, the outside of the quartz tube is cooled by tap water. The sample is outgassed under vacuum at a temperature of 800 °C until the pressure is below $10^{-5}$ mm Hg. The reduction starts at about 900 °C, and is completed at 1350 °C. The produced mixture of CO and $CO_2$ is collected in a calibrated manometer with the help of a diffusion and a Toepler pump. The rate of reduction is controlled by a thermotron. A trap, cooled with a dry ice methanol mixture keeps back impurities. The CO is converted quantitatively into $CO_2$ by a glow discharge between platinum sheets (about 1 $cm^2$). The sheets are kept in position and connected to a tesla inductor through W-wire, melted into the pyrex walls. The long thin end of the conversion tube is cooled by liquid nitrogen. After the conversion is completed, the $CO_2$ is frozen into the sample tube by liquid nitrogen while cooling the glow discharge tube with a dry ice methanol mixture. The oxygen isotope ratio of the sample is then determined relative to a standard in a Atlas M86 mass spectrometer.

## 3. Results

The results are given as $\delta$-values, defined in the usual way by :

$$\delta = \frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{SMOW}}}{(^{18}O/^{16}O)_{\text{SMOW}}} \cdot 10^3 .$$

The standardization was accomplished with the help of a SMOW-water sample from the IAEA in Vienna by equilibration with $CO_2$.

As there was no shortage of material for the experiments, of which the results are reported here, for each run between 5 and 10 mg of magnetite were used. The reproducibility was $\pm 0.1$‰. This accuracy is quite satisfactory, as the uncertainty of the Dole-values ($\delta = 23.0$) is $\pm 0.5$. It could be shown that the same accuracy can easily be achieved for sample sizes down to 2 mg of magnetite, which is of importance for the analysis of the spherule samples.

As test material magnetite from Kiruna (Sweden) iron ore sites was used. The result is

$$\delta_{\text{Kiruna}} = 2.0 .$$

This $\delta$-value is in reasonable agreement with other measurements of terrestrial magnetite from different locations with reported $\delta$-values between 0 and 6 [10].

The $\delta$-values for various iron meteorites are given in Table 1. The two groups, falls and finds, are clearly distinguished by their $\delta$-values.

The "crust" of the finds used for reductions is the result of corrosion and therefore different from the airborne magnetite crust of the falls. The wide scattering of the $\delta$-values of the finds has not been investigated in detail because it is irrelevant with respect to the aim of this paper. With the exception of Tamarugal the $\delta$-values range from 5.3 up to 11.0 and show no correlation with terrestrial age, place of fall or size. (The $\delta$-value of rust from a piece of iron from the backyard of the institute is 11.0.) A possible explanation of the high $\delta$-value of Tamarugal is the dry climate of North Chile, which might result in a higher percentage of $CO_2$ relative to water consumed in the corrosion process.

The meteorite Gundaring can neither be considered a fall nor a find in respect to this investigation. The remarkable corrosion during the seven years between fall and recovery is reflected by the $\delta$-value of 12.9.

The remaining four meteorites fallen in the last hundred years have not been selected for this investigation. They were available at the institute. It is intended to extend the measurements to all available falls. Although a significant change is not expected, the average $\delta$-value reported here has to be considered preliminary.

The mean $\delta$-value of the crust of the four meteorites differs from $\delta = 23.0$, the Dole-value, by 5.4. The oxidation therefore occurs with an isotope effect:

$$\alpha_{M-O} = \frac{(^{18}O/^{16}O)_{\text{meteorite}}}{(^{18}O/^{16}O)_{\text{atmospheric oxygen}}} = 0.9946 \pm 0.0005 .$$

The uncertainty in the Dole-value is about the same as the mean deviation of the meteorite crust values.

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Table 1. Results.

| meteorite | year of fall[12] (terrestrial age [a])[11] | country[12] | weight (found)[12] [kg] | height of[3] retardation [km] | $\delta$ |
|---|---|---|---|---|---|
| *Falls* | | | | | |
| Braunau | 1847 | CSSR | 39 | 14.8 | $+17.2$ |
| N'Goureyma | 1900 | West Africa | 37 | — | $+17.5$ |
| Treysa | 1916 (found 11 months later) | Germany | 63 | 16.0 | $+18.2$ |
| Sikhote Alin | 1947 | Russia | 23000 | 4.4 | $+17.3$ |
| | | | | average | $+17.6 \pm 0.4$ |
| Gundaring | 1930 (found 7 years later) | Australia | 125 | — | $+12.9$ |
| *Finds* | | | | | |
| Canon Diablo | $(< 10^5)$ | USA | crater | | |
| Odessa | $(< 10^5)$ | USA | crater | | |
| Trenton | $(< 10^5)$ | USA | 60 | | |
| Toluca | $(0.6 \cdot 10^5)$ | Mexico | large | | $+5.3 - 11.0$ |
| Carbo | $(1.3 \cdot 10^5)$ | Mexico | 500 | | |
| Bristol | $(2.0 \cdot 10^5)$ | USA | 20 | | |
| Arispe | $(2.4 \cdot 10^5)$ | Mexico | 200 | | |
| Tamarugal | $(27 \cdot 10^5)$ | North Chile | 320 | | $+15.1 - 16.5$ |

## 4. Discussion

The small range of $\delta$-values for the crusts of the four different meteorites allows conclusions on the mechanism causing the isotope effect of 5.4‰. As discussed above the atmosphere is uniform in respect to the oxygen isotope ratio up to about 80 km and it is assumed that the value of the Dole-effect has not changed in the last hundred years. Although the meteorites differ in income velocities, mass, break-up height and height of retardation, the temperature change on the surface will be rather similar at least as far as the oxidation process is concerned. There will be a continuing ablation with temperatures above the melting point of iron until retardation and then a quite fast cooling. The oxidation processes for the four meteorites occurred at different densities of the atmosphere, because of differences in the height of retardation. The small range of the $\delta$-value shows that the density has no influence on the isotope effect. Because of the similarity in temperature a possible explanation would be that an equilibrium and not a kinetic isotope effect is responsible for the oxygen isotope ratio in airborne magnetite. There is support for this conclusion. The separation factor $\alpha_{M-O}$ between magnetite and molecular oxygen can be written as:

$$\ln \alpha_{M-O} = \ln \alpha_{M-W(l)} + \ln \alpha_{W(l)-W(v)} + \ln \alpha_{W(v)-O}$$

where $\alpha_{M-W(l)}$ is the separation factor between magnetite and water (liquid), $\alpha_{W(l)-W(v)}$ between liquid water and water vapor and $\alpha_{W(v)-O}$ between water vapor and molecular oxygen. These three $\alpha$-values are known from experimental and theoretical investigations for certain temperature ranges as shown in Fig. 2. All three isotope effects show crossovers in the temperature range between 400° and 600 °K. From detailed studies of temperature dependances (see e. g. SPINDEL, STERN, and MONSE[16]) it can be expected that $\alpha_{W(l)-W(v)}$ and $\alpha_{W(v)-O}$ show a minimum and a maximum respectively at about 1000 °K. While the calculations of $\alpha_{W(v)-O}$ by UREY[15] could be extended to higher temperatures, a quantitative discussion is still not possible because a theoretical extension of the measurements of $\alpha_{W(l)-W(v)}$ by UVAROV, SOKOLOV, and ZAVORONKOV[13] to higher temperatures seems to be quite complicated[17]. Since the contributions of $\alpha_{W(v)-O}$ and $\alpha_{W(l)-W(v)}$ will only partly cancel, $\ln \alpha_{M-O}$ will become slightly more negativ then $\ln \alpha_{M-W(l)}$ for temperatures above 400 °K. The conclusion drawn from Fig. 2 is that at temperatures between 1000 °K and the melting points of iron and magnetite the separation factor

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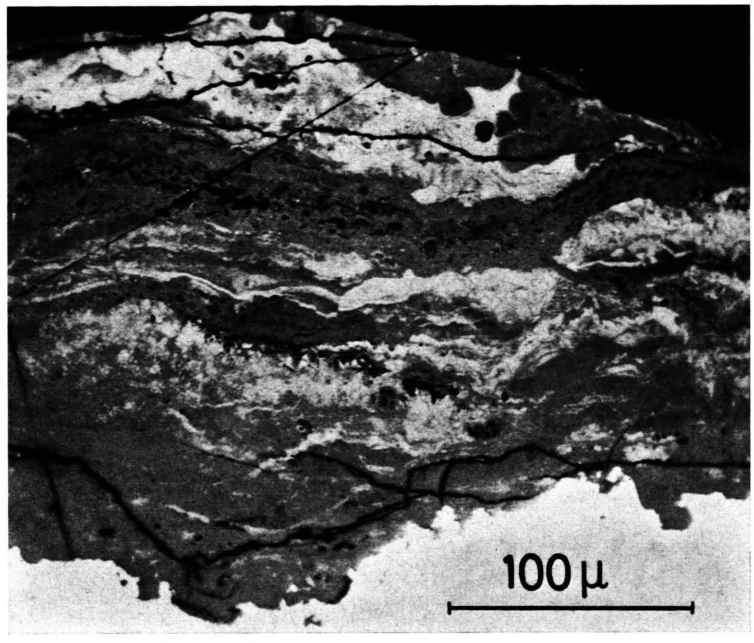


Fig. 3. Typical picture of the weathering crust of an iron meteorite (Trenton) showing colloform aggregates of goethite (grey) with intercalated bands and patches of maghemite (light-grey). The irregular boundary line between the iron core (white) and the crust is characteristic of a corrosion process. — Polished section, oil immersion, 320 ×.

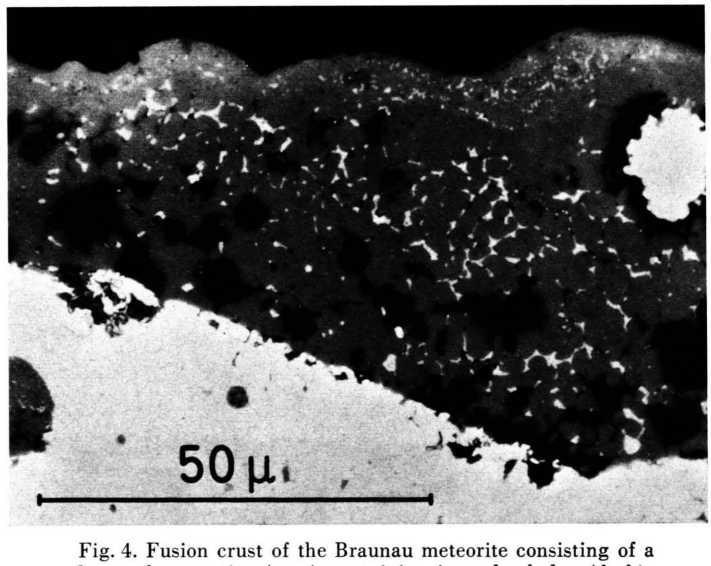


Fig. 4. Fusion crust of the Braunau meteorite consisting of a layer of magnetite (grey) containing irregular holes (dark). The underlying iron (white) shows faint indications of a thermal reconstitution. Note characteristic "pavement" texture of the magnetite with iron and troilite occupying the interstices. — Polished section, oil immersion, 1050 ×.

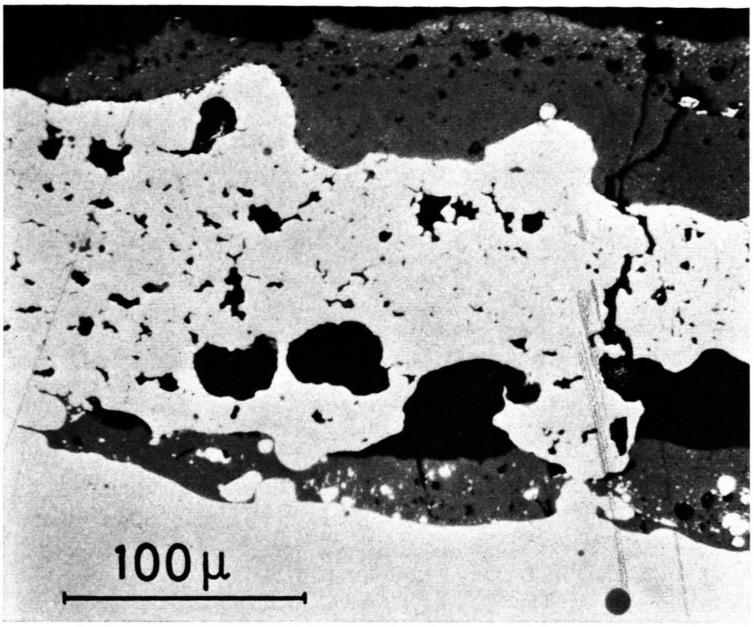


Fig. 5. Double-layer fusion crust (ablation deposit) of the Braunau meteorite. A marginal seam of magnetite (grey, upper part of picture) is followed by a layer of thermally affected iron of a "spongy" appearance. Below the latter a second magnetite seam (enclosing numerous iron blebs) and the iron core of the meteorite. Dark: Holes in the crust. — Polished section, oil immersion, 320 ×.

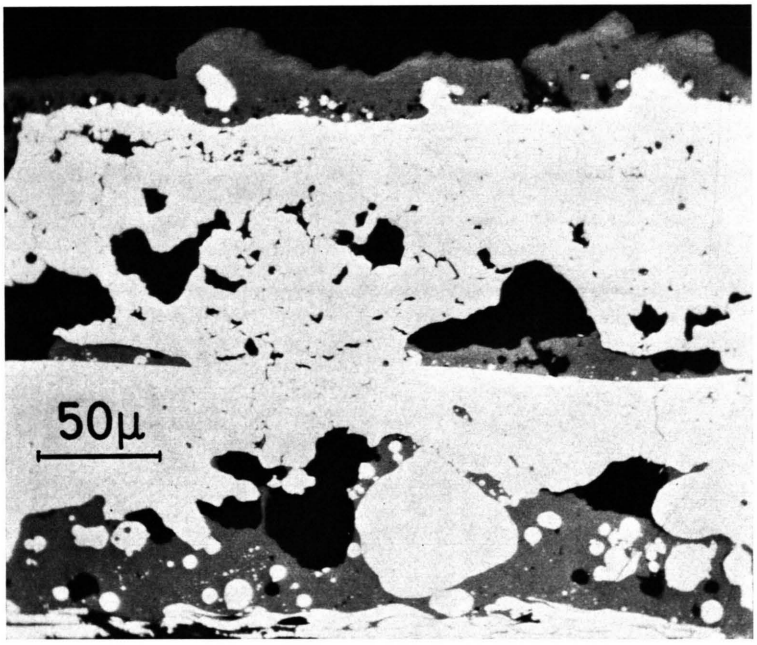


Fig. 6. Ablation deposit forming the crust of the Braunau meteorite. The deposit consists of alternative layers of magnetite (grey) and iron (white), the latter being mostly thermally reconstituted (spongy texture!). Note delicate iron lamellae in the lowermost part of the picture which indicate that the material has flown along the surface of the meteorite. Dark: Holes in the crust. — Polished section, oil immersion, 320 ×.

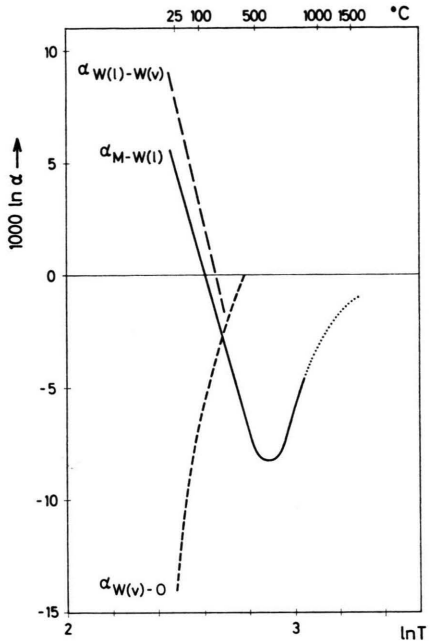


Fig. 2. Temperature dependence of separation factors $\alpha_{A-B} = (^{18}O/^{16}O)_A / (^{18}O/^{16}O)_B$. M = magnetite; W(l) = liquid water; W(v) = water vapor and O = molecular oxygen. —— —— $\alpha_{W(l)-W(v)}$ [13]; ———— $\alpha_{M-W(l)}$ [14] (····· extrapolated); — — — — $\alpha_{W(v)-O}$ [15].

of the oxygen isotopes between magnetite and molecular oxygen in case of isotopic equilibrium will have at least once the value $\ln \alpha_{M-O} = -5.4$ determined in this work. As mentioned above the narrow range of $\delta$-values in Table 1 strongly suggests equilibrium conditions although a lack of knowledge about the exchange rate of oxygen with $F_3O_4$ [18] makes it difficult to estimate how rapidly equilibrium may be reached.

The conclusion that the isotopic composition of meteoritic magnetite represents equilibrium conditions is a very important one because only in this case it can be expected that the separation factor determined for the crust of iron meteorites is also valid for spherules. And only in this case it can be expected to determine the oxygen isotope ratio of atmospheric oxygen from the measured oxygen isotope ratio of the spherules.

An independent check of this conclusion would be possible by comparison of the oxygen isotope ratio in the crust of a larger piece of Sikhote Alin with the oxygen isotope ratio of the spherules found in the area where the meteorite came down.

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If these findings are confirmed, they do not only provide the possibility to study the Dole-effect by spherules but may also prove useful in distinguishing magnetite material formed within the atmosphere from material originating from other sources. Terrestrial magnetite will have $\delta$-values between 0 and 6, extraterrestrial material $\delta$-values near 17.5.

## 5. Mineralogy of the Crust

Some of the oxidation crusts selected for oxygen isotope investigation were, furthermore, subjected to an ore-microscopic inspection. As a result of this work it can be stated that in the case of iron meteorites, a definite distinction between the *fusion crusts* of falls (produced by aerodynamic heating) and the *weathering crusts* of finds is always possible by means of mineragraphic techniques.

Figure 3 * shows a typical weathering or corrosion crust consisting of banded colloform aggregates of goethite [$\alpha$-FeO(OH)] with intercalations of maghemite [cubic $\gamma$-$Fe_2O_3$]. Other corrosion crusts investigated also contained lepidocrocite [$\gamma$-FeO(OH)] and sometimes varying amounts of magnetite (e. g., Cañon Diablo). This magnetite is, however, very seldom the relic of an original fusion crust, but has to be interpreted generally as a low-temperature mineral formed during the weathering process of iron (Ramdohr, pers. communication). By the absence of "pavement" textures typical for the high-temperature magnetite of fusion crusts (cf. Fig. 4), this low-temperature magnetite can be readily identified. It is interesting to note that the $\delta$-values of corrosion crusts containing a considerable fraction of low-temperature magnetite (Cañon Diablo, Table 1) lie within the normal range of the other finds and do not show "mixed" values hinting at the presence of airborne magnetite. As for the exceptional oxygen isotope value yielded by the Tamarugal meteorite (Table 1), there is no indication of this in the mineralogy of the crust which does not differ significantly from that of the other finds.

A peculiar feature of all terrestrial oxidation crusts is the preferential corrosion of $\alpha$-iron (kamacite) as compared with $\gamma$-iron (taenite), schreibersite, and troilite. Relict bodies of the latter phases are often encountered within the corrosion rims.

* Figures 3, 4, 5, and 6 on p. 1488 a, b.

In contrast to the weathering crusts with their marked preponderance of hydrated oxides of ferric iron, primary fusion crusts of iron meteorites consist almost wholly of pure magnetite showing – in particular at high magnification – a significant "pavement" texture (Fig. 4). These magnetite crusts contain numerous holes and are often dissected by various crack systems; sometimes incipient hematite formation has been observed at or near the outer margin. Compared with the broad corrosion seams which often measure 1 mm and more, the magnetite crusts produced by aerodynamic heating are relatively thin. The iron beneath these crusts normally shows the characteristics of a "heat-affected zone" in which the metal has been thermally reconstituted [19].

The fusion crust of the Braunau meteorite depicted in Figs. 5 and 6 represents a typical ablation deposit as described by MARINGER [20]. Here successive layers of magnetite and (mostly heat-affected) iron are piled up one upon another, the magnetite entrapping numerous blebs of iron. On the other hand, the metal contains oxide inclusions, too, often of a spherical type (Fig. 5, lower part of picture). There can be no doubt that this material has been swept away in a molten state by the air flow from the front of the meteorite, freezing again on the less-exposed parts of the surface. Often iron lamellae displaying excellent flow lamination have been observed near the border of the unaltered iron core of the meteorite. Some indications of this lamellar structure (iron parted by minute films of magnetite) may be recognized in the lowermost part of Fig. 6.

*Acknowledgements*

We wish to thank Prof. Dr. F. BEGEMANN, Prof. Dr. H. HINTENBERGER, Dr. W. SCHILLY, Prof. Dr. W. WEISKIRCHNER, Prof. Dr. H. WÄNKE, and Dr. F. WLOTZKA for supply of meteorites and helpful discussions. The able help of G. JOSTEN and Dipl.-Phys. B. MAIWALD during the measurements is gratefully acknowledged.

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