SEARCH FOR POSSIBLE EXTRATERRESTRIAL MATTER AMONG SHINY SMALL IRON OXIDE SPHERULES.

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Introduction: Small magnetic shiny iron oxide spherules have been found in a great variety of geological and glacial (snow and ice) samples (e.g. [1-7] and this study), and the problem of their possible extraterrestrial origin is still a matter of debate.

Some iron oxide spherules have been proven to be of extraterrestrial origin, like the type I cosmic spherules found in the deep sea sediments [8]. However, in some cases a possible loss of platinum-group element (PGE)-rich nuggets [9] prevents an easy assessment of their extraterrestrial origin by identification of a chondritic siderophile element composition. The exact identification of the terrestrial vs. extraterrestrial origin of these spherules could have important implication in the measurement of the flux of extraterrestrial matter onto the Earth, as they are found in very large amounts. One notes that the high abundance of this type of iron oxide spherules with respect to that of the silicate spherules can also prejudge against the extraterrestrial origin of a large proportion of them.

Building on previous work by [10-13] which clearly proved the effect of atmospheric entry heating on type I deep sea cosmic spherules, we performed oxygen isotopic analyses of iron oxide spherules collected in Antarctica, in order to identify possible extraterrestrial spherules and to try to correlate this identification with a chemical and/or textural criterion.

Samples and methods: Thirteen iron oxide spherules were selected from sediments recovered during micrometeorite collections in Antarctica [14, 15], in the blue ice of the Astrolabe Glacier (9 grains) and in the surface snow at Concordia (Dome C) station (4 grains). They range from ~ 25 to ~ 60 µm in size.

External surfaces were observed with a scanning electron microscope before samples were polished. The chemical composition of 12 spherules was measured by electron microprobe with the Cameca SX100 at the University of Vienna.

The oxygen isotopic composition of 13 iron oxide spherules was measured with the Nancy ims1270 ion microprobe at high mass resolution following the procedure described in [16]. The beam diameter was ~ 10 µm, and typical uncertainty for the $\delta^{18}O$ analyses is ~ 1‰. However, due to a large OH interference with the ^{17}O signal, probably due to a poor quality of the vacuum in the sample chamber at the time of the analyses and to the possible presence of OH in the samples, the precision on the $\delta^{17}O$ analyses is only about 2‰. Instrumental mass fractionation was corrected using a terrestrial magnetite standard.

The iron isotopic composition was measured only for the Dome C samples (4 grains) with the Cameca ims1270 ion microprobe at high mass resolution, using a primary negative oxygen ion beam. The beam diameter was ~ 15 µm. We measured the isotopic abundances of ^{54}Fe, ^{56}Fe, ^{57}Fe, and the precision on the delta values are on the order of 1-1.5‰. A correction for the isobaric ^{54}Cr interference with ^{54}Fe was made by measuring the Cr isotopic composition (^{52}Cr, ^{53}Cr) and assuming a "normal" isotopic chromium composition to infer the ^{54}Cr contribution. Instrumental mass fractionation was corrected using a terrestrial magnetite standard.

Texture and mineralogy: External surfaces reveal dendritic structures for most of the samples. After polishing and exposure of the interior of samples, however, a fine dendritic texture is observed in only half of the spherules. Circular- to oblate-shaped cavities were observed in most of the samples. Major elements are iron and oxygen. Minor elements contents determined with EMPA range from below detection (b.d.) to 1.17 wt% for SiO_2 (average 0.50), b.d. to 1.20 wt% for Al_2O_3 (average 0.15), b.d. to 0.12 wt% for Cr_2O_3 (average 0.05), 0.54 to 1.53 wt% for MnO (average 0.85), b.d. to 0.05 wt % for NiO (average 0.03).

Oxygen and iron isotopic composition: The oxygen three isotope diagram for the iron oxide spherules is represented in Figure 1. The $\delta^{18}O$ values range from -11.7‰ to +15.6‰, with $\delta^{17}O$ values from -4.9‰ to +8.3‰. They lie on the terrestrial fractionation (TF) line within analytical uncertainty. Small deviations from the TF line for some analyses are thought to result from a slightly inaccurate correction of the tailing of the OH interference on the ^{17}O signal (see methods).

Our present data split into two "groups", with one spherule showing $\delta^{18}O$ = +15.6‰ and $\delta^{17}O$ = +8.3‰, and 12 spherules exhibiting $\delta^{18}O$ values ranging from -11.7‰ to +6.4‰ and $\delta^{17}O$ from –4.8‰ to +4.1‰. There is no clear correlation between either the texture, the size or the chemical composition of the spherules and their oxygen isotopic composition.

The iron isotopic composition measured for the 4 Dome C samples does not show any fractionation as would be expected from atmospheric entry heating and evaporation and as was found for deep sea type I spherules [11-13].

Origin of the samples: Dendritic textures are known for iron oxides from terrestrial environments as well as for extraterrestrial spherules, thus the textures of the spherules cannot help discriminating for their origin. All the minor elements present are known to easily substitute for iron in terrestrial and extraterrestrial iron oxides (e.g. [17, 18]). Chemistry does not help identifying the origin of the small spherules.

A heavy oxygen isotopic composition correlated with a heavy iron isotopic composition is expected for extraterrestrial samples, as observed by [10-13] for deep sea type-I spherules. This heavy oxygen isotopic composition is observed only for one sample (#98-14-9). A terrestrial origin that could explain such a high $\delta^{18}O$ value is doubtful. The nature and shape of this spherule precludes a volcanic origin, as does its isotopic value. The oxygen isotopic composition of air in Antarctica is at $\delta^{18}O \sim 0‰$, thus a formation of this iron oxide spherule in Antarctica seems unlikely. The most straightforward explanation for such high $\delta^{17,18}O$ values is an extraterrestrial origin for this spherule. Indeed, its heavy isotopic composition is easily explained by Rayleigh distillation due to an evaporation of only ~ 10% of the sample during atmospheric entry heating, considering an atmospheric oxygen isotopic composition of $\delta^{18}O \sim 13‰$, at ~100 km of altitude [12]. This value is lower than that determined by [19] as it could include a fractionation from atmospheric oxygen value due to the oxidation of iron metal into iron oxide. Confirmation of this extraterrestrial origin will be possible by further measuring the iron isotopic composition of this spherule.

A terrestrial origin is preferred for the samples with low $\delta^{18}O$ values. As already said, a volcanic origin is unlikely for these iron oxide spheres. A factory origin (like welding spheres) is also unlikely since homogeneous compositions would be expected for the spheres collected at the same site. Spheres with low $\delta^{18}O$ values may originate from diesel engine fumes which are actually collected at the same time as the sediments or the snow. The isotopic composition we measure is compatible with this last possibility, if we hypothesize the existence of an isotopic fractionation from atmospheric oxygen during the oxidation of the spherules. This assumption can be checked by intentionally collecting engine fumes and checking for the presence, as well as the chemical and isotopic compositions of iron oxide spheres.

We would like however to emphasize on the great care taken to collect and handle the samples in a clean way, at least for this study. On the same note, the fact that such small iron oxide spherules are found in samples collected in very different places and by different methods (e.g. [1-7]) weakens the hypothesis of an anthropomorphic origin. However, their small sizes probably favor their transport over long distances.

To ascertain the terrestrial or extraterrestrial origin of such small iron oxide spherules, the measurement of the iron isotopic composition may be the best criterion, as fractionation by Rayleigh distillation would produce isotopic values that are not observed on Earth, since the terrestrial variation of the iron isotopic composition is usually very small [20].

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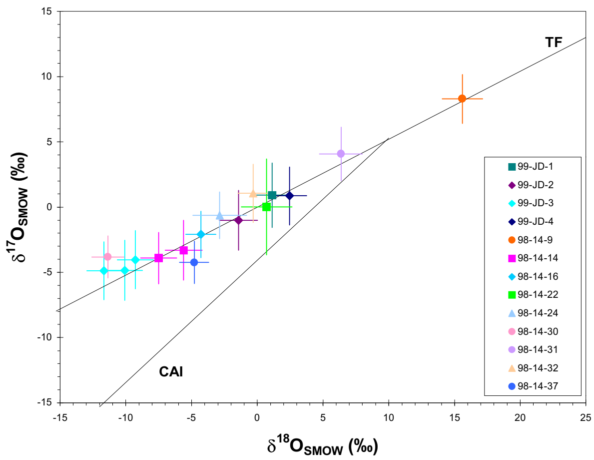

Figure: Oxygen three isotope diagram for the iron oxide spherules. The analyses made by ion microprobe (Cameca ims1270, Nancy). The terrestrial fractionation line (TF), and the line defined by the analyses of Allende CAIs (CAI) are indicated for reference.