

SIMS CHEMICAL AND ISOTOPIC ANALYSIS OF IMPACT FEATURES FROM LDEF EXPERIMENTS AO187-1 AND AO187-2

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SUMMARY

Previous secondary ion mass spectrometry (SIMS) studies of extended impact features from LDEF capture cell experiment AO187-2 showed that it is possible to distinguish natural and man-made particle impacts based on the chemical composition of projectile residues. The same measurement technique has now been applied to specially prepared gold target impacts from experiment AO187-1 in order to identify the origins of projectiles that left deposits too thin to be analyzed by conventional energy-dispersive x-ray (EDX) spectroscopy. The results indicate that SIMS may be the method of choice for the analysis of impact deposits on a variety of sample surfaces. SIMS was also used to determine the isotopic compositions of impact residues from several natural projectiles. Within the precision of the measurements all analyzed residues show isotopically normal compositions.

INTRODUCTION

Among the most noticeable effects of the space environment on spacecraft are impacts produced by the bombardment with small particles from various sources. Several experiments on board the Long Duration Exposure Facility (LDEF) satellite dealt with the analysis of impact craters and projectile debris. There are two basic objectives for such experiments. One is the study of

micrometeoroids in order to determine the flux of interplanetary particles in space and to learn about their nature and origin. The other is the assessment of possible hazards to space flight posed by such impacts. For this purpose it is important to determine (a) the absolute number of impacts and (b) the ratio of natural (micrometeoroids) to man-made (orbital debris) impact particles. Various attempts have been made to estimate this ratio, *e.g.*, by comparing particle fluxes on differently oriented LDEF surfaces. However, a more direct approach to this problem is based on the chemical characterization of particle residues. Since micrometeoroids and orbital debris particles have distinct chemical properties, it is possible to determine the relative contribution of either type to the total particle flux by analyzing the composition of impact debris on LDEF surfaces.

Although all outer surfaces of the LDEF satellite are covered by impact features of various types and sizes, only a few are suited for micro-chemical analysis. What can usually be seen on space exposed materials are only the *effects of hypervelocity impacts* such as craters, dents, and cracks, but not remnants of the impacting particle. Due to the high velocities of impacts (typically several km/sec), practically no projectile material survives the collisions unaltered and only rarely chunks of projectile material can be found within or in the vicinity of impact craters that are large enough for energy dispersive x-ray analysis (EDX). However, frequently there is a thin layer of debris around impact features where some fraction of the particle material re-condensed after being vaporized during impact. This layer of debris is generally too thin to be seen in either optical or scanning electron microscopes (SEM), but secondary ion mass spectrometry (SIMS) can often be used to analyze this material even when its thickness is only a few atomic monolayers.

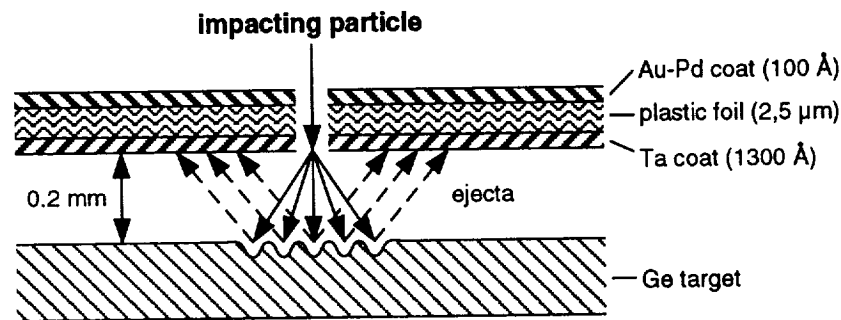


Figure 1. Schematic of capture cell experiment AO187-2.

In principle, impacts on all kinds of surfaces can be analyzed to determine the nature of the projectile material. In practice, however, most accurate analytical results can be achieved from impacts on clean substrates and with relatively large amounts of deposited debris. These conditions are satisfied in the capture cell experiment AO187-2, which was specifically designed for this kind of investigation. The principle of that experiment is shown in Figure 1. A target plate of high-purity germanium is covered with a thin foil separated by a small distance. A high velocity particle of sufficient size penetrates the foil and may be disrupted in the process, spreading out into a debris

shower. This shower impacts the target plate and is further disrupted, melted and vaporized. Some of the projectile material is retained in the impact region on the germanium plate. The projectile material ejected from the impact zone is collected on the backside of the foil and on the surrounding area of the germanium plate. Since only a small amount of material can escape through the impact hole in the cover foil, most impact debris stays in the capture cell and can be analyzed after the cell has been disassembled.

In our previous studies analyses were focused on samples from capture cell experiment AO187-2 (refs. 1, 2). Because most foils did not survive the 5¹/₂ years of exposure in space, we analyzed extended impact features on the germanium plates, produced by projectiles which had arrived while the plastic foils were still in place. First, several different types of extended impact features were identified during optical and SEM analyses. The chemical compositions of the deposits were then determined by SIMS step scans across the impact features. At each step the composition of the surface layer was measured with an O⁻ primary beam of 1-2 nA that was rastered over an area of 40 μm x 40 μm. The width of individual steps was chosen between 35 and 60 μm each. Since each measurement consisted of up to 50 steps, these traverses had a typical length of several hundred μm and a width of about 40 μm. The secondary ion signals of the elements O, Mg, Al, Si, Ca, Ti, Fe, Ni, Ge, and Ta were monitored during the scans. These elements were chosen because they are the most abundant elements in cosmic dust particles and/or in the capture cells themselves. Typical results from one of these scans are shown in Fig. 2. The increase in secondary ion signals near the center of the impact can clearly be correlated with impact deposits.

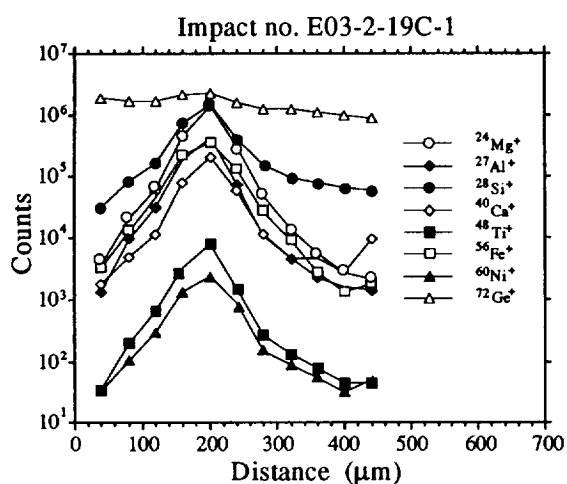


Figure 2. Secondary ion signals of different elements in a traverse across an impact feature on a Ge plate. The center of the impact is located near the 200 μm distance mark.

To date more than 60 extended impacts on germanium plates from experiment AO187-2 have been analyzed by SIMS for the chemical composition of the projectiles. Ion signals associated with material from the impacts could be detected in almost all analyzed impact areas despite serious problems with contamination. It was possible to discern the most likely origins of the projectiles by comparing the compositions of the deposits to those of cosmic dust particles and well known types of man-made debris. Thus we could show that at least 75% of the impacts on the trailing edge of LDEF were caused by micrometeoroids while virtually all analyzed impacts on the leading edge were caused by man-made debris particles (ref. 2).

After having established that SIMS is a useful analytical technique for the determination of the chemical composition of thin layers of impact deposits on the germanium capture cells, we undertook an investigation of its applicability to the analysis of impacts on other LDEF surfaces. We also used SIMS for the measurement of the isotopic compositions of certain impact debris fragments. Such measurements have not yet been possible on thin deposition layers on the germanium plates of the capture cells due to the thinness of the layers, which causes the signal at a given isotopic mass to change rapidly with time.

CHEMICAL ANALYSIS OF GOLD TARGETS FROM EXPERIMENT AO187-1

Next to samples from the capture cell experiment, impacts on witness plates of high-purity Au from experiment AO187-1 appeared particularly interesting because debris analyses on these surfaces had already been performed by conventional SEM-EDX techniques (ref. 3). Unfortunately, in more than 50% of all Au impacts studied no detectable EDX signals could be found, obviously complicating the statistical interpretation of the data. We tried to improve this situation by analyzing these Au samples with the same SIMS analysis technique that we had used earlier on the Ge impacts. For a preliminary investigation Fred Hörz generously provided us with 15 Au samples that had previously been studied by SEM-EDX (ref. 3). Eleven of those impact projectiles had been classified as "natural", one as "man-made" and the origins of the other three were still unknown.

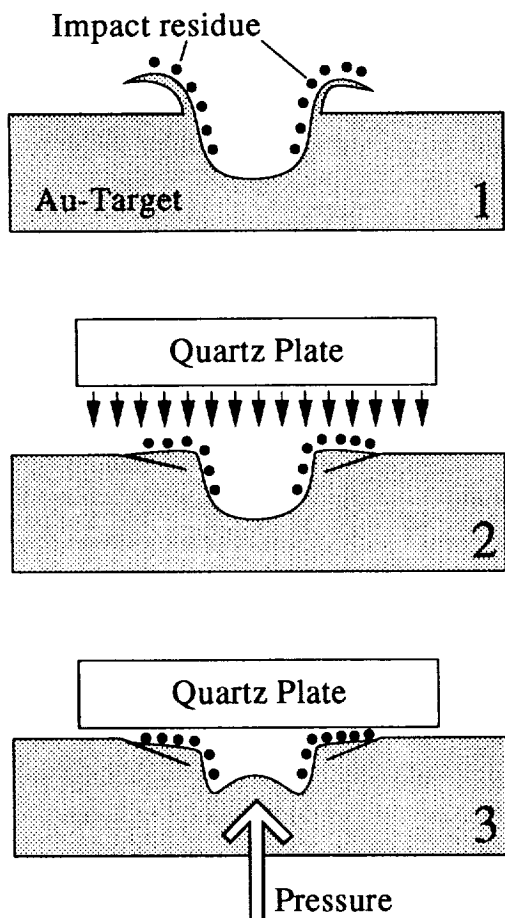


Figure 3: Steps in the sample preparation of Au targets from LDEF.

SIMS measurements of the Au impacts posed some analytical problems. The impact craters in the Au foil are generally relatively deep and are surrounded by a "lip" of Au that rises above the original sample surface. Since SIMS requires a flat sample surface it was necessary to develop a new sample preparation technique for the analysis of these kinds of impact craters (Fig. 3). Preliminary studies had shown that the most interesting areas to analyze in the Au samples are impact residues located inside the crater and on the lip. In order to flatten the lip a quartz plate was pressed onto the sample surface. After the surface was even, a needle was carefully pressed against the underside of the thin Au sheet to push the bottom of the crater up. The entire procedure was monitored under a

stereomicroscope through the quartz disk. That way the surfaces from inside the crater walls became accessible to SIMS measurements on a flat surface. After these preparations, the SIMS scanning technique was applied to the Au witness plates.

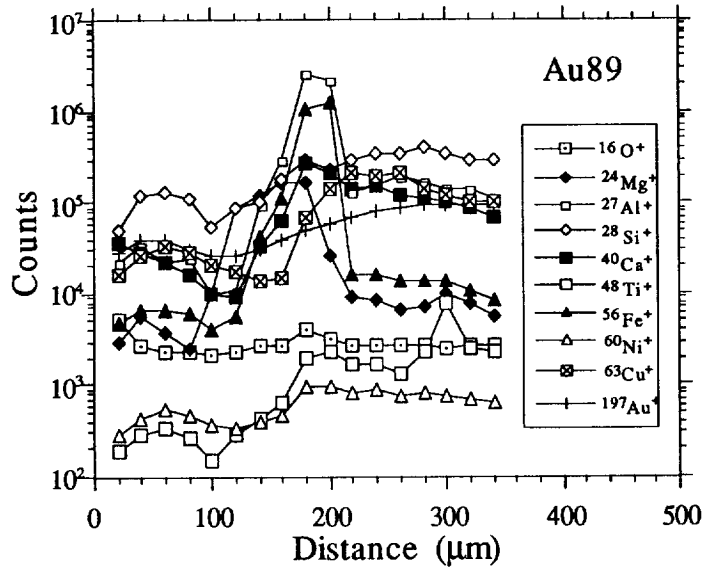


Figure 4: Secondary ion count rates from a SIMS scan across AO187-1 impact "Au89".

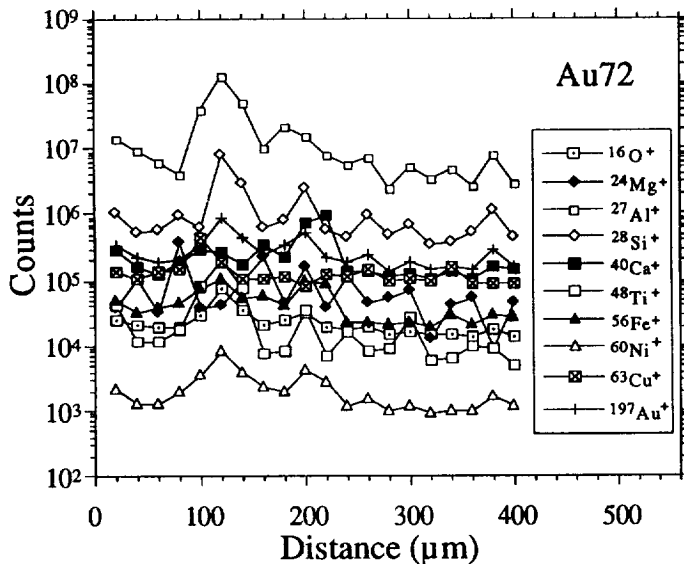


Figure 5: Secondary ion count rates from a SIMS scan across AO187-1 impact "Au72".

The SIMS scans of these "high-purity" Au substrates revealed high levels of contamination that cannot be attributed either to the impacts themselves or to contamination originating from the LDEF spacecraft (see Figs. 4–6). Instead, it appears that the Au target itself contains significant amounts of trace contaminants. In spite of this problem, which led to generally higher background level in most of the measurements, it was indeed possible to determine the origin of the projectiles in several of the Au target impacts. To date SIMS scans have been made across seven flattened craters from experiment AO187-1. Examples of the results are shown in Figures 4–6.

Impact "Au89" (Fig. 4) had originally been classified as "natural" based on the EDX analysis of small chunks of debris that had been found in the crater. The SIMS scan shows a complex pattern with several elements—such as Al, Fe, Ca, and Mg—clearly enriched in the vicinity of the crater whose center is located near the 200 μm distance mark. An elemental signature like this is typical for a natural particle (micrometeoroid). The EDX classification of this impact can therefore be confirmed.

Figure 5 shows data from a scan across impact "Au72" that was classified as "man-made" before. Here too, that classification could be confirmed by the SIMS measurements.

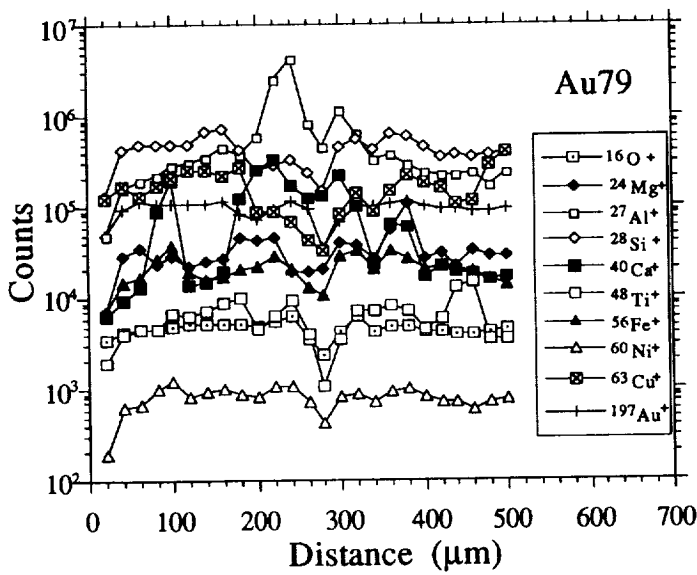


Figure 6: Secondary ion count rates from a SIMS scan across AO187-1 impact "Au79".

The most enriched element at the center of the crater (near the 120 μm mark) is Al, accompanied only by a smaller enrichment of Si. Such a prominent Al-rich composition is highly indicative of an aluminum-oxide particle from rocket exhausts.

The origin of the projectile that caused impact "Au79" was unknown because no debris could be found in the SEM-EDX study that was large enough for a determination of the chemical composition. Here the strength of SIMS as a highly sensitive micro-analytical technique becomes obvious (Fig. 6). Only aluminum is significantly enriched near the position of the crater at the 240 μm distance mark. This impact can unambiguously be classified as "man-made".

The SIMS measurements did not always allow the identification of hitherto unknown projectiles, but the total number of "unknowns" was reduced. It appears that SIMS is the method of choice for the analysis of impact debris on various surfaces, provided the samples can be suitably prepared for SIMS analysis.

In an effort to characterize the chemical composition of some of the "natural" impact projectiles on the Au target plates in more detail, we measured the relative abundances of 24 elements in two chunks of debris from the impacts "Au104" and "Au280". The results of these measurements are shown in Figures 7 and 8, together with values of the meteoritic abundances of C1 chondrites. These C1-abundances are well known from the study of meteorites (ref.4) and there is reason to expect that natural projectiles, *i.e.*, micrometeoroids, have compositions that are similar to those of C1 chondrites (ref. 5). Since only relative abundances can be measured with SIMS, all elements are normalized to Si, whose concentration was arbitrarily set to its C1-abundance.

Since two fragments were analyzed from each impact an upper limit of the precision of the measurement can be estimated from the variation between both measurement runs (inherent heterogeneities in the sample would lead to even bigger variations between the two measurements). The precision appears to be quite good for the majority of the elements. However, the accuracy of the determinations is not as good, possibly due to the inherent problems of quantification in the SIMS technique. Still, the similarity between the compositions of the projectiles and the C1-abundances is striking. Since all elemental abundances are normalized to Si, an overabundance of

this element would lead to seemingly lower abundances of the other elements. Interestingly, in impact "Au280" Ca is depleted while in impact "Au104" Fe, Co, and Ni concentrations are lower than the C1-abundances. Both observations agree with earlier measurements of certain cosmic dust particles that were collected in the stratosphere (ref. 5). Clearly, this determination of the abundances of 24 elements leaves no doubt about the natural origin of the particles that caused these impacts.

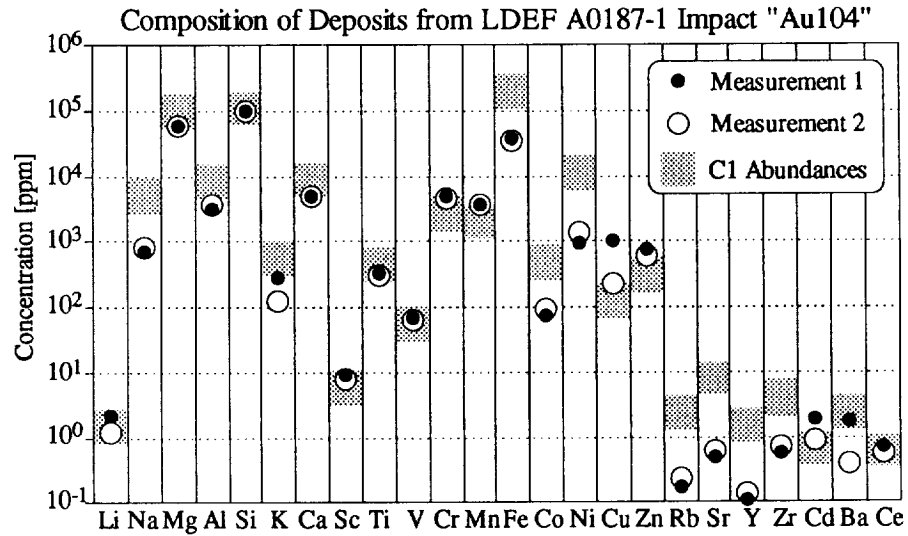


Figure 7: Elemental abundances of two fragments normalized to a chondritic Si value and compared to C1-abundances.

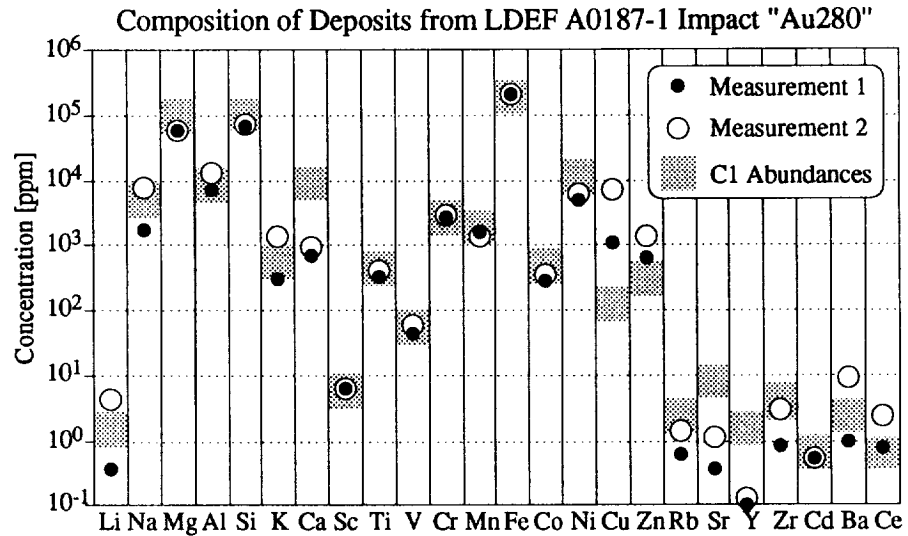


Figure 8: Elemental abundances of two fragments normalized to a chondritic Si value and compared to C1-abundances.

ISOTOPIC MEASUREMENTS IN IMPACTS FROM AO187-1 AND AO187-2

We were also able to perform the first isotopic measurements of impact debris on LDEF. Isotopic analysis of LDEF impacts was one of the original objectives of experiment AO187-2. The isotopic composition of projectile material is of special interest since natural particles (micrometeoroids) are found to have isotopic compositions that sometimes are very different from normal, terrestrial values (refs. 6, 7). If similar anomalies could be found in impact debris that would be one more piece of evidence for an extraterrestrial origin of the projectile material. Moreover, the LDEF impacts represent a different, and possibly isotopically distinct, sampling of the total infall of extraterrestrial material than do micrometeorites recovered in the stratosphere. The results of the isotopic measurements are given here in the δ -notation, which denotes the deviation of the measured isotopic ratio from the normal ratio (*i.e.*, the ratio of a terrestrial standard) in permil (‰). Example: If a measured $^{15}\text{N}/^{14}\text{N}$ ratio were 5% higher than normal, the corresponding δ -value would be $\delta^{15}\text{N} = 50\text{‰}$. Small variations of the isotopic compositions can also be observed in terrestrial material. Therefore all results have to be compared to the maximum observed range of isotopic compositions in terrestrial material and only an object with isotopic compositions clearly outside of that range can unequivocally be classified as extraterrestrial. On the other hand, a normal isotopic composition does not necessarily imply a terrestrial origin.

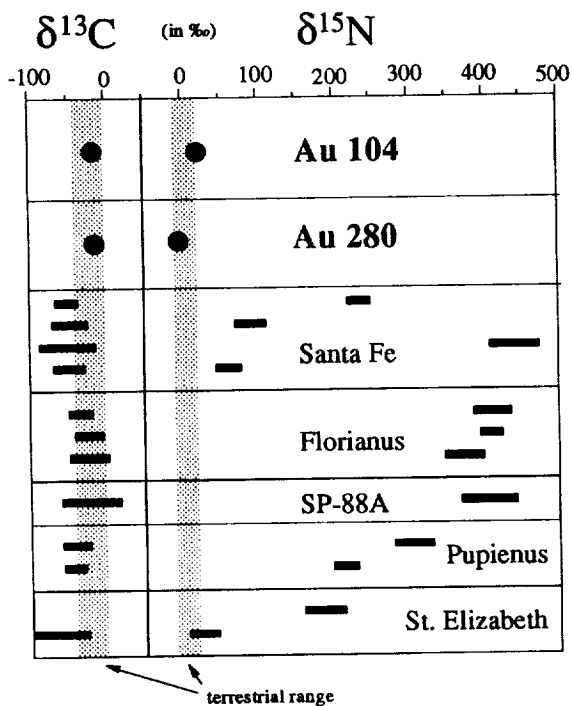


Figure 9: Average C and N isotopic compositions of impact residue from "Au104" and "Au280" and values of IDPs for comparison.

From the Au-foils from LDEF experiment AO187-1 we selected impacts Au104 and Au280 because both have large amounts of apparent projectile residues and both had been classified as "natural" according to the EDX analyses. As shown above, this classification was confirmed by the SIMS measurements of major and trace elements.

In Figure 9 the C and N isotopic compositions of impact residues are compared to the values measured in interplanetary dust particles (IDPs) collected in the stratosphere (ref. 7) and to the range of ratios found in terrestrial samples. Although both projectiles are clearly of natural origin their C and N isotopic compositions are close to normal. This is not very surprising since only one third of all analyzed IDPs show isotopic anomalies in N and none show anomalies in C. The particle "Santa Fe" which is shown for reference has the largest N anomaly among all measured particles of that kind.

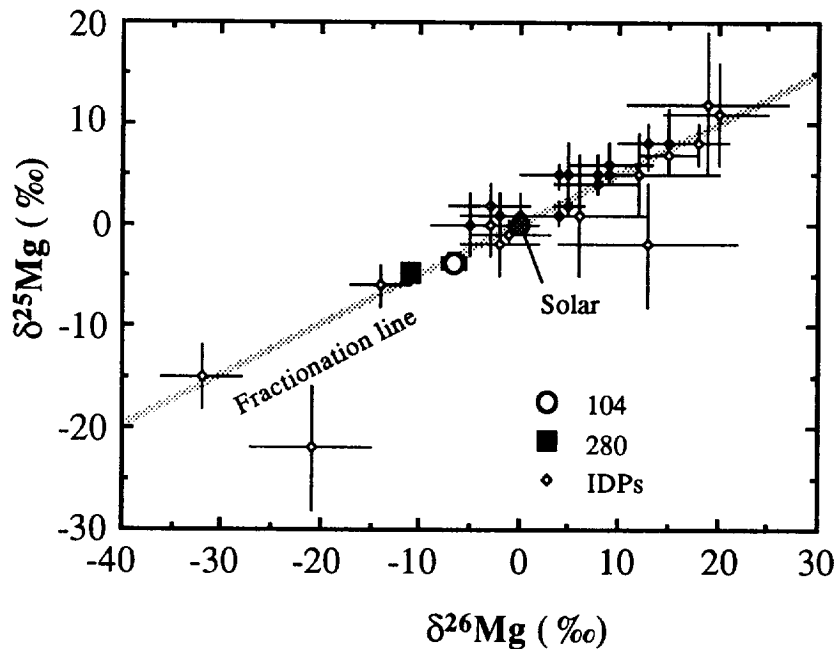


Figure 10: Three-isotope-plot of the Mg isotopic compositions of impact deposits from two AO187-1 impacts and those of Interplanetary Dust Particles (IDPs). The errors shown are 1σ .

Figures 10 and 11 show the Mg and Si isotopic compositions of impact debris from AO187-1 impacts "Au104" and "Au280" in three-isotope-plots. The isotopic compositions of elements with 3 stable isotopes are usually displayed in this way. The $\delta^{25}\text{Mg}$ and the $\delta^{26}\text{Mg}$ values refer to the $^{25}\text{Mg}/^{24}\text{Mg}$ ratio and the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio, respectively ($^{29}\text{Si}/^{28}\text{Si}$ and $^{30}\text{Si}/^{28}\text{Si}$ for silicon). The normal isotopic compositions are denoted "Solar" in the diagrams. Small linear mass-dependent isotopic fractionations –which occur frequently, even in the terrestrial environment– would lead to isotopic compositions that are shifted from the "Solar" composition along a slope- $1/2$ -line in a three-isotope-plot. This line is denoted "Fractionation line" in the diagrams. Any isotopic composition that differs only little from the "Solar" composition and that plots on that line is considered terrestrial while composition that are clearly off that line are indicative of an extraterrestrial origin. As can be seen, the measured impact debris has isotopic compositions of Si and Mg that are essentially terrestrial. The degree of Mg fractionation is also much smaller than the range observed in IDPs collected in the stratosphere, whose compositions are shown for comparison.

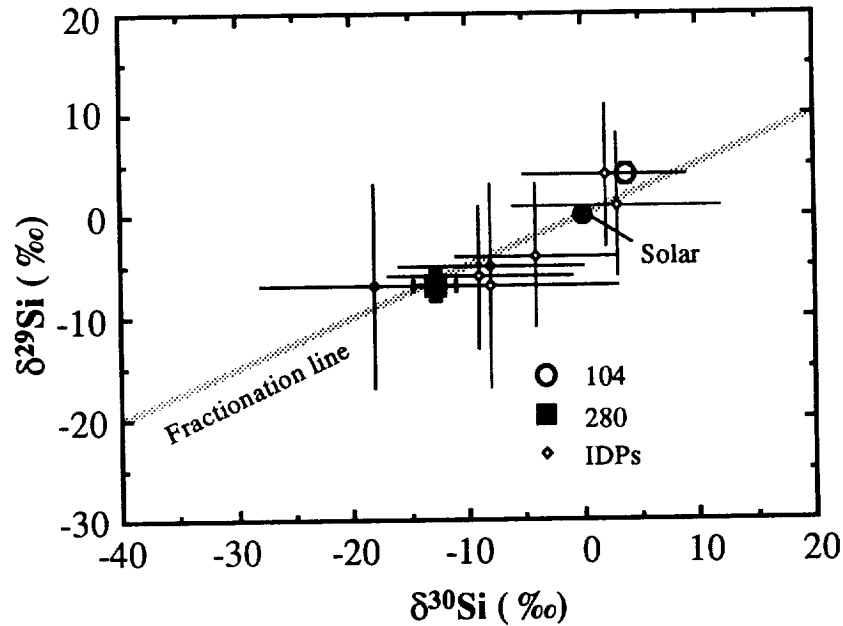


Figure 11: Three-isotope-plot of the Si isotopic compositions of impact deposit and those of Interplanetary Dust Particles (IDPs). The errors shown are 1σ .

Unfortunately, the isotopic analysis of projectile material in extended impacts on germanium plates from experiment AO187-2 is extremely difficult. The reason is the thinness of the impact deposits. An exception is impact C02-2-17C-1, where several solid fragments were found on the rim of the impact feature. The results of the Mg and Si isotopic analysis of these fragments are shown in Figures 12, 13, and Table 1. The isotopic compositions of the fragments plot close to the terrestrial values. Here too, the measured isotopic compositions do not have an identifiably extraterrestrial signature.

	$\delta^{25}\text{Mg}$ (‰)	$\delta^{26}\text{Mg}$ (‰)	$\delta^{29}\text{Si}$ (‰)	$\delta^{30}\text{Si}$ (‰)
Fragment a	30 ± 13	17 ± 9	-2 ± 14	6 ± 21
Fragment b	13 ± 12	13 ± 9	-6 ± 13	14 ± 17
Fragment c	-2 ± 10	-10 ± 10	-14 ± 13	-16 ± 16
Fragment d	-1 ± 7	28 ± 10	9 ± 12	-11 ± 12
Fragment e	10 ± 11	-7 ± 12	-8 ± 14	27 ± 17
Fragment f	-24 ± 8	-6 ± 8	3 ± 10	7 ± 9

Table 1. Results of the Mg and Si isotopic measurements of individual fragments on the rim of impact C02-2-17C-1. The errors are 1σ .

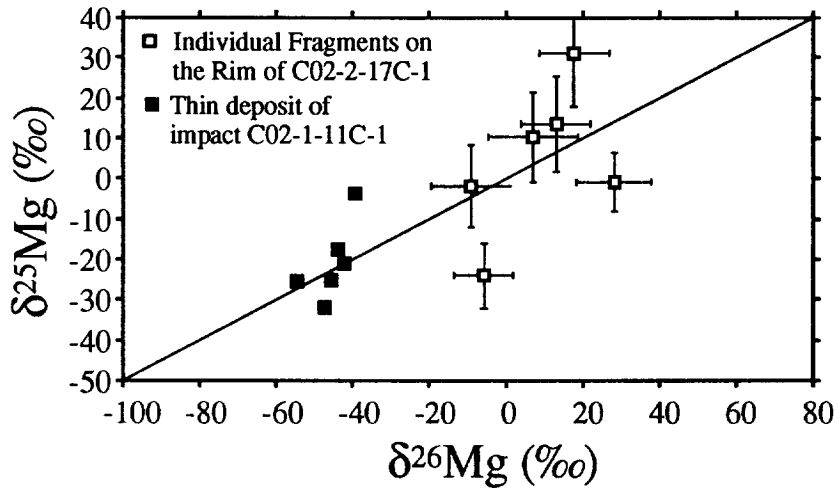


Figure 12. Three-isotope-plot of the results of the Mg isotopic measurements of fragments on the rim of impact C02-2-17C-1 and of deposits in the extended impact C02-1-14C-2. The errors shown are 1σ and the diagonal line is the Terrestrial Fractionation Line.

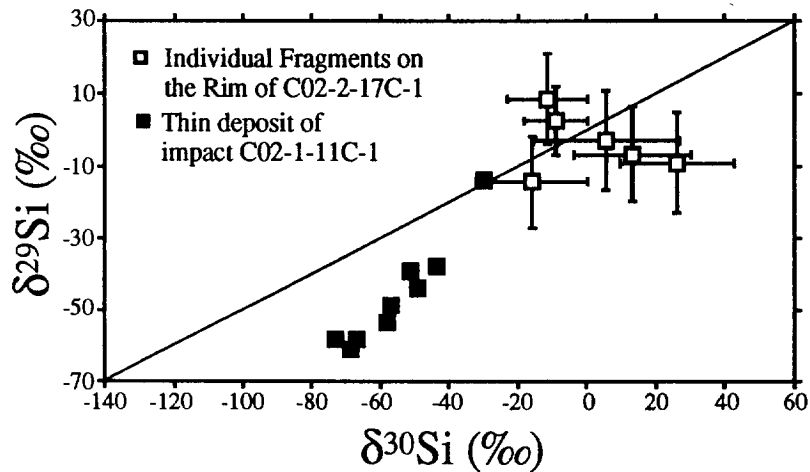


Figure 13. Three-isotope-plot of the results of the Si isotopic measurements of fragments on the rim of impact C02-2-17C-1 and of deposits in the extended impact C02-1-14C-2. The errors shown are 1σ and the diagonal line is the Terrestrial Fractionation Line.

Impact C02-2-17C-1 was the only case of an extended impact from experiment AO187-2 in which we found projectile fragments that had apparently survived the impact. In contrast to the isotopic analyses of these fragments are the analyses of a thin debris layer from impact C02-1-14C-2 (Figures 12 and 13). Here both the Mg and Si isotopic data show large negative (shifts to the lower left, *i.e.* toward more negative δ -values) mass fractionation effects; in addition, the Si data show substantial deviations from the terrestrial mass fractionation line.

A more detailed analysis of these data revealed that these large fractionations and the deviations from the fractionation line are not genuine isotopic effects in the measured material but are artifacts resulting from the small thickness of the impact deposits. Because the layer of deposited projectile is sputtered away during SIMS analysis, the secondary ion signal from a thin layer is not constant but decreases rapidly as a function of time. Since the isotopes of Mg and Si are measured in sequence, the non-linear nature of this decrease can produce the effects shown by the C02-1-14C-2 data. High throughput (large magnet), multiple collector SIMS instruments capable of accurate isotopic measurements are currently being developed for the study of extraterrestrial materials (K. McKeegan, UCLA, private communication). Such instruments may have the required sensitivity and measurement capabilities to permit isotopic measurements of very thin impact deposits.

The extended impacts of LDEF experiment AO187-2 that have already been partially studied by existing SIMS techniques *represent an extremely important scientific resource for future work*. In particular, some of these impacts may make it possible to measure the isotopic composition of cometary material. Dust particles from long-period comets encounter the earth with very high velocities and are thus preferentially destroyed relative to slower, asteroidal particles during atmospheric entry (ref. 8). Cometary particles may thus be grossly under-represented in the stratospheric micrometeoroid collections. In contrast, high velocity particles produce extended impacts with high efficiency and should thus be well represented in the existing collection of capture cell impacts.

Because of their potential scientific importance, continued care should be taken to store the relevant surfaces of experiment AO187-2 under clean conditions so they may be properly analyzed by future, improved analytical instruments.

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