

# Accretion Rates of Meteorites and Cosmic Dust in the Early Ordovician

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Abundant fossil meteorites in marine, condensed Lower Ordovician limestones from Kinnekulle, Sweden, indicate that accretion rates of meteorites were one to two orders of magnitude higher during an interval of the Early Ordovician than at present. Osmium isotope and iridium analyses of whole-rock limestone indicate a coeval enhancement of one order of magnitude in the influx rate of cosmic dust. Enhanced accretion of cosmic matter may be related to the disruption of the L chondrite parent body around 500 million years ago.

Thirteen fossil meteorites were recently found in condensed Lower Ordovician [~480 million years ago (Ma)] marine Orthoceratite Limestone from the Thorsberg quarry in southern Sweden (1) (Fig. 1). A conservative estimate, assuming only four different falls and extremely low sedimentation rates and using the known volume of quarried limestone, indicated one to two orders of magnitude higher meteorite influx rates in the Early Ordovician than today. The extraordinary meteorite density is accompanied by nondetrital Ir enrichments in the Orthoceratite Limestone (1). However, the Ir source could not be identified, and hydrogenous as well as extraterrestrial Ir enrichment are viable explanations. Osmium is unique among the noble metals because the decay of  $^{187}\text{Re}$  to  $^{187}\text{Os}$  produces variations in the isotopic composition of Os that can be used to distinguish detrital and hydrogenous Os sources from extraterrestrial and mantle-derived sources. Here, we present Os isotope data for the Orthoceratite Limestone to determine the origin of the excess noble metals (2). We also report four additional fossil meteorite findings, trace element data for seven fossil meteorites, Os isotope data for one of the meteorites, and Sr isotope data for biogenic calcite (3).

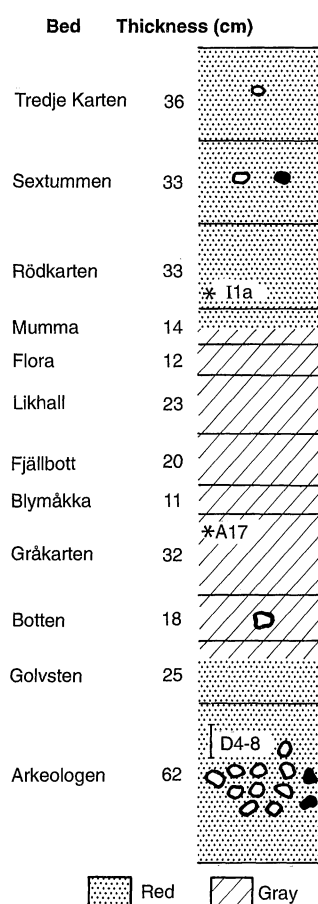
The diagenetically altered fossil meteorites have been identified by their high Ir, Au, and Cr concentrations (Table 1), their generally chondritic Au/Ir ratios, the occurrence of chromite grains with meteoritic

composition, and the presence of chondrule-like structures (4, 5). An age-corrected  $^{187}\text{Os}/^{186}\text{Os}$  ratio of 1.058 and Os/Ir ratio of ~1 in the center of the Österplana Ark 009 meteorite [identical to Österplana 9 in (1)] are comparable to present-day chondritic meteorites (Tables 1 and 2). The findings of four additional meteorites after July 1996 support the meteorite accumulation rates estimated for the Early Ordovician in (1). The most important new find is a large meteorite in the Sextummen bed in the upper red interval (Fig. 1 and Table 1). This meteorite was recovered after quarrying <600 m<sup>2</sup> of the Sextummen bed in addition to the ~1700 m<sup>2</sup> that yielded the first large meteorite before July 1996 (1) (Table 1). Two additional meteorites (diameter in cross sections = 5 by 4.5 by 3.5 cm and 5 by 4 by 3.5 cm) were found in the meteorite-rich Arkeologen bed, increasing the number of meteorites recovered from this bed to 12. With these findings, the sea-floor density of meteorites is calculated at 1 per 150 m<sup>2</sup> in the Arkeologen bed and 1 per <1150 m<sup>2</sup> in the Sextummen bed. These meteorite densities are high relative to those in recent meteorite-strewn fields (6). However, we do not know the exact vertical position of the different meteorites in the two beds, and the meteorites may represent more than two fall events. A fourth meteorite (diameter ~3 cm) was discovered in the red limestone floor of a public building in southern Sweden. The floor was quarried in the Thorsberg quarry in 1994. It is uncertain from which bed this meteorite derives.

Osmium isotope analyses were performed on three whole-rock samples from the Arkeologen, Gråkartan, and Rödkartan beds, representing the lower red, middle gray, and upper red intervals in the Thorsberg quarry, respectively (Table 2 and Fig. 1). The samples were collected in the abandoned Hälleklis quarry, 4 km away from the Thorsberg quarry. The stratigraphy and li-

thology over the meteorite-yielding interval is the same in the two quarries. Esser and Turekian (7) demonstrated that Os in marine sediments can be considered a three-component mixture of detrital, hydrogenous, and meteoritic Os. Riverine particulate matter and loess, representing eroded upper continental crust, are characterized by radiogenic  $^{187}\text{Os}/^{186}\text{Os}$  ratios of ~10.5.

The Os isotopic composition of seawater (hydrogenous component) varies as a function of the balance among dissolved Os inputs from riverine, sea floor hydrothermal, and extraterrestrial sources. During most of the Cenozoic, seawater Os isotopic ratios varied between 3.5 and 8.6 (8). Only at the Cretaceous-Tertiary boundary were ratios as low as ~2. Information on Mesozoic and Paleozoic seawater, although missing, is important for interpreting marine



**Fig. 1.** Quarried interval at Kinnekulle with positions of fossil meteorites and samples studied for Os isotopic composition (Table 2). Solid meteorite symbols represent additional finds after July 1996 (1). A fourth new meteorite from the Thorsberg quarry could not be assigned to any particular bed. Traditional quarry workers' names for different beds are given. Thicknesses of beds vary somewhat along the outcrop. The entire quarried interval corresponds to ~1.75 My; however, only an interval corresponding to ~1.17 My is being used for the production of sawed slabs (1).

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**Table 1.** INAA results for fossil meteorites [data for Österplana Ark 001 and 009 from (1); other results, (3)]. Names of fossil meteorites (locality + abbreviated name of bed of origin) are preliminary. The relative analytical accuracies are estimated at 5 to 15% (n.a., not analyzed). Parts of some of the meteorites are missing.

| Meteorite                     | Size (cm)     | Ir (ng/g) | Au (ng/g) | Cr (μg/g) | Fe (mg/g) | Ni (μg/g) | Co (μg/g) | Ca (mg/g) | Ba (mg/g) |
|-------------------------------|---------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Österplana Ark 001            | 5 × 4 × >1.5  | 147       | n.a.      | 5540      | 2.47      | 335       | 14.2      | n.a.      | n.a.      |
| Österplana Ark 007            | 9 × 7.5 × 6   | 630       | 264       | 4710      | 2.54      | 372       | 18.3      | 18.8      | 25.3      |
| Österplana Ark 009            | 4 × >3 × >1.5 | 800       | 550       | 4400      | 0.871     | 560       | 12.1      | 36.4      | 9.98      |
| Österplana Ark 011            | 5 × 4.5 × 3.5 | 200       | <2        | 4350      | 6.43      | 366       | 26.5      | 30.5      | 4.65      |
| Österplana Bot 001            | 9 × 5.5 × 3   | 880       | 390       | 7230      | 3.12      | 969       | 2100      | 9.3       | 29.0      |
| Österplana Sex 002 (sample 1) | 6.5 × >5 × 5  | 180       | 102       | 3040      | 4.77      | 235       | 16.4      | 31.7      | 0.01      |
| Österplana Sex 002 (sample 2) | 6.5 × >5 × 5  | 130       | 8         | 3230      | 6.25      | 196       | 19.6      | 29.3      | 0.01      |
| Österplana Sex 001 (rim only) | 8 × 7 × 6     | 32        | 15        | 679       | 2.41      | <50       | 8.1       | 38.2      | 0.18      |

sedimentary Os isotope data from these eras. On the basis of the correlation of the marine <sup>187</sup>Os/<sup>186</sup>Os and <sup>87</sup>Sr/<sup>86</sup>Sr isotope records during the Cenozoic (8), we use the Ordovician marine Sr isotope record as a proxy for the coeval Os isotope record. Present-day seawater isotope ratios of Os and Sr are radiogenic, ~8.6 and ~0.7091, respectively. Marine Sr isotope records (9) and our Sr isotope analyses (Table 3) show that Early Ordovician seawater had similarly radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratios of ~0.7088. This indicates that the marine Os isotope composition may have been radiogenic as well. Existing cratering and paleontological records show no evidence for a major asteroid impact during the Early Ordovician that could have resulted in nonradiogenic seawater Os isotope ratios because of dissolution of extraterrestrial Os from the impactor (8, 10). We therefore interpret the nonradiogenic, age-corrected <sup>187</sup>Os/<sup>186</sup>Os ratios of 1.67 and 3.13 for two samples of the lower and upper red interval as indicators of a large particulate meteoritic or mantle-derived Os fraction. Re concentrations in the red intervals are low (23 and 7.5 pg/g), and decay-corrected <sup>187</sup>Os/<sup>186</sup>Os ratios do not differ much from the measured ratios. Immobile element ratios such as Zr/TiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> indicate average upper continental crustal composition for the detrital fraction (1). This is consistent with the depositional environment of the Orthoceratite Limestone in an epicontinental sea or intracratonic basin (11). This fact and

the association of excess Ir and Os with fossil meteorites favor an extraterrestrial rather than a mantle origin of the excess noble metals. A simple isotope mass balance calculation assuming a two-component mixture of detrital Os (<sup>187</sup>Os/<sup>186</sup>Os ~ 10.5) and extraterrestrial Os (<sup>187</sup>Os/<sup>186</sup>Os ~ 1.05) yields an extraterrestrial Os fraction of 93% and 76% for the lower and upper red intervals, respectively. With the use of the measured Os concentrations in the two samples, the Os concentration of the detrital fraction (~10 to 15% of the whole rock) can be calculated at 20 to 40 pg/g, typical for weathering-exposed continental crustal material (12, 13). In contrast to the red limestone, a radiogenic <sup>187</sup>Os/<sup>186</sup>Os ratio of 30.9 and Re concentrations of 2.14 ng/g have been measured in the gray, organic-rich interval. High Re concentrations and Re/Os ratios reflect hydrogenous Re enrichment typical for organic-rich sediments (14). Decay correction yields a negative initial Os isotope ratio indicative of open-system behavior. For this reason, the extraterrestrial fraction of noble metals in the gray interval cannot be estimated using Os isotope data. Diffusive loss of noble metals from the fossil meteorites may have contributed to excess concentrations of these elements in the limestones. However, our estimates suggest that <0.5% of the excess Ir in the limestone is derived from fossil meteorites, with the remainder related to influx of extraterrestrial dust (15). In the following, we

use the average Ir content (67 pg/g) of 31 samples of red limestone (1) to estimate the flux of excess Ir to the sea floor. Chondritic Os/Ir ratios in the limestone and the Os isotope mass balance calculated above indicate that ~85% of the Ir (mean value of 93% and 76% Os) is extraterrestrial in origin. We estimate a minimum extraterrestrial Ir accumulation rate of ~30 ng cm<sup>-2</sup> My<sup>-1</sup> (My = million years) for the Early Ordovician, based on the average excess Ir concentration of 57 pg/g and minimum net sedimentation rates of 0.2 cm per 1000 years for the red limestone (1). On the basis of Os isotope analyses of deep-sea sediments, it was estimated that extraterrestrial Os today accumulates at rates of 1.3 to 3 ng cm<sup>-2</sup> My<sup>-1</sup> (12, 16). Similar accumulation rates prevailed throughout the Cenozoic (17). Our Os isotope data support an enhancement of an order of magnitude in the influx of extraterrestrial dust in the Early Ordovician relative to the present. The difference cannot be accounted for by uncertainties in the sedimentation rate estimates, which are critical in all flux calculations. The Lower Ordovician Orthoceratite Limestone at Kinnekulle is about 20 m thick, and according to conventional paleontologic-stratigraphic information, the section represents 10 ± 5 My (1). Any attempt to account for the excess Ir by an order of magnitude lower sedimentation rate would result in an unrealistic depositional time span of ~100 My for the 20 m-thick section.

**Table 2.** Os isotopic ratios and Os and Re analyses. 1σ uncertainties are given on the basis of counting statistics. Initial <sup>187</sup>Os/<sup>186</sup>Os values are calculated using a depositional age of 480 Ma for all samples and decay constant λ = 1.64 × 10<sup>-11</sup> year<sup>-1</sup> (20).

| Sample                           | <sup>187</sup> Os/ <sup>186</sup> Os (measured) | <sup>187</sup> Os/ <sup>186</sup> Os (initial) | <sup>187</sup> Os/ <sup>188</sup> Os (measured) | Os (ng/g)       | Re (ng/g)       |
|----------------------------------|-------------------------------------------------|------------------------------------------------|-------------------------------------------------|-----------------|-----------------|
| <i>Fossil meteorite</i>          |                                                 |                                                |                                                 |                 |                 |
| Österplana Ark 009, central part | 1.068 ± 0.001                                   | 1.058                                          | 0.12852 ± 0.00012                               | 838 ± 8         | 25.3 ± 1.3      |
| <i>Whole-rock limestone</i>      |                                                 |                                                |                                                 |                 |                 |
| D4-8 (lower red interval)        | 1.819 ± 0.005                                   | 1.674                                          | 0.21886 ± 0.00061                               | 0.0514 ± 0.0054 | 0.0233 ± 0.0012 |
| A17 (gray interval)              | 30.89 ± 0.17                                    | -6.229                                         | 3.719 ± 0.021                                   | 0.0268 ± 0.0003 | 2.14 ± 0.11     |
| I1a (upper red interval)         | 3.269 ± 0.02                                    | 3.125                                          | 0.3934 ± 0.0024                                 | 0.0171 ± 0.0002 | 0.0075 ± 0.0004 |

Estimates in (1) indicate that meteorites >500 g accumulated during the Early Ordovician at a rate two orders of magnitude higher than today. The discrepancy between this estimate and the order of magnitude enhancement for extraterrestrial dust accretion may be related to the greater statistical uncertainty for the meteorite flux calculations. The Ordovician meteorite flux represents an average for 1.17 My, whereas accretion rates based on recent meteorite distributions in desert areas represent only the past ~0.05 My (18). If meteorite influx to Earth is episodic, this would be an important circumstance to consider. Alternatively, the discrepancy could be related to differences in the dynamic behavior of the different source regions for meteorites and extraterrestrial dust. Meteoroids are products of parent body fragmentation in the asteroid belt, whereas extraterrestrial dust is derived from asteroidal as well as cometary (the Kuiper belt, the Oort cloud) and interstellar sources.

We do not know to what extent the ~1.75-My period we studied represents an anomaly in terms of extraterrestrial matter influx, or whether it is representative of a much longer time interval. However, it is likely that the abundant meteorites reflect a short event such as a catastrophic breakup of a meteorite parent body in the asteroid belt. Analyses of chromite grains from the Österplana Ark 001 meteorite indicate that it is an H or L chondrite (5). Studies of recent meteorites have revealed a high abundance of heavily shocked and degassed L chondrites with Ar-Ar ages around 500 Ma, suggesting a major impact on the L chondrite parent body at this time (19). It is possible that the high meteorite density on the Early Ordovician sea floor is somehow related to the disruption of the L chondrite parent body at ~500 Ma. If this is correct, the early Paleozoic limestone record may contain important further information about the timing, causes, and effects of this major event in the history of the solar system.

**Table 3.** Results of  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic analyses of biogenic calcite. The first two samples are unidentified shells; the third sample at +3.5 m is a trilobite pygidium. All values are normalized to a value of 0.710140 for NBS 987 standard. Errors are  $2\sigma$  of the mean of repeated measurements. Depth is relative to the base of the gray interval (Fig. 1).

| Depth (m) | $^{87}\text{Sr}/^{86}\text{Sr}$ |
|-----------|---------------------------------|
| -3.9      | 0.708858 $\pm$ 12               |
| +0.9      | 0.708792 $\pm$ 11               |
| +3.5      | 0.708820 $\pm$ 12               |

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3. Element results were obtained by instrumental neutron activation analysis (INAA) at ACTLABS, Ontario [see (7)].  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were determined with a Finnigan MAT 261 mass spectrometer as described (B. Schmitz, S. L. Ingram, D. T. Dockery, G. Åberg, *Chem. Geol. Isotope Geosci.*, in press).
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## Measurements of $^{12}\text{C}/^{13}\text{C}$ , $^{14}\text{N}/^{15}\text{N}$ , and $^{32}\text{S}/^{34}\text{S}$ Ratios in Comet Hale-Bopp (C/1995 O1)

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The  $^{12}\text{C}/^{13}\text{C}$ ,  $^{14}\text{N}/^{15}\text{N}$ , and  $^{32}\text{S}/^{34}\text{S}$  isotope ratios in comet Hale-Bopp (C/1995 O1) were determined through observations taken with the James Clerk Maxwell Telescope. Measurements of rare isotopes in HCN and CS revealed isotope ratios of  $\text{H}^{12}\text{CN}/\text{H}^{13}\text{CN} = 111 \pm 12$ ,  $\text{HC}^{14}\text{N}/\text{HC}^{15}\text{N} = 323 \pm 46$ , and  $\text{C}^{32}\text{S}/\text{C}^{34}\text{S} = 27 \pm 3$ . Within the measurement uncertainties, the isotopic ratios are consistent with solar system values. The cometary volatiles thus have an origin in the solar system and show no evidence for an interstellar component.

The isotopic abundances of abundant elements (C, N, O, S, and others) may reveal where cometary material originated. In the current paradigm, cometary matter was captured from the solar nebula at the time of the formation of the planetary system and

should preserve a record of isotopic abundance ratios in the nebula  $4.5 \times 10^9$  years old (1). Isotopic anomalies in comets, if they exist, might reveal patterns of pollution of the solar nebula by nearby supernovae, or gas phase reactions in the pre-planetary disk, or even the existence of interstellar comets.

Nearly-solar isotope ratios were measured by spacecraft passing through the coma of P/Halley (2, 3). The  $^{12}\text{C}/^{13}\text{C}$  ratio has been determined in a few other comets from ground-based data [Ikeya 1963a (4), Kohoutek 1973f (5), and Kobayashi-Berger-Milon 1975IX (6)], and the ratio is consistent with a solar system origin for all. Many of these measurements relied on high-reso-

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