Reports

Iodine-129/Xenon-129 Age of Magnetite from the Orgueil Meteorite

Abstract. *Magnetite from the Orgueil C1 chondrite is only 2.0 ± 2.4 million years older by the iodine-xenon method than the next oldest meteorite, the Karoonda C4 chondrite. This age ties the primitive C1 chondrites to the extensive iodine-xenon chronology of normal chrondrites. If Karoonda and Orgueil magnetite formed from similar material, then the age difference is an upper limit to the formation time of these meteorites—and by customary extension, the solar system. Condensation, chondrule formation, accretion, and metamorphism of the Karoonda parent body all seem to have been completed within a few million years.*

Type 1 carbonaceous chondrites (C1) have a very primitive chemical composition, close to that of the sun, except for the most volatile elements (*1*). Yet they are not necessarily the oldest of all meteorites. They may be isochronous or even younger if they comprise the last solid matter to condense from a cooling solar nebula.

Conventional dating methods (K-Ar, Rb-Sr, Pb-Pb) are of no use here, as they lack the necessary resolving power. A more promising technique is the I-Xe method, based on extinct ^{129}I [see (*2*) for a recent review of the method]. Some 21 meteorites have been studied by this method (*2–5*) and all except the achondrites began to retain ^{129}Xe within 15 million years of each other. The place of C1 chondrites in this hierarchy could not be determined, though, because the radiogenic ^{129}Xe in these chondrites is swamped by large amounts of trapped xenon. Recently, however, Jeffery and Anders (*6*) devised a method for separating the principal minerals of the C1 chondrite Orgueil—hydrated silicates and magnetite—and found that radiogenic ^{129}Xe was nearly 100-fold enriched in the magnetite relative to trapped ^{132}Xe. This opened up the possibility of obtaining an I-Xe date for material from a C1 chondrite.

As in the procedure of Jeffery and Anders (*6*), the submicrometer-sized intergrowth of silicate flakes and magnetite was disaggregated with a strong electrolyte. Lithium chloride was used instead of NaOH (*6*) on the assumption that it was less likely to etch the minerals and cause gas loss. We added 75 ml of a saturated (20°C) solution of LiCl to 2.05 g of powdered Orgueil (stone 9419 from the Musée d'Histoire Naturelle, Montauban, France). After stirring the mixture at 55° ± 5°C for 6 days, we isolated a magnetite fraction which stuck to the magnetic stirring bar. Three subsequent ultrasonic cleanings in H_2O removed some of the clinging silicates, which contain large amounts of interfering trapped xenon (*7*). The purified material (0.22 g) was washed with water, then acetone, and finally dried in a desiccator.

A portion of the magnetite and a Co-doped Al wire were then sealed in an evacuated quartz capsule. The quartz capsule and a similar capsule containing a sample of the St. Séverin (LL6) chondrite were irradiated to a nominal neutron fluence of 1.9×10^{19} neutron/cm^2 (*8*). After the samples had "cooled" for several months, the xenon was extracted from both samples in a stepwise heating experiment. Experimental method and data reduction were as described by Podosek and Lewis (*3*).

In Fig. 1 we have plotted the high-temperature ^{128}Xe/^{130}Xe and ^{129}Xe/^{130}Xe ratios from the heating experiments on Orgueil magnetite and St. Séverin (*9*). Data were normalized to ^{130}Xe because the spallation corrections for ^{130}Xe for St. Séverin were smaller (4 percent maximum, 1300°C) than the fission corrections for ^{132}Xe (approximately 50 percent maximum, 1200°C). In order to keep our St. Séverin data directly comparable to

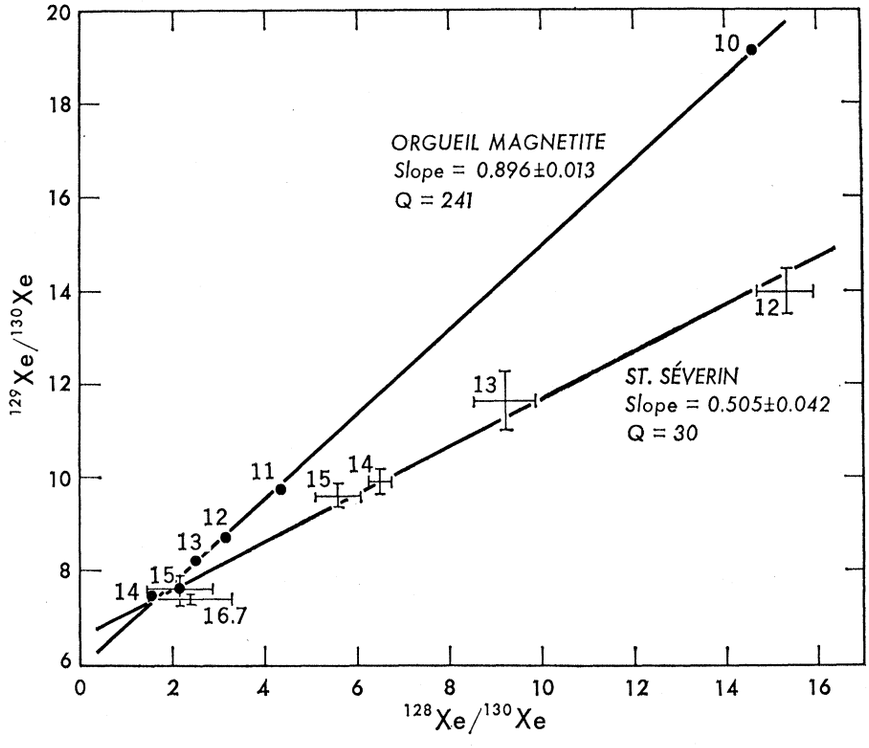

Fig. 1. Correlation of ^{129}Xe/^{130}Xe with ^{128}Xe/^{130}Xe for Orgueil magnetite and St. Séverin. The numbers indicate the release temperature of each fraction, in units of 100°C. Slopes are equal to ^{129r}Xe/^{128s}Xe (see text). The Q values listed are the "confidence parameters" as defined in (*2*). The low-temperature points in both meteorites fall below and to the right of the isochrons. This behavior is typical of other meteorites (*2–5*).

Podosek's (*2*), we used his spallation ratios to calculate the spallation corrections. No spallation corrections were necessary for Orgueil magnetite since all of the observed $^{124}Xe/^{130}Xe$ and $^{126}Xe/^{130}Xe$ ratios were within experimental errors of average carbonaceous chondrite (AVCC) xenon (*10*). The St. Séverin data are less accurate due to instrumental difficulties encountered during the analysis and because St. Séverin contains roughly 100 times less xenon than does Orgueil magnetite.

Slopes in Fig. 1 were calculated according to York's (*11*) regression method. The slope of each line is the quantity $^{129r}Xe/^{128*}Xe$, where ^{129r}Xe is xenon from the decay of extinct ^{129}I and $^{128*}Xe$ is xenon from the neutron reaction $^{127}I(n,\gamma,\beta^-)^{128*}Xe$. The slopes are related to $^{129}I/^{127}I$, the isotopic ratio of iodine at the time the meteorite or mineral began to retain ^{129r}Xe, by the equation

$$^{129}I/^{127}I = (^{129r}Xe/^{128*}Xe)\ (^{128*}Xe/^{127}I) \quad (1)$$

where $^{128*}Xe/^{127}I$ is the fraction of ^{127}I converted to $^{128*}Xe$ in the reactor (*12*). In the absence of an independent determination of $^{128*}Xe/^{127}I$ (*13*) it is possible to calculate the $^{129}I/^{127}I$ ratio of Orgueil magnetite relative to that previously determined (*2*) for St. Séverin by using the formula

$$(^{129}I/^{127}I)_m = \frac{(^{129}I/^{127}I)_s\ (^{129r}Xe/^{128*}Xe)_m\ (N)}{(^{129r}Xe/^{128*}Xe)_s} \quad (2)$$

where the subscripts m and s stand for Orgueil magnetite and St. Séverin, respectively, and the factor N is the ratio of neutron fluences received by the two meteorites. Using the slopes listed on Fig. 1, $(^{129}I/^{127}I)_s$ from (*2*), and $N = 0.976 \pm 0.0024$ (determined from the Co-doped Al flux wires), we calculate $^{129}I/^{127}I = (1.40 \pm 0.13) \times 10^{-4}$ for Orgueil magnetite at the start of xenon retention. This confirms the prediction of Jeffery and Anders (*6*) that Orgueil magnetite would have "a high age, a high degree of correlation, or both" (*14*). The $^{129}I/^{127}I$ ratio of Orgueil magnetite is the highest determined for a chondrite so far, but its error (1 S.D.) overlaps the range of previously measured values (*2*), 1.3×10^{-4} to 0.7×10^{-4}.

This experiment represents the first well-defined I-Xe isochron determined for type 1 or type 2 carbonaceous chondrite material and as such ties the C1 chondrites to the extensive I-Xe chronology of normal chondrites. The principal observation is that the I-Xe age of Orgueil magnetite is similar to that of all other classes of chondrites dated thus far. This observation is of special interest in view of the much debated possibility that Orgueil contains pristine interstellar matter which escaped vaporization during collapse of the solar nebula (*15*). Such material, not having been outgassed since the last nucleosynthetic event, should have an I-Xe age perhaps 10^8 years older than that of run-of-the-mill meteorites (*16*). Apparently the magnetite does not contain significant amounts of material predating the collapse of the solar nebula. The low cosmic-ray exposure age of Orgueil, 11 million years (*6*), had already cast doubts on this possibility. Orgueil magnetite clearly is made from the same batch of material as the other chondrites.

Three sequential events in the history of meteorites can reset the I-Xe clock by depletion of Xe relative to I, or isotopic homogenization of I or Xe.

1) Condensation and growth of dust grains in the cooling solar nebula (*17*).

2) Chondrule formation, presumably by remelting of the dust (*18*).

3) Metamorphic reheating, presumably in asteroidal parent bodies after accretion of the chondrule-matrix mixture (*19, 20*).

Let us designate the onset of ^{129}Xe retention after each of these stages by t', t'', t'''. Most meteorites dated thus far have experienced all three processes and the last event seems to have been intense enough to completely reset the I-Xe clock. Thus, their I-Xe ages reflect differences in t''', the cooling times of their parent bodies. Orgueil, however, escaped the last two processes. It contains no chondrules and shows no signs of metamorphism. Thus, the I-Xe age of Orgueil magnetite is recording the formation time of the magnetite, t'.

Orgueil magnetite probably formed from primary condensates (metal, magnesium silicates) by reactions (*6, 17*) such as

$$3Fe + 4H_2O(g) \xrightarrow[<405°K]{} Fe_3O_4 + 4H_2 \quad (3)$$

$$12(Mg,Fe)_2SiO_4 + 14H_2O(g) \xrightarrow[\leq 380°K]{} 2Fe_3O_4 + 2H_2 + 3(Mg,Fe)_6(OH)_8Si_4O_{10} \quad (4)$$

Magnetite made by the first reaction freely equilibrates with ambient noble gases (*21*). It therefore seems likely that the I-Xe clock was completely reset during the formation of magnetite (*22–24*). In addition, an extended nebula cools rapidly, in less than 10^3 years (*25*), and so the entire condensation stage must have been short. Hence, t' for Orgueil magnetite probably is identical to t' for all other meteorites, within the resolving power of the $^{129}I/^{127}I$ method.

If we combine the I-Xe age of Orgueil magnetite with that of a less primitive meteorite, we can determine the interval between condensation, t', and the end of metamorphism, t'''. (The "end" of any process in this context means the time when the system became closed to I and Xe.) The age difference between any two meteorites is given by the equation (*2*):

$$\Delta t_{1-2} = \tau[\ln(^{129}I/^{127}I)_2 - \ln(^{129}I/^{127}I)_1] \quad (5)$$

where Δt is the age difference between meteorites 1 and 2, τ is the mean life of ^{129}I (25 million years), and the $^{129}I/^{127}I$ ratios are calculated from Eq. 1 or Eq. 2. The oldest meteorite with a well-defined $^{129}I/^{127}I$ ratio listed by Podosek (*2*) is Karoonda. Karoonda is a carbonaceous chondrite like Orgueil, is of petrologic type 4 rather than 1, contains chondrules, and has a value of $^{129}I/^{127}I = (1.29 \pm 0.03) \times 10^{-4}$ (*2*). From Eq. 5 we calculate that Karoonda began to retain ^{129}Xe 2.0 ± 2.4 million years later than Orgueil magnetite (at the 68 percent confidence level) (*26*).

The major part of this interval must have been taken up by metamorphism. Even a body as small as 30 km in radius takes 8 million years to cool from 800°C to 500°C, a typical temperature range for chondrite metamorphism (*27*). Although we do not know the peak metamorphic temperature experienced by Karoonda or the size of its parent body, no reasonable choice of parameters will bring this time down to less than 1 million years. Thus, a significant part of the time span of 2.0 ± 2.4 million years was taken up by postaccretional processes: heating and cooling of the Karoonda parent body. The preceding nebular stage, involving condensation, chondrule formation, and accretion, must have lasted less than 2.0 ± 2.4 million years, perhaps much less.

GREGORY F. HERZOG*
EDWARD ANDERS
Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637
E. C. ALEXANDER, JR.
P. K. DAVIS
R. S. LEWIS†
Department of Physics, University of California, Berkeley 94720

References and Notes

1. A. E. Ringwood, *Rev. Geophys.* **4**, 113 (1966); E. Anders, *Geochim. Cosmochim. Acta* **35**, 516 (1971).
2. F. A. Podosek, *Geochim. Cosmochim. Acta* **34**, 341 (1970).
3. ——— and R. S. Lewis, *Earth Planet. Sci. Lett.* **15**, 101 (1972).
4. F. A. Podosek and C. M. Hohenberg, *ibid.* **8**, 443 (1970).
5. E. C. Alexander, Jr., B. Srinivasan, O. K. Manuel, *ibid.* **6**, 355 (1969); *ibid.* **8**, 188 (1970); F. A. Podosek, *Geochim. Cosmochim. Acta* **36**, 755 (1972). A complete review of the pre-1969 data is included in (*2*).
6. P. M. Jeffery and E. Anders, *Geochim. Cosmochim. Acta* **34**, 1175 (1970).
7. The purity of the magnetite fraction is estimated to be >95 percent, by assuming that all of the trapped ^{132}Xe observed in the magnetite (1.5×10^{-9} cm^3/g) came from unremoved silicates which have a ^{132}Xe content of $\sim 3 \times 10^{-8}$ cm^3/g.
8. The Orgueil magnetite and St. Séverin samples were irradiated together with several lunar and terrestrial samples as part of an irradiation designated "Vallecitos 4." The St. Séverin sample was included to serve as a monitor of known I-Xe age (*2*).
9. The complete isotope ratios for all temperatures of both samples are too bulky to include in this report. The data have been tabulated and are available on request from the authors. A curious feature of the rest of the data is an excess of the heavy isotopes of xenon, above that of AVCC. The summed $^{134}Xe/^{132}Xe$ and $^{130}Xe/^{132}Xe$ ratios are 0.3902 and 0.3319, respectively, with a total ^{132}Xe content of 1.51×10^{-9} cm^3/g (STP). Neutron induced fission can only account for $\lesssim 30$ percent of this excess, based on a limit for uranium of <10 parts per billion by Krähenbühl *et al.* (U. Krähenbühl, J. W. Morgan, R. Ganapathy, E. Anders, *Geochim. Cosmochim. Acta*, in press). The remainder of the excess could be accounted for either by a very high Pu/U ratio of ≥ 0.06 or by the presence of fission xenon of the carbonaceous chondrite type [M. W. Rowe, *Geochim. Cosmochim. Acta* **32**, 1317 (1968)]. Unfortunately, the anomalies are too small to test these two possibilities.
10. D. Krummenacher, C. M. Merrihue, R. O. Pepin, J. H. Reynolds, *Geochim. Cosmochim. Acta* **26**, 231 (1961).
11. D. York, *Can. J. Phys.* **44**, 1079 (1966).
12. R. A. Fish and G. G. Goles, *Nature* **196**, 27 (1962)
13. A sample of KI salt was irradiated with the samples to give an independent measure of $^{128*}Xe/^{127}I$. However, two independent isotope dilution experiments yielded very discordant values for this quantity. It is evident that the problem is in the isotope dilution experiment and not the irradiation. We have preserved most of the irradiated KI and may eventually be able to obtain an independent calibration of this irradiation, which will reduce the quoted error.
14. Jeffery and Anders (*6*) estimated an $^{129}I/^{127}I$ ratio of 1.3×10^{-4} ($\pm$ a factor of 2), based on the Br content of the magnetite, 0.96 part per million, and an assumed I/Br ratio equal to the cosmic value. Although fortuitously close to our ratio of $(1.4 \pm 0.13) \times 10^{-4}$, it is not really comparable to it, because it refers to total rather than correlated, high-temperature iodine. Our data yield a markedly lower "total" $^{129}I/^{127}I$, 0.41×10^{-4}, but the discrepancy may in part reflect differences in separation procedure [NaOH in (*6*), LiCl in this work].
15. A. G. W. Cameron, *Interstellar Dust Int. Astron. Union Symp. 52nd 1972*, in press; D. C. Black, *Geochim. Cosmochim. Acta* **36**, 377 (1972).
16. H. Reeves, *J. Astron. Astrophys.* **19**, 215 (1972); D. N. Schramm and G. J. Wasserburg, *Astrophys. J.* **162**, 57 (1970); A. G. W. Cameron (private communication) notes, however, that interstellar grains may contain their volatile elements such as ^{129}I in loosely bound surface coatings. Hence, they would not be able to accumulate any ^{129}Xe until remelted or recrystallized in a high-temperature environment, such as a newly forming solar system.
17. J. W. Larimer and E. Anders, *Geochim. Cosmochim. Acta* **31**, 1239 (1967); E. Anders, *Annu. Rev. Astron. Astrophys.* **9**, 1 (1971).
18. F. L. Whipple, *Science* **153**, 54 (1966); in *Nobel Symposium 21, from Plasma to Planet*, A. Elvius, Ed. (Almqvist & Wiksell, Stockholm, Sweden, 1972), p. 211.
19. J. A. Wood, *Icarus* **6**, 1 (1967).
20. ———, *J. Geophys. Res.* **72**, 6379 (1967). A fourth sequential event, namely, breakup of the meteorite parent body, seems to have left no record in the I-Xe chronology of most of the meteorites. The one exception is the shock-heated LL3 chondrite Manych [Podosek and Hohenberg (*4*)]. Manych did not yield a unique I-Xe age, probably because it suffered late reheating to 800°C to 900°C for several weeks [J. A. Wood (*19*, p. 30)] which may have partly reset its I-Xe clock.
21. M. S. Lancet and E. Anders, *Geochim. Cosmochim. Acta*, in press.
22. A possible complication arises from the fact that there are two kinds of magnetite in Orgueil (*23*): submicrometer-sized grains intergrown with silicate and spheres or platelets 5 to 20 μm in diameter associated mainly with $MgSO_4$ and dolomite veins. The fine-grained material most likely formed in the nebula by reaction 2, whereas part or all of the coarse-grained material may have formed in the parent body, during an episode involving liquid water (*24*). Owing to the high water-solubility of iodides, it seems likely that the presence of an aqueous phase would cause less iodine to enter the magnetite lattice. Consequently, one would expect the second-generation magnetite to contribute only a minor part of the total ^{129}Xe, and hence have only a minor effect on the I-Xe age.
23. J. Jedwab, in *Origin and Distribution of the Elements*, L. H. Ahrens, Ed. (Pergamon, Oxford, 1968), p. 467; *Earth Planet. Sci. Lett.* **2**, 440 (1967); J. F. Kerridge, *ibid.* **9**, 299 (1970).
24. E. R. DuFresne and E. Anders, *Geochim. Cosmochim. Acta* **26**, 1085 (1962).
25. A. G. W. Cameron, *Icarus* **1**, 13 (1962).
26. We are tacitly assuming that metamorphism in Karoonda was severe enough to reset the I-Xe clock. In support of this assumption we note that Karoonda is more strongly recrystallized than the L4 chondrite Bjurböle, which is used as a reference meteorite in I-Xe dating; in fact, W. R. Van Schmus [in *Meteorite Research*, P. Millman, Ed. (Reidel, Dordrecht, 1969), pp. 480–491] suggested that Karoonda should perhaps be reclassified to C5.
27. P. E. Fricker, J. I. Goldstein, A. L. Summers, *Geochim. Cosmochim. Acta* **34**, 475 (1970).

28. We thank A. Cavaille for supplying the sample of Orgueil and G. A. McCrory for his assistance in maintaining the equipment. R. Ganapathy first suggested the experiment. This work was supported by AEC contracts AT(04-3)-34 and AT(11-1)-382 and bears the AEC code numbers UCB-34P32-84 and COO-382-122.

* Present address: Department of Chemistry, Douglass College, New Brunswick, New Jersey 08903.

† Present address: Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637.

5 January 1973; revised 7 February 1973

Glaciers and Nutrients in Arctic Seas

Abstract. *Significantly higher concentrations of nitrate and silicate were found in glaciated South Cape Fiord than in unglaciated Grise Fiord, in the Canadian Arctic, or in adjacent Jones Sound. No significant differences in phosphate concentrations were found. Glacial activity apparently enriches the concentrations of those nutrients most critically limiting for arctic phytoplankton requirements.*

The effects of active, moving glaciers discharging into the sea on the nutrient content of adjacent waters have been the subject of some limited speculation. Vibe (*1*), for example, discussing conditions in northwest Greenland, remarked " . . . I hold the view that the glaciers far surpass precipitation as an erosive factor in procuring the inorganic material . . . which renders all organic life possible." Similarly, Sverdrup ". . . suggested that Antarctic waters should also receive much dispersed silica formed by comminution of rock beneath the very large glaciers of the Antarctic continent" (*2*). Hartley and Dunbar (*3*) discussed upwelling and enriching hydrodynamic processes associated with "brown zones" adjacent to glaciers terminating in the sea.

The hypothesis that active coastal glaciers enrich nutrient concentrations in the sea was tested in May 1969 in two of the numerous fiords that indent the southern shore (latitude 76°30'N) of Ellesmere Island, Northwest Territories, Canada. Glaciated and unglaciated fiords provide experimental and control areas, respectively, in which hypothetical effects of glaciation may be isolated and examined without undue external dilution, which might obscure glacial influence. Grise Fiord, the control area, extends inland approximately 38 km and does not have any glaciers reaching its shores. South Cape Fiord, the experimental area, is approximately 25 km long and has three glaciers reaching its shores (see cover photograph). The largest of these, unnamed, is approximately 32 km long and about 3.2 km wide where it reaches the fiord. This glacier evidently is active, calving small icebergs into South Cape Fiord. The cover photograph shows one such berg recently calved from the glacier front. In May 1969, at least 15 icebergs were frozen into the fiord.

At the time of this survey, air temperatures were in the range of −15° to −1°C and the entire area was snow-covered with no signs of spring thaw or melt. There were no effects on the sea of runoff from the land. Throughout the area of this study, Jones Sound and the adjacent waters were completely covered with intact, snow-covered sea ice averaging 0.75 to 1.0 m in thickness.

Grise Fiord has a maximum depth of about 365 m inside a sill depth of