Examination of the data reveals instead a sharply defined, negative acceleration. While this appears to support the Urey hypothesis, it is not necessarily inconsistent with other selelenological theories.

P. M. Muller
W. L. Sjogren
*Jet Propulsion Laboratory,
Pasadena, California*

References and Notes

1. W. H. Michael, Jr., R. H. Tolson, J. P. Gapcynski, *Science* **153**, 1102 (1966); J. Lorell, in *Measure of the Moon,* Z. Kopal, Ed. (Gordon and Breach, New York, 1967); R. H. Tolson and J. P. Gapcynski, *Proc. Int. Space Sci. Symp. 8th* (COSPAR assembly, London, July 1967); J. Lorell and W. L. Sjogren, *Science* **159**, 625 (1968).
2. P. M. Muller and W. L. Sjogren, "Consistency of Lunar Orbiter residual with trajectory and local gravity effects," *Tech. Rep. 32-1072* (Jet Propulsion Laboratory, Pasadena, Calif.).
3. H. C. Urey, in *Vistas in Astronomy,* A. Beer, Ed. (Pergamon Press, London, 1956), vol. 2, p. 1676.
4. M. R. Warner and M. W. Nead, "SPODP—Single precision orbit determination program," *Tech. Mem. 33-204* (Jet Propulsion Laboratory, Pasadena, Calif., 1965).
5. T. M. Lang, "LEASTQ—A program for least-squares fitting segmented cubic polynomials having a continuous first derivative," *Space Programs Summary* (Jet Propulsion Laboratory, Pasadena, Calif., 1968).
6. H. C. Urey, in *Physics and Astronomy of the Moon,* Z. Kopal, Ed. (Academic Press, New York, 1962), pp. 484–486.
7. R. B. Baldwin, *The Face of the Moon* (Univ. of Chicago Press, Chicago, 1958), p. 200.
8. We thank R. W. Davies, W. L. Kaula, J. Lorell, P. Gottlieb, and D. W. Trask for many helpful contributions; D. K. Davies (and staff), R. Hanson, P. A. Laing, C. L. Lawson, and R. N. Wimberly for programming and computer assistance. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under NASA contract NAS 7-100.

1 August 1968

■

Potassium-Feldspar Phenocrysts in the Surface of Colomera, and Iron Meteorite

Abstract. *Silicate aggregates, including large single crystals of potassium feldspar as long as 11 centimeters and sodium feldspar, are embeded in the surface of the medium octahedrite Colomera. Silicate nodules in the interior appear to be much smaller (about 0.3 centimeter). Glass nodules are abundant both on the external surface and in the interior. These observations are evidence that some iron meteorites formed as segregations within a silicate matrix and did not originate in a metallic planetary core.*

The presence of silicates in iron meteorites has been well known for more than a century. Because of the obvious importance of the existence of the metallic iron, interest in the silicate fraction has been rather small until recently. The presence of a wide variety of silicates in iron meteorites (*1*) in much lower abundance than in pallasites and mesosiderites has permitted use of the Rb^{87}-Sr^{87} and K^{40}-Ar^{40} methods for the dating of these objects (*2*). Previous work in our laboratory on silicate inclusions from several iron meteorites showed very regular Rb^{87}-Sr^{87} and K^{40}-Ar^{40} ages of about 4.6×10^9 years. Silicate material taken from slices of Colomera yielded results that did not define an isochron. These anomalous results suggested that this meteorite merited further investigation.

Colomera, first recognized as an iron meteorite in 1934 (*3*), was found buried in a patio in the village of Colomera near Granada (Spain) in 1912. The original mass was reported as 134 kg; it measured roughly 50 by 40 by 16 cm. By courtesy of the Museo Nacional de Ciencias Naturales de Madrid, the main mass was shipped to our laboratory.

Preliminary observations showed that large silicate inclusions, partly obscured by rust, occur on the surface. In order to remove the rust, we cleaned the main mass by "sand blasting" with TiO_2 spherules. During this process it was discovered that the external surface contained at least four large silicate inclusions. One of these exhibited the characteristic reflectance of a single cleavage fragment; it was 11 cm long, 2.5 cm wide, and deeper than 1 cm. In the center of this inclusion were large green pyroxene aggregates (~ 1 cm). Several of the largest of these inclusions were found in depressions or "holes" in the surface. In addition to these large silicate masses, small (~ 0.3 cm) droplike masses were present on the external surface, resembling in size and form the silicate inclusions present in the interior and exposed on the cut surface. These small inclusions also occur in slices of Colomera. Some of the surface pockets are almost covered with silicates that suggest that they are relicts of a continuous filling of silicates. The silicates on the exterior can very easily be overlooked, since they often are rust colored.

The present mass of Colomera is 129.3 kg including all known pieces which are in the Spanish and U.S. National museums. Considering the thickness of the cuts made on this meteorite, and the loss of weight during removal of the rust, we can account for almost all the originally reported mass of 134 kg.

The surface of the meteorite shows clear evidence of subjection to some form of forging; hammer and chisel marks are obvious at several points. The extent to which the marks reflect its history before acquisition by the Spanish Museum is not obvious. Fractures in the meteorite and certain peculiar surfaces suggest that a fragment of iron was ripped away over a single area of about 100 cm^2. We cannot prove that the present surface is primary and was not significantly altered by ablation.

The mean density of the meteorite, determined on the main mass with a dynamometer in a Joly balance experiment, is 7.613 ± 0.048 g/cm^3. Estimating the densities of the metallic iron-nickel and silicate at 7.88 to 7.90 (*4*) and 3.3, respectively, and correcting for the presence of remnant rust, we obtain a range of 4.3 to 5.8 percent (by volume) of silicates in the whole meteorite. Clearly, large amounts of silicate inclusions are incompatible with the density data, the suggestion being that the abundance of large silicate masses on the exterior is not typical of the interior. This idea is supported by the observation that a large surface inclusion, exposed on the cut surface and in the adjacent slices, extends to a depth of only about 1 cm.

Several samples were taken from each of the large external-surface inclusions and from several of the small spheroidal inclusions exposed on both the external surface and the cut surface; they were studied optically, by x-ray diffraction and electron-microprobe techniques. Quantitative chemical analyses were obtained from the microprobe analyses using the procedures described by Bence and Albee (*5*). The average chemical analysis for each phase is reported in Table 1.

Macroscropic examination of the largest of the surface inclusions revealed two distinct phases: the large crystal (11 by 2.5 cm) already mentioned for which a cleavage face was observed, and aggregates or single crystals of green pyroxenes (~ 1 by 1 cm). Samples from various parts of the large crystal showed that it had the composition of a nearly pure potassium feldspar (Table 1); expressed in terms of the feldspar chemical end-members, its composition is $Or_{89}Ab_{10}An_{01}$. No evidence was found to indicate the existence of an exsolved sodic phase. X-ray diffraction patterns, obtained from two areas of the large crystal, showed critical spectral lines at 2θ $(\bar{2}01)$ = 21.05 deg, 2θ (060) = 41.6 deg, and 2θ $(\bar{2}04)$ = 50.8 deg; part of one scan is shown in Fig. 1. Using the indexing procedure outlined by Wright and Wright and Stewart (*6*), the crystal was identified as potassium feldspar having the structural state of high sanidine; the position of the $\bar{2}01$ reflection is consistent with the composition of $Or_{90}Ab_{10}$.

Optical examination of several fragments of the potassium feldspar, which constitutes 60 to 75 percent of the inclusion, revealed that ferromagnesium minerals are completely enclosed within the large feldspar crystal in a poikilitic texture. The minerals include aggregates of chromian clinopyroxene ($En_{47}Fs_{13}$-Wo_{40}) with variable composition, and minor anhedral, calcium-poor pyroxene ($En_{73}Wo_{02}Fs_{25}$). Accessory phases in this inclusion include a polymorph of SiO_2, chromite, ilmenite, calcium phosphate, and carbonate. A zoned olivine crystal (Fa_{27-32}) was found in one of the other large surface inclusions.

In general, the mineralogy and chemistry of the phases found in all the large surface inclusions were similar, except for an inclusion exposed on the cut surface which contains sodium feldspar of composition $Ab_{94}Or_3An_3$ (Table 1); its structural state is that of a high albite, as obtained from $\Delta 2\theta$ $(1\bar{3}0–130)$ = 0.6 to 0.7 deg and $\Delta 2\theta$ $(1\bar{3}1–131)$ = 1.8 to 1.9 deg. The critical spectral lines occur at 2θ $(\bar{2}01)$ = 22.01 deg, 2θ (060) = 42.3 deg, and 2θ $(\bar{2}04)$ = 51.4 deg.

Calcium carbonate present in the large surface inclusions is generally associated with the K-feldspar; none was observed in the globular-type inclusion. The carbonate mineralization is restricted to the surface of the meteorite and must be considered a product of terrestrial weathering.

The small droplike inclusions exposed on both the external surface and the cut face are numerically the most abundant; they consist primarily of alkali-rich glass, with accessory pyroxenes, chromite, and rutile; a few contain abundant chromian clinopyroxene and glass as the major phases, and free SiO_2, calcium-poor pyroxene, calcium phosphate, and chromite as accessories. The glass is characterized by its high soda content (Table 1) and distinct excesses of both alumina and silica over the feldspar formula. Interinclusion variations of soda (up to 20 percent), alumina (7 percent), and silica (3 percent) were noted, but intrainclusion variations are small. The pyroxenes occurring within the glass are small (~ 10 to 20 μ) euhedral crystals distinctly different in composition (Table 1) from the calcium-poor pyroxenes found within the large surface inclusions. Chromite grains of variable composition occur in both the glass globules and the large surface inclusions.

Five inclusions from the interior of the meteorite showed the following phases: abundant glass and chromian clinopyroxene, accessory calcium-poor pyroxene, SiO_2, TiO_2 needles, calcium phosphate, and chromite. No potassium or sodium feldspar was observed although Bunch and Olsen (*7*) found both phases in internal inclusions. While our sampling was extremely limited, it ap-

Table 1. Average compositions (percentages by weight) of Colomera silicates. An ARL-EMX Electronprobe microanalyzer was used, operating at 15-kv acceleration potential. Instrument drift was minimized by use of electron-beam integration rather than fixed-time counting. Analytical error was 1 to 5 percent of the amount present. Abbreviations: LSI, large surface inclusions; Glob, globular inclusions.

Phase	Feldspar (LSI)		Chromian clino-pyroxene (LSI)	Olivine (LSI)	Ca-poor pyroxene		Glass (Glob)	SiO_2 (LSI, Glob)
	K	Na			LSI	Glob		
SiO_2	65.1	67.8	53.6	36.4	54.5	55.6	72.0	99.0
TiO_2	0.05	0.0	0.91	0.07	0.27	0.34	0.41	0.11
Al_2O_3	18.2	20.0	0.63	0.0	0.11	0.90	16.9	0.77
Cr_2O_3	0.0	0.0	1.67	0.0	0.40	0.34	0.0	0.0
FeO	0.13	0.23	7.13	26.7	16.3	11.0	0.11	0.0
MgO	0.0	0.0	15.9	35.6	26.5	30.1	0.09	0.0
MnO			0.60	1.12	1.37	1.13		
CaO	0.12	0.75	18.9	0.07	1.21	0.67	0.47	0.0
Na_2O	1.15	11.2	1.07	0.05	0.14	0.09	8.22	0.33
K_2O	15.0	0.46	0.0	0.0	0.0	0.0	0.97	0.0
Totals	99.8	100.4	100.4	100.0	100.5	100.2	99.2	100.2

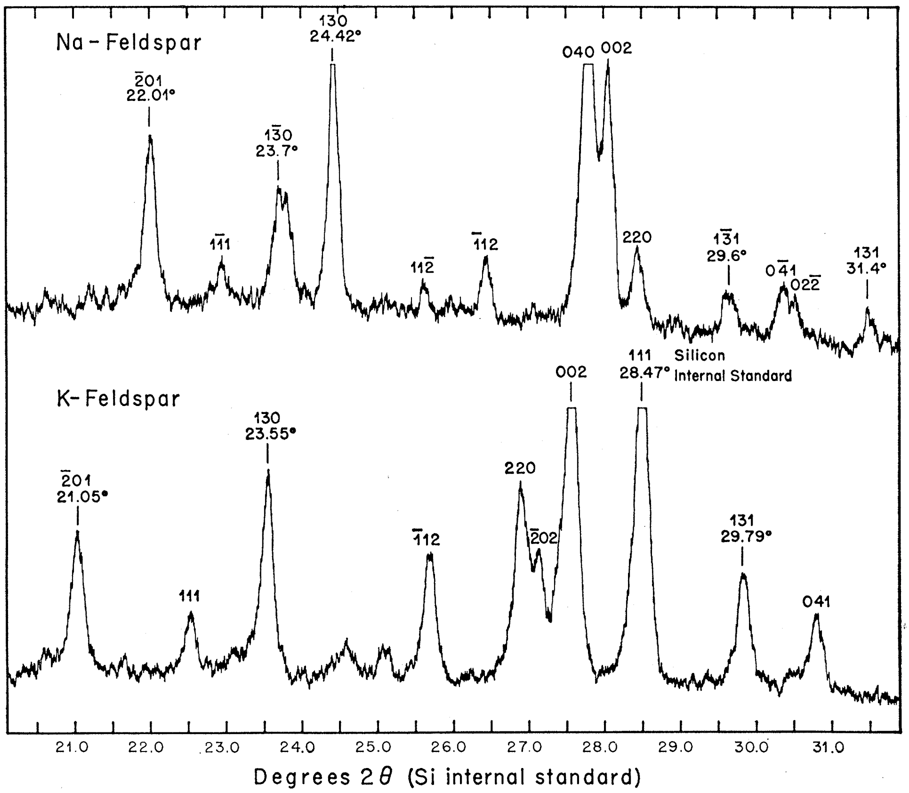

Fig. 1. Part of the x-ray diffraction scans obtained for sodium and potassium feldspars from the large surface inclusions in Colomera; nickel-filtered Cu*Kα* radiation.

pears that the abundance of feldspars, particularly K-feldspar, are far greater in the large surface inclusions than in the small inclusions, both internal and external. The phases found in both the surface and internal inclusions revealed a similar range in composition and showed that, except for the chromite, they were not chemically distinguishable.

Grains ranging up to 50 μ and consisting of almost pure SiO_2 (Table 1) occur in both the large surface inclusions and the globules; they are undoubtedly a polymorph of silica that we have not yet identified optically. This free silica coexists with glass and orthopyroxene in the globules, and with K-feldspar and two pyroxenes in the large surface inclusions.

The presence of large amounts of alkalis (especially potassium) in Colomera implies extreme differentiation from any reasonable parent material, on the basis of studies of other meteorites. The great enrichment in silicon also implies differentiation. The compositions of the feldspars and glass suggest that they cannot be considered to represent a quenched equilibrium assemblage. The coexistence of olivine and SiO_2 within the same inclusion, zoning in the olivine, and variable composition of the pyroxenes within an inclusion point to a lack of equilibration of the silicates.

The scatter in the Rb-Sr data for Colomera (*2*) is not yet understood. Although there is clear evidence of some alteration of the external inclusions, some additional measurements were made on them. A sample of the K-feldspar phenocryst gave 10.1 percent K; 2911 parts per million (ppm) Rb; $Rb^{87}/Sr^{86} = 114.2$; and $Sr^{87}/Sr^{86} = 8.45$. These values yield an age of about 4.7×10^9 years. A fragment of the phenocryst gave an Ar^{40}-K^{40} age of 4.3×10^9 years. Analyses of spallation products in the metal phase have been reported by Hintenberger and Wänke (*8*). A sample of the albite gave 0.61 percent K; 27.5 ppm Rb; $Rb^{87}/Sr^{86} = 0.535$; and $Sr^{87}/Sr^{86} = 0.7354$. The Rb^{87}-Sr^{87} values are compatible with the K-feldspar results. The K/Rb ratios are extremely low in the K-feldspar and show very great fractionation of the alkalis relative to the albite; this result suggests that the K/Rb ratios are controlled by mineral partitioning, and that care must be taken in use of this value as an index of differentiation when sampling is not adequate.

The internal globules in Colomera suggest a silicate melt trapped in a solidifying iron mass. It is our interpretation that these are primary glasses from the time of formation of the iron meteorite and are not the product of shock. Because of the much higher freezing point of the metallic phase it is quite possible for the silicates that were entrapped as liquids to be in complete disequilibrium with the silicates adjacent to the iron mass. The silicate glasses and the high structural states of the feldspars imply quenching in these silicate systems; this finding contrasts with the development of Widmanstätten patterns which implies a cooling rate slow with respect to diffusion recrystallization for the metal system.

From our observations it seems reasonable to conclude that Colomera was originally formed as a molten iron segregation of rather small mass contained within a silicate matrix. This iron and associated molten silicate were cooled so rapidly that the silicate globules included in the iron were trapped (*9*). The entire mass is considered to have been surrounded by silicate, with possible extensions of iron penetrating the silicate. This object would therefore not represent a planetary core or the border zone of a core as has been suggested for the pallasites, but rather an incomplete stage in the segregation of metallic iron from iron-silicate mixtures.

The effects of melting and extreme differentiation are of course manifest in the alkali contents described, so that the total silicate composition of this meteorite is analagous to a diopsidic syenite or granite. These silicates would represent the lowest melting fraction of any reasonable parent material. Iron segregations such as those represented by Colomera presumably may be formed at any depth within a small parent planetary object, but conceivably they may have been formed near the surface of a larger parent.

It is reasonable to believe that, during the collision that broke up the parent body (from which this meteorite came) and exposed the meteorite to cosmic rays, the external silicate fragments were easily dispersed and the iron mass was more readily preserved. The same circumstance would prevail during passage of the meteorite through the atmosphere and subsequent impact with Earth, thereby leaving only a small residue of the external silicate portion.

It has been suggested that many of the large concavities and holes in some iron meteorites reflect the original existence in these voids of silicates that were removed by impact and weathering (*10*). Urey (*11*) has presented reasons why iron meteorites may derive from pools or melts of iron near the surfaces of parent objects. Our observations strongly support this view for at least some meteorites. This model eliminates some of the difficulties associated with the partial segregation of silicates from an iron-nickel melt in a planetary core (*9*).

In distribution of silicates in the interior, Colomera is very similar in gross texture to Weekeroo Station and Kodaikanal in which the silicates mostly appear globular. Kodaikanal, however, is highly deformed, and some of the geometric forms of the inclusions may be secondary. All three meteorites are similar in high enrichment of alkalis, especially potassium, in the silicates. Other meteorites such as Four Corners, Pine River, Toluca, El Taco, Copiapo, and Odessa have silicate inclusions, some of which appear to be much more angular. The geometric forms of some of these inclusions are controlled by the crystallographic planes of the iron, but the fragmental origin for some appears to be reasonable. Such a circumstance is quite possible in a highly plastic iron-silicate mass slightly below the melting point of iron.

All the above iron meteorites may be considered to have originated as plums of iron in a pudding of silicates; they must have been buried sufficiently deeply within their parent bodies for adequate development of the Widmanstätten patterns and the cooling characteristics determined by iron-nickel diffusion models (*12*). The more massive irons, such as Canyon Diablo, also contain rare silicate inclusions (*13*). These massive irons must represent a further stage in the gravitational differentiation of nickel-iron and silicates, but may still be quite far from representing planetary cores.

G. J. Wasserburg
H. G. Sanz*
A. E. Bence
Charles Arms Laboratory, Division of Geological Sciences, California Institute of Technology, Pasadena

References and Notes

1. See, for example, B. Mason, *Mineral Mag.* **36**, 120 (1967).
2. G. J. Wasserburg, D. S. Burnett, C. Frondel, *Science* **150**, 1814 (1965); D. S. Burnett and G. J. Wasserburg, *Earth Planetary Sci. Letters* **2**, 137, 397 (1967); D. D. Bogard, D. S. Burnett, P. Eberhardt, G. J. Wasserburg, *ibid.* **3**, 375 (1968).
3. J. Dorronsoro and F. Moreno Martin, *Anales Soc. Espan. Fis. Quim.* **32**, 1111 (1934).

4. E. P. Henderson and S. H. Perry, *Geochim. Cosmochim. Acta* **6**, 221 (1954).
5. A. E. Bence and A. L. Albee, *J. Geol.* **76**, 382 (1968).
6. T. L. Wright, *Amer. Minerologist* **53**, 88 (1968); ——— and D. Stewart, *ibid.*, p. 38.
7. T. E. Bunch and E. Olsen, *Trans. Amer. Geophys. Union* **49**, 237 (1968) (abstr.); *Science*, **160**, 1223 (1968). These workers report potassium feldspar in Kodaikanal but erroneously reported a feldspar of composition $Ab_{64}An_9Or_{27}$ in Weekeroo Station as potassium feldspar. Discussion of isotopic ages by these workers is obscure because of some misunderstanding.
8. H. Hintenberger and H. Wänke, *Z. Naturforschung* **19a-2,** 218 (1964). These workers report the presence of olivine and suggest that Colomera should be classed as a pallasite; this finding is probably in error because of misidentification of diopside.
9. Some aspects of the gravitational segregation problem are discussed by R. A. Fish, G. G. Goles, E. Anders, *Astrophys. J.* **132**, 243 (1960). This point of view is probably not pertinent to the model we present.
10. E. Henderson, personal communication (1953); ——— and S. H. Perry, *Proc. U.S. Nat. Museum* **107**, 339 (1958).
11. H. C. Urey, *Monthly Notices Roy. Astron. Soc.* **131**, 199 (1966).
12. See, for example, J. I. Goldstein and J. M. Short, *Geochim. Cosmochim. Acta* **31**, 1733 (1967).
13. A. El Goresy, *ibid.* **29**, 1131 (1965).
14. Supported by grants from NSF (GP 3570 and 7976) and NASA (NGR-05-002-044). Philip Carpenter and James Stevens (Jet Propulsion Laboratory) generously aided us in cleaning and weighing the meteorite. Valuable discussions with D. S. Burnett, A. E. Ringwood *et al.* be here acknowledged. We were ably assisted in the microprobe work by A. Chodos. The argon analyses, made by D. D. Bogard, will be reported elsewhere. Contribution 1534 from the Division of Geological Sciences, California Institute of Technology.

* National Aeronautics and Space Administration International University fellow. Permanent address: Junta de Energia Nuclear, Madrid, Spain.

20 May 1968

■

Radiocarbon: Analysis of Inorganic Carbon of Fossil Bone and Enamel

Abstract. *Carbon dioxide from calcium carbonate in fossil bone can be selectively separated from carbon dioxide in bone apatite by hydrolyzing the sample first in acetic acid and then in hydrochloric acid. Radiocarbon analyses of the inorganic carbon dioxide in three samples of known age clearly show calcium carbonate in fossil bone to be secondary and the carbonate of bone apatite to be indigenous and suitable for dating in some cases. Agreement between dates on collagen-bone apatite pairs increases the level of confidence.*

In a previous publication in which radiocarbon analyses of organic fractions of fossil bones was reported (*1*), I concluded that only collagen that has been purified of humic acids and other secondary organic matter gives reliable ages with the C^{14} method. The analyses of inorganic carbon of fossil bone and enamel reported here is a continuation of this research to investigate the reliability of fossil bones and teeth for radiocarbon dating.

It has long been recognized that most of the calcium carbonate in fossil bone is secondary and hence younger than the host. Therefore, carbon from this source is not reliable for age dating the animal (*2*), although it may provide useful geochemical data on secondary carbonate deposition and levels of ancient water tables (*3*).

The precise chemical structure of the inorganic matter of living bone and tooth enamel has been under investigation for over a century. The main constituent of bone and tooth inorganic matter is calcium phosphate (bone apatite) with varying proportions of fluoride, hydroxyl, and carbonate ions (*4*) Unless exchange has taken place the carbonate from bone apatite should be indigenous and reliable for age dating by the radiocarbon method.

In order to analyze the carbonate from bone apatite, that from calcium carbonate must first be completely removed before the bone apatite can be hydrolyzed. Experimentation with mineral specimens of carbonyl apatites, fossil tooth enamel, and calcite revealed that acetic acid would completely hydrolyze calcium carbonate and not appreciably affect apatite even after prolonged treatment. Apatite could then be hydrolyzed with hydrochloric acid and the carbon dioxide thus released analyzed in the standard way for C^{14}.

In order to test the possibility that bone apatite carbonate is indigenous, three of the same bone samples that had been used for analysis of the organic fraction were selected for analysis of bone carbonates. In addition mammoth tooth enamel was included for comparison with bone. The Lehner and Hell Gap samples yielded x-ray powder diffraction patterns typical of bone apatite. The data, including the earlier analyses corrected for fractionation of the standard, are presented in Table 1.

The Lehner archeological site, Arizona, is where Clovis hunters killed mammoths 11,260 years ago, as determined by the radiocarbon method (*5*). Both calcium carbonate (*6*) and bone apatite of mammoth bone from the Lehner site were analyzed. The calcium carbonate (A-806C) is 10,000 years younger than the bone deposit and is obviously secondary, but the bone apatite carbon (A-874C) is only a little more than 1000 years younger than the bone. It is, in fact, the oldest of the four fractions dated, suggesting that under the geochemical conditions at the Lehner site carbon from bone apatite is more stable than collagen.

Table 1. Carbon-14 analyses of organic and inorganic carbon of fossil bone. Laboratory numbers of the samples are given in parentheses.

Fraction	Lehner mammoth bone	Lehner mammoth tooth	Hell Gap bison bone	Murray Springs bovid bone
	C^{14} age*	C^{14} age	C^{14} age	% Modern standard
First $CaCO_3$	1,190 ± 90 (A-806C)		700 ± 260 (A-753C_1)	125 ± 4.6 (A-819C)
Second $CaCO_3$			6,130 ± 500 (A-753C_2)	
Apatite CO_2	9,980 ± 220 (A-874C)	7,780 ± 150 (A-876C)	9,050 ± 160 (A-753C_3)	
Organic residue	5,610 ± 350 (A-806A)†		8,890 ± 110 (A-753A)	103.5 ± 3.0 (A-819A)
Humates and soluble organic carbon	7,930 ± 490 (A-806D)		5,430 ± 110 (A-753D)	102.4 ± 2.8 (A-819B) 100.9 ± 2.4 (A-819D)
Fulvic acids				98.8 ± 6.7 (A-819E)
		Total percentage of organic carbon		
	0.63		3.68	1.28
		Percentage of apatite carbon‡		
	0.82	1.55	0.66	
		True age		
	11,260 ± 360	11,260 ± 360	8,600 ± 300	50 to 500

* Expressed as years B.P. (before 1950). † Not collagen, but probably includes some decay products of collagen. ‡ Based on weight of sample after removal of calcium carbonate.