Allende Meteorite: A High-Voltage Electron Petrographic Study

Abstract. *Electron-transparent sections of the Allende meteorite, a carbonaceous chondrite, have been prepared by ion-thinning and examined by high-voltage (800-kilovolt) transmission electron microscopy. The matrix crystals, mainly olivine, range in size from approximately 5 to approximately 0.01 micrometers; carbon is present as intergranular films of poorly crystalline graphite. The chondrules exhibit extensive radiation damage, a feature lacking in the matrix. In addition, both chondrules and matrix are undeformed and contain negative crystals; submicroscopic exsolution lamellae are present in pyroxenes. Comparison of the substructure in the Allende meteorite with that in the Parnallee meteorite and in lunar and selected terrestrial rocks leads to the conclusion that chondrule irradiation preceded cold accretion during formation of the solar system and that the meteorite has since been undisturbed.*

The Allende meteorite fell near Parral, Chihauhau, Mexico, on 8 February 1969. The size of the fall, the carbonaceous character of the meteorite, and its immediate accessibility for examination for possible short-lived radioactivity have resulted in an intensive study of specimens of this meteorite in several laboratories by optical, petrographic, and chemical techniques (*1*, *2*). This carbonaceous chondrite [Wiik's type III (*3*), Van Schmus and Wood's type C3 (*4*)] consists of a dark gray matrix in which are embedded many spherical aggregates of coarser crystals (chondrules) and less numerous irregular crystal clusters. Although the matrix is too fine-grained to permit full resolution by optical techniques, its dark color has been attributed to finely dispersed carbon. Most of the chondrules are rich in magnesium and consist predominantly of forsteritic olivine (Mg_2SiO_4), commonly accompanied by a pyroxene $(Ca,Mg,Fe)SiO_3$. The crystals in most of the chondrules of the Allende meteorite display igneous textures, that is, they appear to have crystallized from a melt; the remainder have textures suggestive of devitrification (*5*). The present study was undertaken to determine the fine structure of the matrix and of the chondrules, especially with reference to the location of the carbon, by using the improved resolution obtainable from transmission electron microscopy. The advantage of conventional electron microscopy (100-kv accelerating voltage) over that of optical microscopy was further enhanced by the use of higher voltage (800 kv), which gives increased penetration, more precise electron diffraction of selected areas, and reduction of the possibility of specimen damage due to ionization or heating effects under the electron beam. Electron-transparent foils were prepared from standard petrographic thin sections of the meteorite by a low-angle, ion-bombardment process (*6*). Final foil thicknesses ranged up to the order of 1 μm.

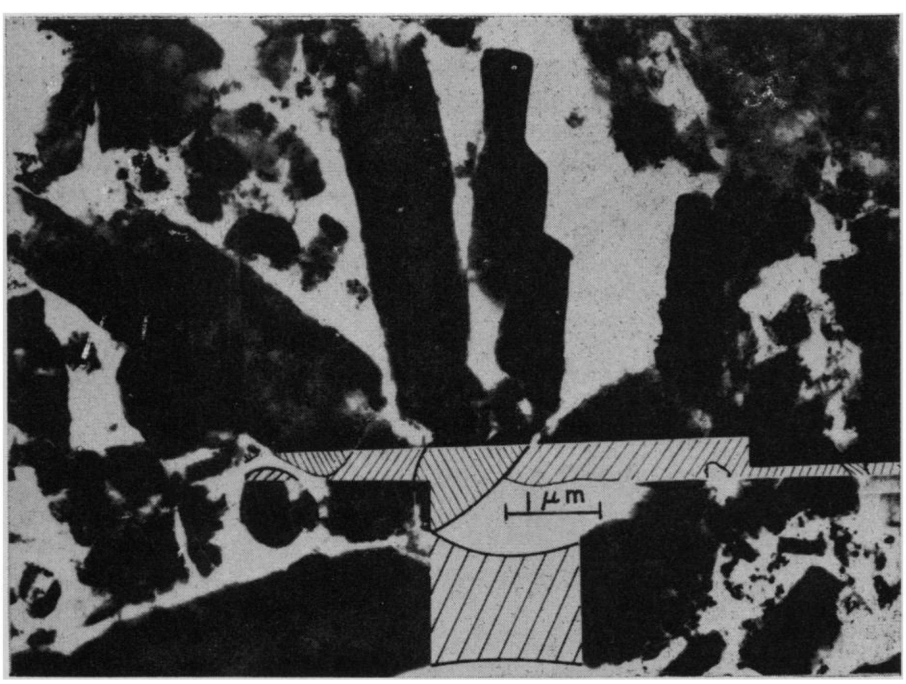

Fig. 1. Electron micrograph mosaic of the Allende matrix showing the radiating group of euhedral olivine crystals elongated parallel to [001]. Bright areas between crystals are holes in the specimen produced by the falling out of extremely small grains during specimen preparation.

In a transmission electron microscope, the Allende matrix is seen to consist mainly of euhedral olivine crystals up to 5 μm long and 1 μm in diameter, with the interstices filled with extremely small crystals, often only a few hundred angstroms in diameter. The olivine crystals, elongated parallel to [001], generally appear to be randomly distributed, but sometimes form radiating groups (Fig. 1). Chemical analysis of matrix foils with an electron microprobe shows these olivines to contain considerable iron substituting for magnesium, in agreement with a previous and more general chemical and x-ray analysis of this meteorite (*2*). Most matrix crystals exhibit relatively little substructure, and there is no evidence of plastic deformation. Some of the larger matrix grains show small precipitates as well as negative crystals. The occasional pyroxene grains that are present show exsolution lamellae on an extremely fine scale—less than 0.1 μm thick (Figs. 2 and 3A).

Although the fine precipitates inside the matrix crystals could not be identified by electron diffraction from selected areas, the diffraction analysis showed no evidence of carbon within the grains. In contrast, diffraction from small areas (0.25 μm in diameter) centered about grain boundaries produces the single ring pattern characteristics of poorly crystalline graphite (Fig. 2 and inset). In some instances a broad, but definite, graphite ring appears [at the (0002) graphite spacing], but elsewhere the structure is sufficiently disordered to mask the ring. Thus it appears that the carbon in the Allende meteorite is located primarily at grain boundaries in the matrix and occurs as highly disordered graphite. No structural features of possible biological nature were found (*7*).

The negative crystals are small intracrystalline bubbles, bounded by low-index crystal faces, and are apparently empty or gas-filled (no evidence of liquid, glass, or crystalline phases was found). The absence of negative crystals in the finer matrix grains suggests that the negative crystals arose from the nucleation and growth of gas bubbles after crystallization, since the preferential escape of gas atoms to nearby grain boundaries in the finer grains would inhibit such nucleation. Alternatively, the negative crystals could represent the incorporation of gas bubbles absorbed on the crystal surfaces during growth. However, their absence in the finer grains, the lack of any apparent growth-related distribution of bubbles in the coarser crystals, and the absence of included, nongaseous phases in the bubbles causes us to doubt this possible origin.

Four different types of olivine-bearing chondrules were examined: polycrystalline olivine, olivine phenocrysts (large crystals bounded by low-index faces) surrounded by fine-grained anorthite ($CaAl_2Si_2O_8$) and an exsolved pyroxene pair, olivine-pyroxene aggregates, and barred olivine (*8*). Despite the pronounced differences visible optically, these different chondrules exhibited markedly similar substructures. As in the matrix, chondrule crystals are undeformed and contain small precipitates, negative crystals (Fig. 4), and thin exsolution lamellae (~ 0.1 μm) in pyroxenes (Fig. 3A). However, in addition to these features, four of the five chondrules examined showed a fine-scale black-spot structure, typical of coalesced point defects (Fig. 3B). This structure is prominent in olivine and anorthite; it also may be present in the pyroxenes but, if so, it is obscured there by the complex diffraction contrast arising from the exsolution lamellae. As many as 10^{13} spots per cubic centimeter were counted, with individual spots ranging up to 0.1 μm in diameter. (The actual sizes of the defect clusters responsible for these images are, however, much smaller.) No relationship between spot density and location within crystals or chondrules was evident. Only one chondrule, composed exclusively of barred olivine, contained no black-spot structure. Electron diffraction patterns from selected areas containing the black-spot structure show no evidence of another phase, thus ruling out the possibility that these features are caused by strain contrast around small precipitates. It is likely, therefore, that this structure originated either from the quenching of vacancies during extremely rapid cooling or from displacement damage caused by irradiation.

In an effort to better understand the features observed in the Allende meteorite, we have conducted a comparative examination of the Parnallee meteorite, a partially equilibrated ordinary chondrite [type LL3 of Van Schmus and Wood (*4*)] and also compared the results for the Allende meteorite with similar results from studies of the same minerals in lunar basalts (*9*) and selected terrestrial rocks (*9, 10*). The Parnallee chondrules show much the same features in the electron microscope as the chondrules from the Allende meteorite, with two striking exceptions—no black-spot structure was found, and the crystals show abundant evidence of deformation. In common with the meteorites, fine-scale exsolution phenomena have recently been observed to occur extensively in both terrestrial and lunar pyroxenes. Although not reported in lunar and most types of terrestrial rock, submicroscopic negative crystals in olivine are abundant in terrestrial peridotites (*11*). Examples of black-spot structures have been observed in pyroxene from a lunar basalt (*9*) and in the lunar fines (*12*), but not in terrestrial rocks (*9, 10*).

Of the two possible interpretations of the black-spot structure—quenched-in vacancies or radiation damage—the latter is preferred. The quenching origin is doubted because this type of substructure has not been found (*9*) in Hawaiian basalts that are known to have been rapidly cooled (from the fact that they are glass-bearing). Quenched-in and clustered vacancies have thus far been observed only in simple metals, and it appears likely that the energies needed to form vacancies and the diffusion kinetics in nonmetals are unfavorable for the formation of vacancy clusters. The observation of the spot structure in lunar material gives added strength to the interpretation that the black-spot structure results from radiation damage because, unlike the surface of the earth which is protected by its atmosphere and magnetic field, the surface of the moon receives large doses of radiation from cosmic rays and the solar wind.

Radiation damage in silicates in the form of tracks revealed by chemical etching has been reported for several meteorites (*13*), and a large amount of radiation damage has been reported for the lunar fines (*12, 14*), but this particular type of radiation damage has not yet been reported for the Allende mete-

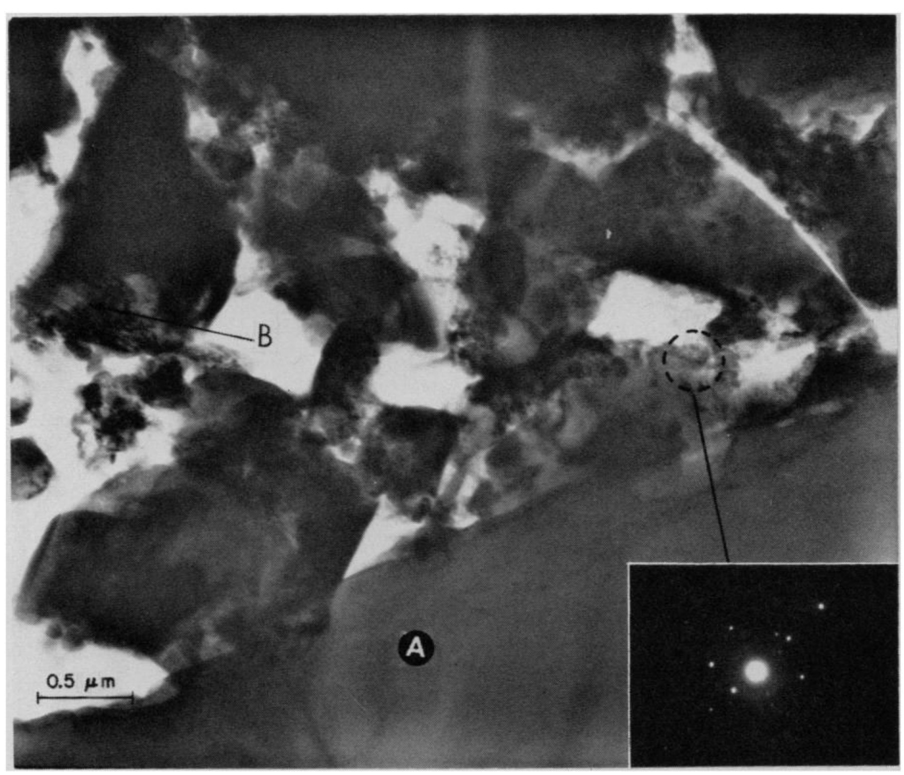

Fig. 2. Detail of the Allende matrix showing the electron diffraction evidence (inset from the selected area is indicated) of poorly ordered graphite on grain boundaries of the fine crystallites. The micrograph also shows examples of (*A*) the substructure-free larger olivine and (*B*) fine-scale exsolution in pyroxene crystallites.

orite. The damage structure which gives rise to such tracks is difficult to see by diffraction contrast in the electron microscope and is usually revealed by chemical etching, which enlarges the tracks so that detection by optical and scanning electron microscopy is possible. It is possible that such damage structures do exist in the Allende meteorite; however, we have not used etching techniques thus far. On the other hand, the presence of black-spot damage in the meteorites studied previously by surface etching procedures cannot be ascertained at the present time (*15*). In the case of the lunar fines, for which it is possible to select individual particles small enough for direct observation by transmission electron microscopy, occasional regions of black-spot damage in conjunction with tracks have been observed recently (*12*). The sporadic occurrence of black-spot damage in the lunar fines and its occasional occurrence in the lunar basalts point to the considerable variations in the types or conditions of radiation or post-radiation history, or both, in these several materials.

The nature of the damage structure in the Allende meteorite has not yet been identified, but presumably the radiation originated in the proto-sun. The presence of radiation damage in chondrule olivine and other phases and its absence in matrix olivine indicate that the irradiation occurred after chondrule solidification, but that it preceded accretion to form the parent meteorite body. Unless submicroscopic matrix crystals dispersed in space before accretion do not register detectable radiation damage (*16*), the irradiation must also have preceded formation of those crystals. Our observations also indicate that accretion occurred at temperatures sufficiently low ($< 500°K$) that the radiation damage in the chondrules was not annealed out (*13*). The euhedral nature of the matrix olivines, their occasional clustering into radiating groups, and the exceedingly fine grain size of other matrix crystals suggests the possibility of crystallization directly from the circumsolar plasma. All of this evidence appears to be incompatible with the "impact-ignimbrite" hypothesis for chondrite formation (*17*).

The Parnallee meteorite has apparently experienced a mild metamorphism, inasmuch as ratios of magnesium to iron in olivines and pyroxenes from different chondrules in it show a slight tendency toward equilibration (*18*). The thermal event reflected by this partial equilibration probably reflects autometamorphism in the later stages of accretion, but could conceivably represent a separate, subsequent heating. In either case, the elevated temperature responsible for partial chemical homogenization of the olivines and pyroxenes would probably have been sufficient to anneal out any black-spot damage originally present. The abundant deformation features indicate at least one deformation event, such as might result from collision in space.

The lack of complete ordering of matrix carbon to graphite, the extremely fine grain size of the matrix, and the preservation of the black-spot structure since before the formation of the parent meteorite body all argue strongly that the Allende meteorite has experienced no significant thermal event since its origin (*19*). At the same time, the lack of deformation suggests that the meteorite has suffered no significant collisions in that time as well. These observations are in complete agreement

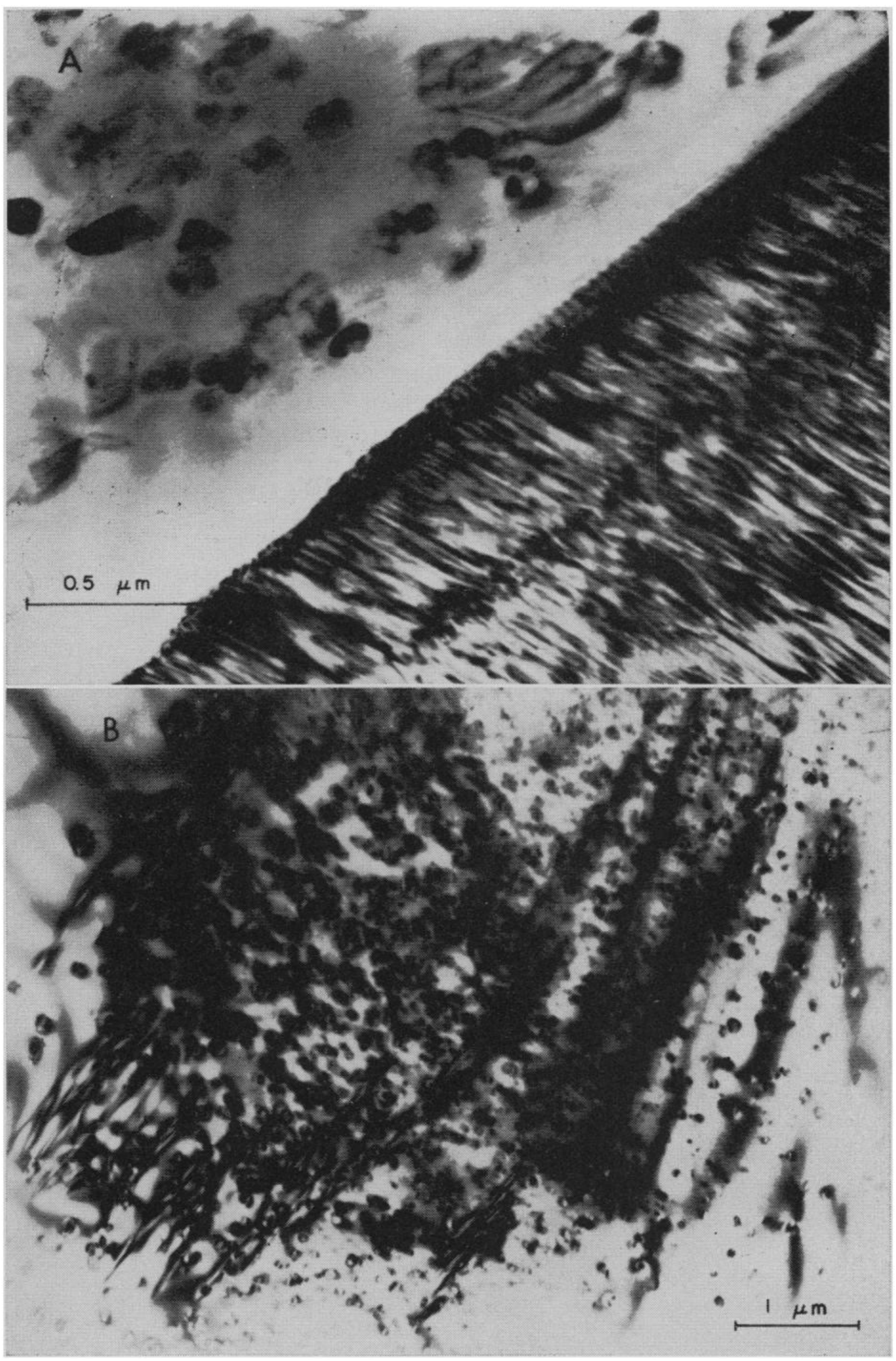

Fig. 3. Chrondrule substructure. (A) An interphase boundary between anorthite (upper left) and pyroxene (lower right). The anorthite contains precipitates and black-spot structure (dark contrast) and negative crystals (light contrast), whereas exsolution lamellae can be seen in pyroxene. (B) Black-spot structure in olivine.

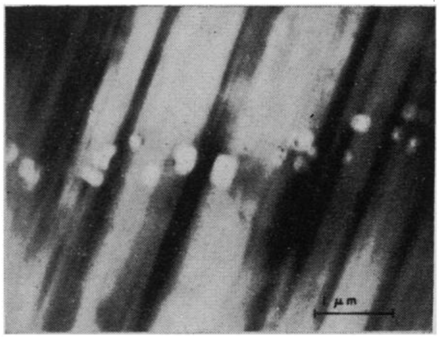

Fig. 4. Negative crystals (bubbles bounded by low-index crystal faces) in chrondrule pyroxene showing exsolution.

with and amplify those of Van Schmus (*20*), from which he concluded that type III (C3) carbonaceous chondrites have not been produced by metamorphism of type II (C2) carbonaceous chondrites. We thus conclude that the Allende meteorite consists of virgin planetary material. Its low content of water and some other volatile species indicates either formation in a region of the early circumsolar plasma deficient in these elements, or accretion under conditions unfavorable to condensation or entrapment of these components.

Note added in proof: Fireman, DeFelice, and Norton (*21*) have recently reported U, Th-^{4}He, and K-^{40}Ar ages for Allende in which the chondrules date older than the whole rock (and hence the matrix). These results are consistent with the results reported here.

H. W. GREEN II*
Department of Geology and *Division of Metallurgy and Materials Science, Case Western Reserve University, Cleveland, Ohio 44106*

S. V. RADCLIFFE
A. H. HEUER
Division of Metallurgy and Materials Science, Case Western Reserve University

References and Notes

1. E. A. King, Jr., E. Shonfeld, K. A. Richardson, J. S. Eldridge, *Science* **163**, 928 (1969); J. Oro and E. Gelpi, paper presented at the 32nd annual meeting of the Meteoritical Society [*Meteoritics* **5** (1969)]; L. H. Fachs, *Amer. Mineral.* **54**, 1645 (1969).
2. R. S. Clarke, Jr., E. Jarosewich, B. Mason, J. Nelen, M. Gomez, J. R. Hyde, *Smithson. Contrib. Earth Sci.* **5**, 1 (1970).
3. H. B. Wiik, *Geochim. Cosmochim. Acta* **9**, 279 (1956).
4. W. R. Van Schmus and J. A. Wood, *ibid.* **31**, 747 (1967).
5. There has been considerable controversy over the origin of chondrules. Two schools of thought exist, one favoring crystallization of liquid droplets and the other supporting growth in the solid state from the vapor (or plasma) phase. It is our belief that at least those chondrules which contain olivine phenocrysts (large crystals bounded by low-index faces) surrounded by finer grained crystals were originally liquid droplets, and that many other chondrules probably share that origin. Apparently, some were quenched to a glass and subsequently devitrified, instead of being crystallized from the melt.
6. M. Paulus and F. Reverchon, *J. Phys. Radium* **22**, 103A (1961); N. J. Tighe, in *Ultrafine-Grain Ceramics*, J. J. Burke, N. L. Reed, V. Weiss, Eds. (Syracuse Univ. Press, Syracuse, 1970), p. 109; D. J. Barber, *J. Mater. Sci.* **5**, 1 (1970); A. H. Heuer, R. Firestone, J. Snow, H. W. Green, R. Howe, J. M. Christie, *Rev. Sci. Instrum.*, in press.
7. We cannot completely rule out the possibility that the intergranular film consists of nonbiogenic organic material, but we prefer to believe that it consists of graphite because of the correspondence of the lattice spacing indicated by the diffraction ring to the (0002) spacing of graphite.
8. Barred olivines are dendritic crystals with parallel tabular inclusions of glass or of extremely fine-grained material. A section cut through this structure reveals parallel "bars" of olivine in crystallographic continuity, separated by "bars" of the included material. They probably are the result of crystallization during very rapid cooling, having much in common with the structure found in quenched melts by E. Roedder and P. Weiblen [*Proceedings of the Apollo 11 Lunar Science Conference*, A. A. Levinson, Ed. (Pergamon, New York, 1970), vol. 1, p. 818, figures 30 and 31].
9. S. V. Radcliffe, A. H. Heuer, R. M. Fisher, J. M. Christie, D. T. Griggs, *Science* **167**, 638 (1970); in *Proceedings of the Apollo 11 Lunar Science Conference*, A. A. Levinson, Ed. (Pergamon, New York, 1970), vol. 1, p. 731; J. M. Christie, J. S. Lally, A. H. Heuer, R. M. Fisher, D. T. Griggs, S. V. Radcliffe, *Proceedings of the Apollo 12 Lunar Science Conference*, A. A. Levinson, Ed. (Pergamon, New York, in press).
10. H. W. Green, S. V. Radcliffe, A. H. Heuer, *Trans. Amer. Geophys. Union* **51**, 341 (1970); C. Arceneaux, Ed., *Proceedings of the 28th Annual Meeting of the Electron Microscopy Society of America* (Claitor, Baton Rouge, 1970); H. W. Green and S. V. Radcliffe, *Trans. Amer. Geophys. Union*, in press.
11. Larger, optically visible bubbles are common in the lunar basalts and in many terrestrial igneous rocks, especially in peridotites. These inclusions commonly contain glass and silicate crystals, and the ones from peridotites usually contain liquid carbon dioxide under pressure. E. Roedder [*Amer. Mineral.* **50**, 1746 (1965)] and E. Roedder and P. Weiblen [*Proceedings of the Apollo 11 Lunar Science Conference*, A. A. Levinson, Ed. (Pergamon, New York, 1970), vol. 1, p. 801] interpret these bubbles to be droplets of an immiscible liquid incorporated during crystallization. Most of these larger inclusions are not negative crystals, but are subspherical. The shape of the bubbles in Allende crystals and the lack of condensed phases within them suggest the different origin suggested above, that is, intracrystalline precipitation of a gaseous phase.
12. J. Borg, J. C. Dran, L. Durrieu, C. Jouret, M. Maurette, *Earth Planet. Sci. Lett.* **8**, 379 (1970); D. Barber (personal communication) has seen black spots in olivine and other phases from the fines but finds their occurrence extremely sporadic.
13. R. L. Fleischer, P. B. Price, R. M. Walker, *J. Geophys. Res.* **70**, 2703 (1965); D. Lal and R. S. Rajan, *Nature* **223**, 269 (1969); P. Pellas, G. Poupeau, J. C. Lorin, *ibid.*, p. 272; L. Wilkening, D. Lal, A. M. Reid, paper presented at the 32nd annual meeting of the Meteoritical Society [*Meteoritics* **5** (1969)]; J. C. Dran, L. Durrieu, C. Jouret, M. Maurette, *Earth Planet. Sci. Lett.* **9**, 391 (1970).
14. D. J. Barber, I. Hutcheon, P. B. Price, *Science* **171**, 372 (1971).
15. This work is currently in progress.
16. It is well known that the production of radiation damage is most pronounced at the end of the "range" of the particles in the radiation flux, when the rate of energy loss is highest. Passage through the initially isolated submicroscopic crystallites may not attenuate cosmic rays or other damage-producing particles sufficiently for them to produce damage. We do not presently understand the absence of the black-spot structure in the barred olivine chondrule; the structure was found in other chondrule olivine crystals which contain similar inclusions. Although perplexing, these observations are in accord with the sporadic occurrence of black-spot structures in the lunar material (*9*, *12*).
17. A. E. Ringwood, *Geochim. Cosmochim. Acta* **24**, 159 (1961); K. Fredriksson, *Trans. N.Y. Acad. Sci.* **25**, 756 (1963); K. Fredriksson, J. Nelen, W. G. Melson, *Proceedings of the Apollo 11 Lunar Science Conference*, A. A. Levinson, Ed. (Pergamon, New York, 1970), vol. 1, p. 419.
18. R. T. Dodd, Jr., and W. R. Van Schmus, *Geochim. Cosmochim. Acta* **31**, 921 (1967).
19. We emphasize that this may be concluded regardless of the origin of the black-spot structure. Our evidence indicates the spots are point-defect clusters which would anneal out at elevated temperatures.
20. W. R. Van Schmus, paper presented at the 31st annual meeting of the Meteoritical Society [*Meteoritics* **4** (1968)]; in P. Millman, Ed., *Meteorite Research* (Reidel, Dordrecht, Holland, 1969), p. 480.
21. E. L. Fireman, J. DeFelice, E. Norton, *Geochim. Cosmochim. Acta* **34**, 873 (1970).
22. Supported by NSF grant GA13409. We thank Dr. B. R. Simoneit, Space Sciences Laboratory, University of California, Berkeley, for donation of the Allende specimen, and the Geology Department of Case Western Reserve University for the Parnallee specimen. We also thank G. Arrhenius for helpful discussion and suggestions. R. Criss prepared many of the petrographic sections; R. Wittkop assisted with the electron microprobe. This work could not have been completed without the assistance and cooperation of R. M. Fisher and his staff at the Bain Fundamental Research Laboratory, U.S. Steel Corporation.
* Present address: Department of Geology, University of California, Davis 95616.

28 December 1970; revised 22 March 1971

A Mechanism for Producing Magnetic Remanence in Meteorites and Lunar Samples by Cosmic-Ray Exposure

Abstract. *An irradiation of 3×10^{17} neutrons per square centimeter in a reactor core produced an increase in the coercive force of iron and kamacite of 16 to 21 percent. The alternating-current demagnetization spectrum of saturation isothermal remanence was shifted toward higher coercive forces. Similar neutron fluences produced by cosmic-ray exposure may be capable of converting soft isothermal remanence in meteorites and lunar samples to remanence with a higher coercive force.*

A new mechanism is proposed by which magnetically soft isothermal remanence acquired by meteorites and lunar samples may be converted to remanence with a higher coercive force. The mechanism is the creation of lattice defects and their associated stress fields by exposure of iron and kamacite to cosmic radiation. Centers of internal stress are known to be ef-