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METASTABLE CARBON IN TWO CHONDRITIC POROUS INTERPLANETARY DUST PARTICLES.

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An understanding of carbonaceous matter in primitive extraterrestrial materials is an essential component of studies on dust evolution in the interstellar medium and the early history of the Solar System. We have suggested previously that a record of graphitisation is preserved in Chondritic Porous (CP) aggregates and carbonaceous chondrites [1, 2] and that the detailed mineralogy of CP aggregates can place boundary conditions on the nature of both physical and chemical processes which occurred at the time of their formation [2, 3]. In this letter, we report further Analytical Electron Microscope (AEM) studies on carbonaceous material in two CP aggregates which suggest that a record of hydrocarbon carbonisation may also be preserved in these materials. This suggestion is based upon the presence of well-ordered Carbon-2H in CP aggregates W7029*A and W7010*A2. This carbon is a metastable phase resulting from hydrous pyrolysis of pre-existing hydrocarbons below 300-350°C and may be a precursor to poorly graphitised carbons (PGC's) in primitive extraterrestrial materials [2].

Chondritic porous aggregates are samples of unmelted micrometeorites that survived atmospheric entry without appreciable effects of thermal metamorphism due to pulse-heating [3 - 5]. Broadly based classification studies and chemical analyses of stratospheric dust collections show that fluffy aggregates of small-sized grains (<100nm) with a chondritic bulk composition are commonly of extraterrestrial origin [6, 7]. The bulk carbon content of CP aggregates can range up to 5 wt% in carbon-rich CP aggregates [6] and possibly includes hydrocarbon compounds [8]. For this study we selected two CP aggregates from the Johnson Space Center (JSC) Cosmic Dust Collection. Detailed information on collection, curation and processing procedures at the JSC Curatorial Facility are given by Rietmeijer and Mackinnon [3] and references therein.

Chondritic porous aggregate W7029*A is a carbon-rich, uncontaminated sample of primitive extraterrestrial material [3]. In this CP aggregate, ~44% of the grains are carbonaceous material [2, 3] and the remainder are predominantly low-temperature minerals [3]. The presence of kaolinite [3] and cubic Bi_2O_3 [4] in this CP aggregate suggests that temperatures on atmospheric entry were no higher than ~300°C. In CP aggregate W7010*A2 only ~5% of the grains are carbonaceous material. However, its bulk carbon content is higher because the fine-grained (1 to ~150nm) platey silicates and sulfides in the matrix of this CP aggregate are embedded in carbonaceous, possibly hydrocarbon, material [9].

Analyses were performed with a modified JEOL 100CX AEM [10] equipped with a Princeton Gamma Tech (PGT) System IV Energy Dispersive Spectrometer (EDS) operating at an accelerating voltage of 100kV. All EDS spectra are consistent with the presence of low-atomic number ($Z<11$) elements only. For selected grains we confirmed the carbon chemistry using a JSM-35CF Scanning Electron Microscope fitted with a PGT Windowless EDS (WEDS) operating at an accelerating voltage of 10kV and by WEDS and Electron Energy Loss Spectroscopy (EELS) using a Philips EM 420T operating at 120kV. The samples are not provided with a conductive surface coating (e.g. Au/Pd or C) prior to analysis. Sample contamination with carbon materials during laboratory handling or in the AEM is negligible [3, 11]. Identification of phases is possible through a combination of AEM imaging, Selected Area Electron Diffraction (SAED), EDS, WEDS and EELS analyses. The diffraction spacings shown in TABLE 1 have a relative error of ~1%. For individual particles we obtained SAED data at various sample tilt angles relative to the incident electron beam.

The majority of carbonaceous material in CP aggregate W7029*A is present as clumped masses of thin sheets and as irregular fluffy grains. The morphology and crystallographic properties of material in these occurrences are consistent with poorly graphitised carbon [2]. Thin, amorphous carbon rims on pre-existing minerals similar to those observed in other CP aggregates [12] are also present in CP aggregate W7029*A [4]. In addition, a small fraction (~10%) of carbonaceous material in this CP aggregate occurs as thin (<100Å) electron transparent sheets which range from 0.2μm x 0.3μm to 0.6μm x 2.0μm in size (Figures 1 and 2). In general, these sheets have lobate circumferences, but in rare cases show a subhedral outline. Most of this carbonaceous material occurs as single sheets, although stacking of sheets is occasionally observed. When exposed to the electron beam the smooth surfaces of these sheets may become slightly wrinkled, suggesting loss of volatiles. In CP aggregate W7010*A2, the morphology of carbonaceous grains which are not part of the matrix, is similar to the thin sheets shown in Figure 3. SAED data shown in Table 1 are for the carbon phase in these sheets for each aggregate and are consistent with crystalline carbon-2H.

We have shown previously [2] that the morphology of carbonaceous material in CP aggregate W7029*A appears to undergo a gradual transition from thin sheets, to clumped masses of stacked sheets, and then to fluffy PGC grains. The SAED data (Table 1) show that carbons in CP aggregate W7029*A, and to a lesser extent in CP aggregate W7010*A2, occur primarily in two distinct forms as carbon-2H and PGC. In these PGC's the d_{002} basal spacing is typically at 3.50 + 0.03Å. However, the majority of PGC particles in both CP aggregates also show carbon-2H interplanar spacings and this suggests that these carbon particles are a mixture of PGC and carbon-2H. For comparison, interplanar spacings for carbon residues from carbonaceous chondrites are also listed in Table 1. Carbons in these meteorites are primarily PGC [13].

We have previously suggested that PGC in CP aggregate W7029*A and in carbonaceous chondrites results from graphitisation of a carbon phase [2]. The graphite reflection, d_{101} (2.10Å), in PGC from CP aggregates W7029*A and W7010*A2 is more diffuse and less defined when compared to the same reflection from PGC in carbonaceous chondrites. This reflection is in fact a composite of the (101) and (100) reflections (d = 2.03Å and 2.13Å) and is a sensitive indicator of the onset of graphitisation [14]. The value of the (002) spacing in PGC is a measure of the degree of order, or the extent of graphitisation, for PGC [2, 14]. The above observations suggest that graphitisation in carbonaceous chondrite PGC is better developed than that observed for PGC in CP aggregates.

In order to understand the occurrence of carbon-2H in CP aggregates, we refer to literature on low-temperature alteration of hydrocarbon compounds under natural conditions [15, 16]. We will discuss the formation of carbon-2H as a low-temperature metastable phase, because other processes for the formation of stable carbon-2H in an interstellar, or early Solar System, environment are not readily invoked for primitive extraterrestrial materials such as CP aggregates. For example, carbon-2H is a stable high-temperature/high pressure polymorph of carbon that can form from pure graphite at temperatures >1000°C and static pressures >130 kbar [17]. Carbon-2H may also form via intense shock metamorphism of pure graphite [18, 19]. However, solar flare track [5] and noble gas [20] data show that CP aggregates are not part of larger (e.g. meteoroid size) bodies during Solar System transit. Thus, intense shock events through impact with meteoroids, or larger-sized bodies, are unlikely formation mechanisms for carbon-2H in CP aggregates. In addition, parent bodies for CP aggregates are probably porous and of low density (e.g. cometary-like [21] and would not provide an environment suitable for high-temperature and/or high pressure transformations. These arguments indicate that carbon-2H formed at, or before, the accretion of CP aggregates into planet-sized bodies.

Catalytically activated hydrous pyrolysis of hydrocarbons may be a likely process for the formation of some carbon phases in CP aggregates. This mechanism may be appropriate if temperatures are below 300 to 350°C [22]. Indeed, temperatures during formation of CP aggregates, and even carbonaceous chondrite parent bodies, are considered low [3, 23-25]. Catalytically activated hydrous pyrolysis of hydrocarbons, particularly kerogens, is an important process for the diagenesis of terrestrial hydrocarbon deposits below temperatures of 350°C [15, 16]. Kerogen is thermodynamically unstable and in a terrestrial environment, with increasing time and temperature, will decompose into successively more stable phases such as graphite, CO_2, CH_4 and N_2. This irreversible decomposition process may proceed along complex pathways with a variety of intermediate phases [22, 26]. At the low temperatures for primitive extraterrestrial parent bodies, the kinetics of alteration reactions will dominate this catalytic hydrous pyrolysis mechanism.

Few studies on the kinetics of hydrous pyrolysis are available but some general conclusions may be drawn from current work: : (a) reasonable yields of pyrolysis products are obtained on geological timescales up to $\sim 10^7$ years [15]; (b) hydrous pyrolysis is catalytically activated by layer silicates [15]; (c) the efficiency of the catalytic process depends, among other parameters, on the possibility of readsorption of pyrolyis products onto the surface of catalysts [15] and (d) the pyrolysis temperature of the reactions is more important than the effect of total pressure or the presence of a catalyst [16, 22]. Most importantly, only pyrolysis in the presence of an aqueous phase produces the soft, i.e. well-graphitisable, carbons [22] which with continued heat-treatment can transform to PGC [14].

We propose that carbon-2H forms as a crystalline metastable product of catalytically activated hydrous pyrolysis of hydrocarbons (following the Ostwald Step Rule) in primitive extraterrestrial materials. This proposition can be supported by the mineralogy of CP aggregates and may even prove tenable for carbons in many carbonaceous chondrites [27]. For example, a variety of low-temperature minerals including layer silicates have been observed in five CP aggregates [cf. ref. 3] and layer silicates are abundant in CI and CM carbonaceous chondrites [25, 28]. In addition, previous observations on carbon phases in both types of primitive extraterrestrial materials [2] as well as the possible conditions of their formation [1, 21, 27] suggest that low-temperature diagenesis involving catalytic reactions may be a primary mechanism for the formation of the mineralogy observed in many CP aggregates. This mechanism may also prove viable for some components of carbonaceous chondrites, as suggested by Anders and co-workers [29], provided these catalytic reactions go to completion. In addition, a precise understanding of the complex pathways for the formation of carbonaceous compounds and carbon phases may allow detailed interpretations of isotopic variations (e.g. changes in D/H ratios [cf. ref. 26]) noted for CP aggregates [30] and carbonaceous chondrites [31].

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hkil	W7029*A	W7010*A2	CARBON-2H*	hkl	W7029*A	ALLENDE CV3	COLD BOKKEVELD C2	ORGUEIL C1
				002	3.50 (3.47-3.53)	3.47 (3.39-3.51)	3.6 (3.4-3.9)	3.8 (3.5-4.1)
$10\bar{1}0$	2.185 ± 0.015	2.17	2.18		2.18 ± 0.03	--	--	--
				100	2.09	2.10	2.10	2.09
0002	--	--	2.06					
$10\bar{1}1$	--	--	1.93					
				004	1.75 ± 0.03	1.73	--	--
					1.635	--	--	--
$10\bar{1}2$	--	--	1.50					
$11\bar{2}0$	1.26 ± 0.01	1.265	1.26		1.265 ± 0.015	--	--	--
	1.195 ± 0.01	1.19		110	1.19 ± 0.02	1.22	1.21	1.21
$10\bar{1}3$	--	--	1.17	006	1.16	1.16	--	--
$11\bar{2}2$	1.085 ± 0.015	1.09	1.075	200	1.09 ± 0.02	1.06	1.05	--
				106	1.01	--	--	--
					0.92	--	--	--
					0.87	--	--	--
2110	0.81 ± 0.02	--	--	210	0.82 ± 0.02	0.83	--	--
	0.72 ± 0.015	--	--	300	0.725 ± 0.015	0.71	--	--

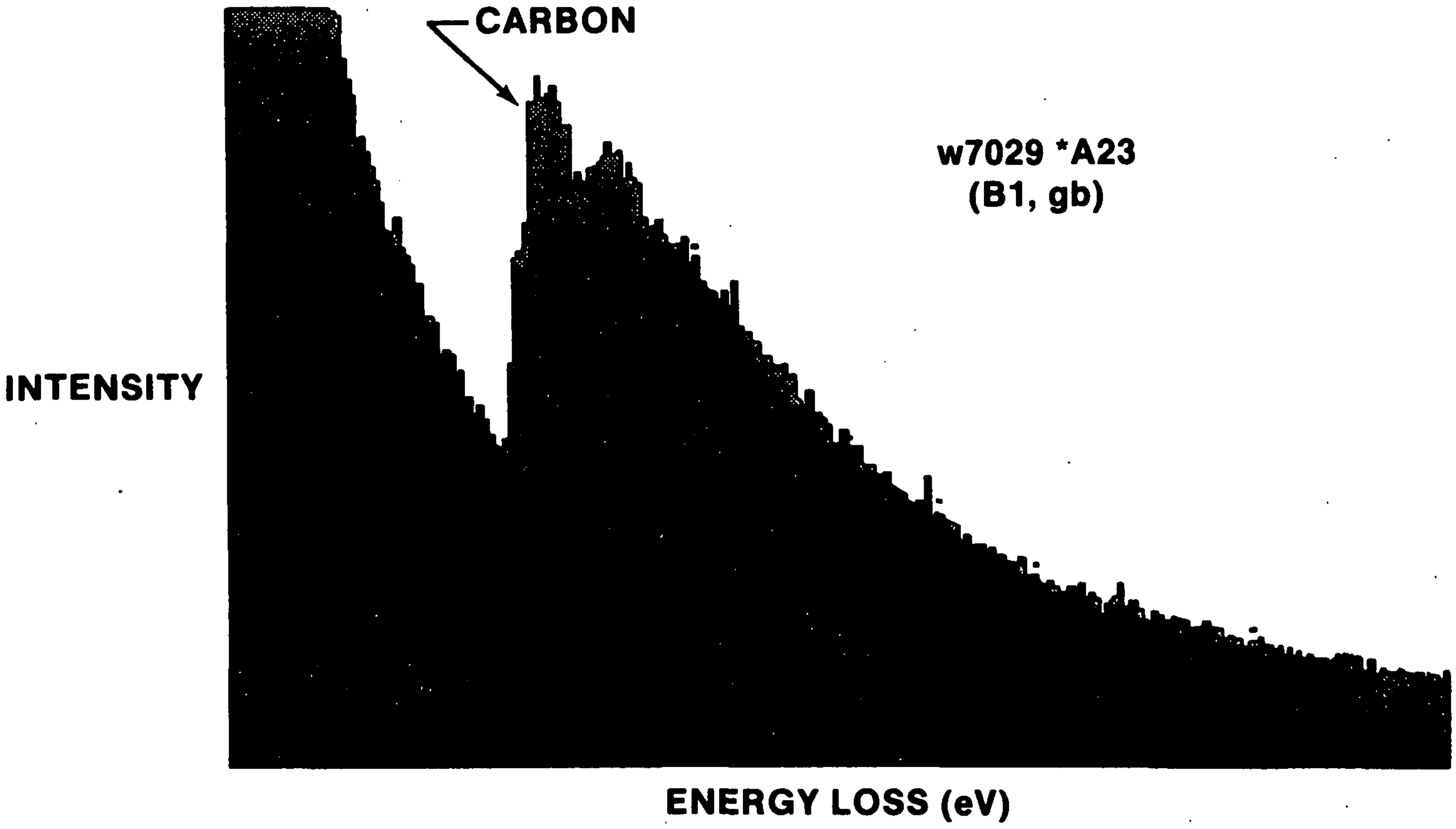
CARBON
w7029 *A23
(B1, gb)
INTENSITY
ENERGY LOSS (eV)

TABLE 1: Interplanar spacings (Å) for carbon sheets from CP aggregates W7029*A and W7010*A2 compared with interplanar spacings (Å) for carbon-2H [18] and poorly graphitised carbons in CP aggregate W7029*A [2] and selected carbonaceous chondrites [13].

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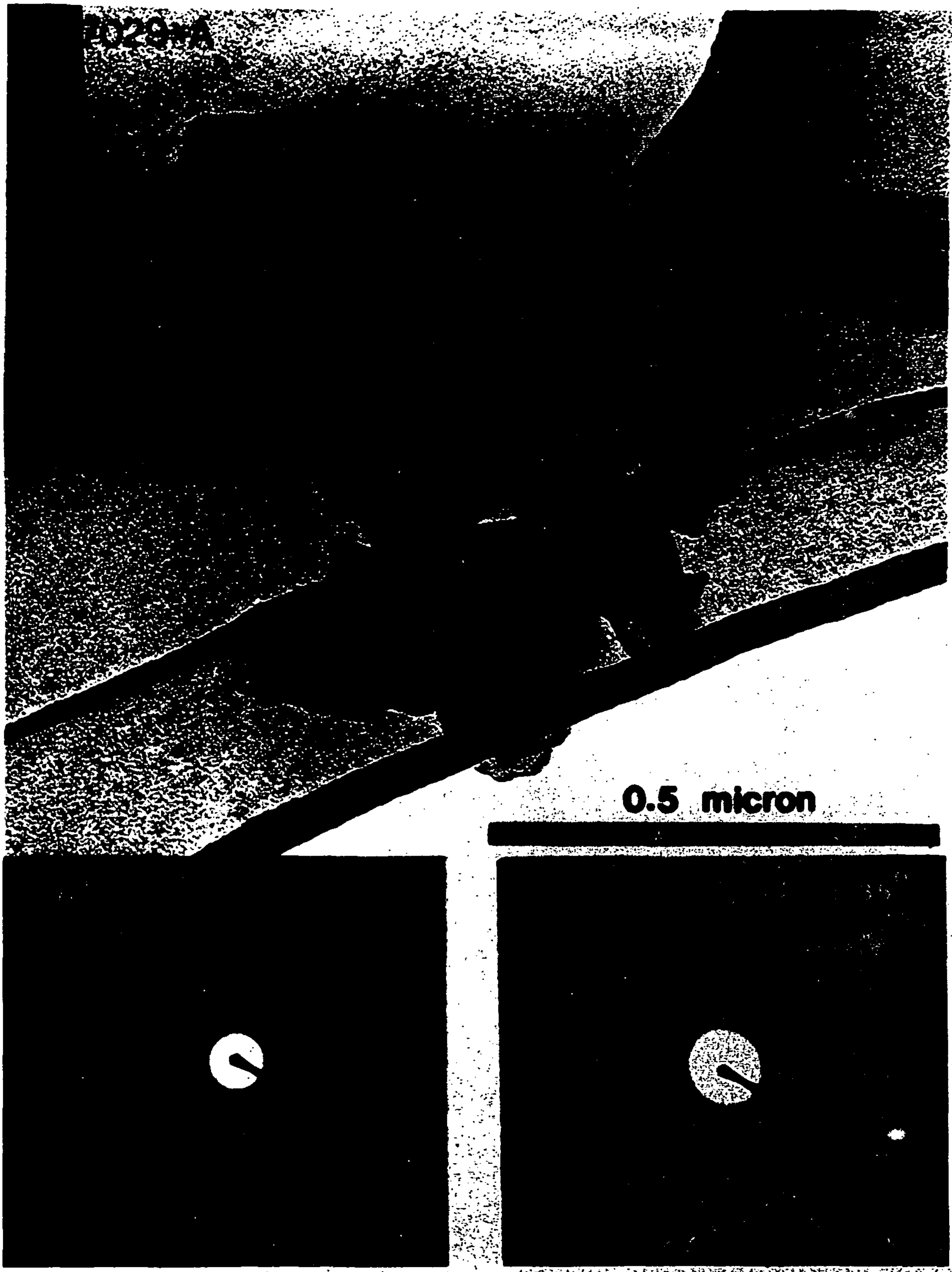

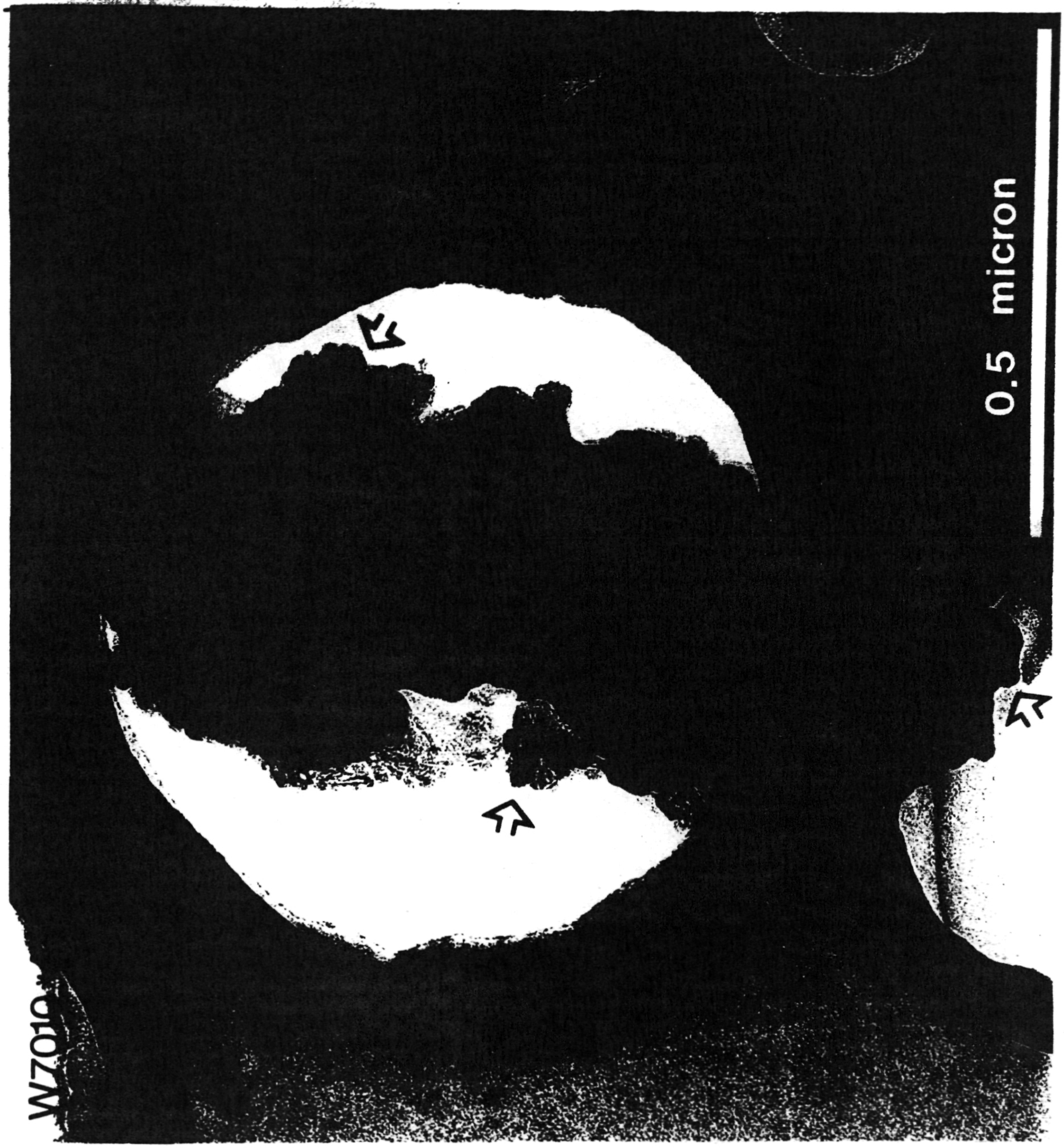
0.5 micron
W7010

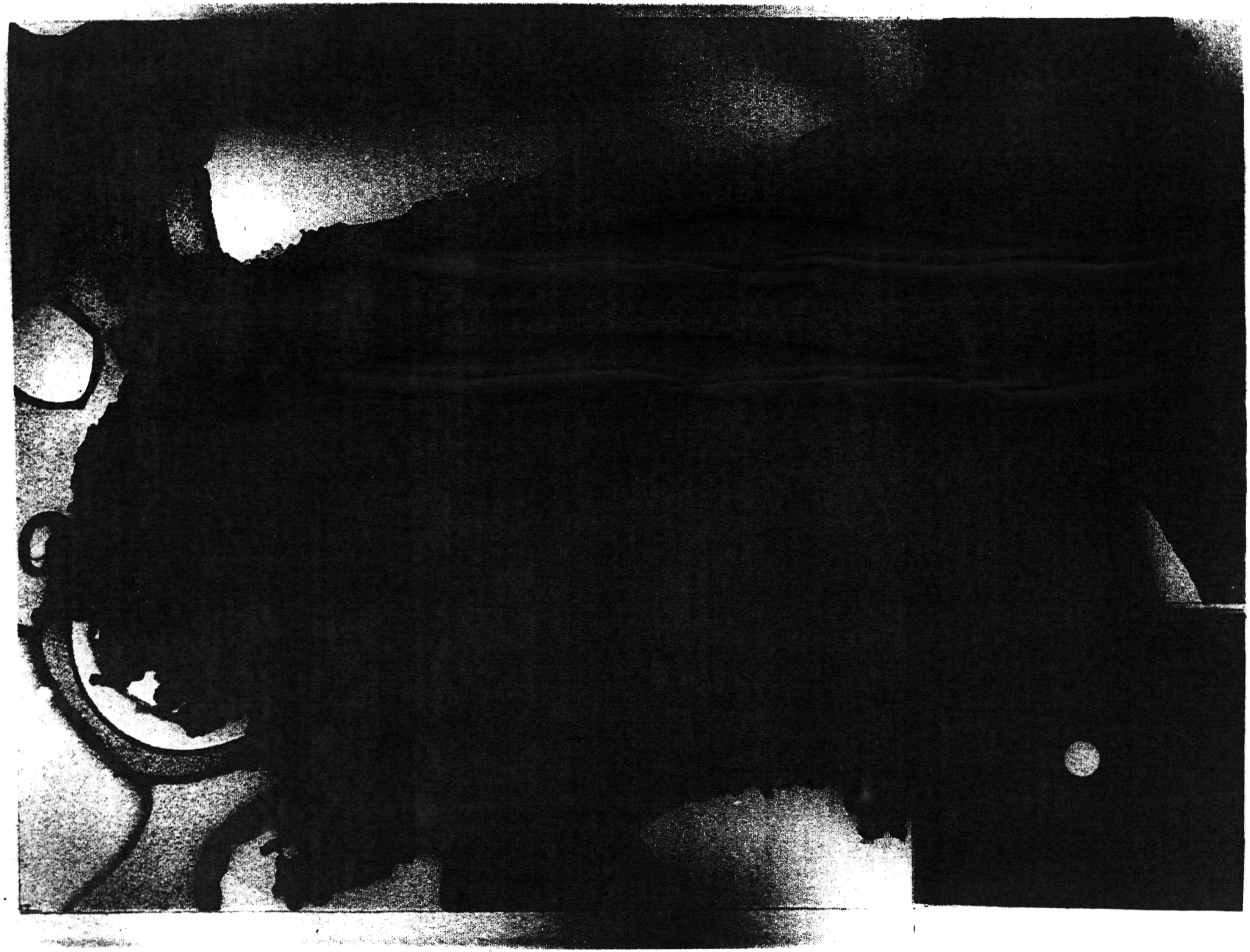

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FIGURE 1: [A] Large carbon-2H with domains of poorly graphitised carbon (left-hand side). The SAED pattern (inset) is consistent with carbon-2H.

[B] Electron energy loss spectrum on thin, smooth carbon-2H grain shown in Figure 1A.

FIGURE 2: Carbon-2H in CP aggregate W7029*A showing small areas of electron beam damage (arrowed). SAED patterns are shown for two different tilt orientations relative to the incident electron beam and are typical for carbon-2H.

FIGURE 3: Carbon-2H occurrence in CP aggregate W7010*A2 showing small areas of electron beam damage (arrowed).