carotenoid and chlorophyll pigments in natural photosynthetic assemblies are held in place by strong noncovalent interactions with membrane proteins. Large-amplitude motions by the carotenoid and chlorophyll molecules are probably much more restricted in their natural environment than in solution. Thus if a carotenoid is not in a favorable relationship with a chlorophyll molecule before generation of the triplet, it will not be able to compete favorably for it with the small, mobile oxygen molecule.

The observation that antenna function and photoprotection both ultimately require very close approach of chromophores is germane to recent work by Parson and Monger (*9*) with bacterial reaction center preparations. They found that sensitization of the carotenoid triplet ceases at very low temperature (< 20 K) and suggested that temperature-induced structural changes shift the electronic energy levels of the pigments so that population of the carotenoid triplet is unfavorable. Although not reported to date, the persistence of antenna function at these temperatures would strongly support this interpretation. An alternate interpretation, a structural change affecting the orientation and distance between the chromophores, would be indicated by concomitant loss of antenna function at very low temperatures.

These results and those reported previously (*3*) suggest that photoprotection through quenching of the chlorophyll triplet by carotenoids can be extremely effective if protection is accorded to key chlorophyll molecules (such as those in the energy transduction pathway and in the reaction centers) which are likely to undergo intersystem crossing under saturating conditions in vivo. Scavenging of previously formed singlet oxygen by carotenoids (*10*) likely also occurs, but is inherently less efficient because the carotenoid must compete with all other potential reactants for this deleterious species.

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Carbyne Forms of Carbon: Do They Exist?

Abstract. *Almost 15 years have passed since carbynes entered the literature as new forms of elemental carbon. They recently attracted attention as possible interstellar dust constituents and as carriers of presolar noble gases in meteorites. Their existence and that of the related mineral chaoite are questioned, and a reevaluation of previous data is suggested.*

In 1967 Kasatochkin *et al.* (*1*) reported the synthesis of a new polymorph of elemental carbon, known as carbyne, with a structure consisting of linear chains of carbon atoms linked by alternating single and triple bonds. In subsequent studies (*2*) the Russian group suggested the existence of two polymorphs, α- and β-carbyne, and proposed a hexagonal crystal structure in which the carbon chains are aligned parallel to the crystallographic *c*-axis. A naturally occurring form of carbon, described in 1968 by El Goresy and Donnay (*3*) and given the mineral name chaoite by El Goresy (*4*), is considered by Whittaker and Kintner (*5*) to belong to the carbyne series. More recently, Whittaker (*6*) reported the synthesis of eight or more polymorphs of carbyne and found several of these occurring as intergrowths in natural graphites (*7*). Carbynes have also been suggested as possible constituents of the interstellar dust (*8*).

Interest in the carbynes was heightened 2 years ago with the report that they are carriers of isotopically anomalous noble gases in carbonaceous chondrite meteorites, including some noble gas components believed to be of presolar origin (*9, 10*). However, recent work by Smith and Buseck (*11, 12*) and by Lumpkin (*13*) casts doubt on the identification of carbyne; these authors find instead that the carbon in such meteorites is predominantly a poorly ordered graphite.

Carbynes have generally been recognized by their characteristic hexagonal [0001] electron diffraction patterns; however, as we pointed out previously (*12*), the sheet silicate minerals give rise to hexagonal diffraction patterns with a similar range of interplanar spacings (*14*). Because of this potential for misidentification and because of the questions raised by the studies of carbon in meteorites, we reexamined some reported occurrences of carbynes, including chaoite. We used a transmission electron microscope (TEM) equipped with an energy-dispersive x-ray spectrometer (EDS) to check the chemical composition of possible carbyne grains.

Chaoite was first discovered as thin (3 to 15 μm wide) lamellae in graphite in a shock-fused gneiss from the Ries meteorite crater (West Germany) (*3*). We obtained a polished section of this material from A. El Goresy, who identified a graphite-chaoite intergrowth for us. Our observations of this sample by reflected light microscopy differ in two respects from the previous account (*3*), so we describe them here. The chaoite lamellae are optically isotropic and have a poorer polish and much lower reflectivity than the graphite. The graphite lamellae stand up slightly in relief, suggesting that chaoite is the softer of the two phases. Our observations concerning the reflectivity and hardness thus differ from those of El Goresy and Donnay (*3*), who described the chaoite as much more strongly reflecting than graphite and also slightly harder.

Analyses of this sample, made with a scanning electron microscope equipped with an EDS, show the presence of silicon (1.0 to 2.5 percent by weight) and aluminum (0.3 to 1.0 percent by weight) together with a trace of iron. These impurities are not concentrated in either component of the lamellar intergrowth, although their distribution is not completely uniform. The graphite-chaoite intergrowth grains that were made available to us are too small (~ 10 μm in diameter) to permit their safe removal from the rock slice for study by TEM. However, in order to characterize the phase or phases responsible for the impurities noted above, we extracted a somewhat larger grain that appeared optically to consist entirely of graphite. We crushed this grain between two clean glass slides and transferred it to a perforated amorphous carbon support film for examination by TEM.

The graphite crystals give single-crystal [0001] electron diffraction patterns, but most areas also give a superposed powder diffraction pattern resulting from a second phase. The five measured *d*-spacings for this powder phase are in reasonable agreement with the strongest *hk*0 reflections for a nontronite clay with a *b*-cell dimension of 8.98 ± 0.02 Å (Table 1). EDS spectra from areas that give the powder diffraction rings show peaks for silicon and iron with minor aluminum and calcium; the EDS spectra are similar to those obtained from a nontronite standard. Thus it appears that the impurities noted above are due to finely dispersed nontronite crystals oriented with their *c*-axes parallel to that of the host graphite; because of the preferred orientation only the *hk*0 reflections occur in the electron diffraction patterns. The nontronite has presumably been deposited along cleavage planes in the graphite; it may well have formed by alteration of the glassy matrix of the rock. We also found minor amounts of kaolinite, another clay mineral, associated with the graphite.

If the (001) reflections for a typical nontronite are included it appears that the nontronite associated with the graphite could account for five of the *d*-spacings of chaoite observed by El Goresy and Donnay (*3*). A sixth reflection, that at 4.12 Å, was observed for two nontronite samples by Gruner (*15*), but has not been reported subsequently.

In addition to the possible interference by nontronite, many of the reflections reported for chaoite correspond to quartz lines, as noted by Fleischer (*16*). The correspondence is striking: 11 of the 22 reflections listed for chaoite agree to within 0.4 percent or better with *d*-spacings for quartz (Table 1). Many of these reflections fit better with quartz than they do with *d*-spacings calculated for chaoite. Five quartz peaks of moderate to strong intensity are absent from the chaoite pattern reported by El Goresy and Donnay (*3*), but these all lie very close to peaks for graphite and would therefore have been excluded from the published data. El Goresy (*17*) feels that contamination of the sample by quartz is unlikely since chaoite was found only in rocks in which the silicates are fused to glass. However, there is still much quartz present in the sample that we examined and we suspect that quartz may inadvertently have been included in the x-ray mount that was used in the previous study (*3*).

Since we were not able to examine the lamellar intergrowth grains by TEM, our observations provide only circumstantial evidence concerning the identity of chaoite. However, it is clear that nontronite and quartz contaminants could account for all but five of the x-ray reflections previously attributed to chaoite. We therefore consider that the x-ray data of El Goresy and Donnay (*3*) provide insufficient evidence on which to base the identification of a new mineral.

Table 1. Complete powder diffraction pattern (*d*-spacings in angstroms) for chaoite (*3*), showing the correspondence with reflections for quartz (*26*) and for the nontronite contaminant in the Ries graphite. The reference pattern for nontronite is sample D of Eggleton (*27*).

Chaoite	Quartz	Nontronite in Ries graphite	Nontronite (*hkl*)
4.47		4.48	4.52 (020, 110)
4.26	4.26		
4.12*			
3.71			3.71 (004)
3.22			
3.03			3.02 (005)
2.94			
2.55		2.57	2.59 (200, 130)
2.46	2.458		
2.28	2.282		
2.24	2.237		2.26 (040, 220)
2.10			
1.983	1.980		
1.910		1.70	
1.496		1.50	1.522 (060, 330)
1.370	1.375, 1.372		
1.289	1.288	1.30	1.31 (400, 260)
1.26	1.256		1.26 (420, 170, 350)
1.197	1.200		
1.184	1.184		
1.080	1.082		
0.8642			

*Possibly due to an impurity (*3*).

A more recent report of chaoite is that of Setaka and Sekikawa (*18*), who examined shock-compressed synthetic glassy carbon by TEM. They found a few grains that gave hexagonal electron diffraction patterns with a *d*-spacing of 4.47 ± 0.02 Å. We examined a sample of this material, which was kindly provided by N. Setaka. In a search of one TEM mount we located eight grains that give hexagonal diffraction patterns, but chemical analysis by EDS shows that these grains are all muscovite mica. Using an internal diffraction standard, we measured a *d*-spacing of 4.52 ± 0.02 Å for these grains, consistent with the identification as muscovite. We consider that the error limits in the diffraction measurement quoted by Setaka and Sekikawa are probably overoptimistic, since they did not use an internal standard, and that the chaoite reported in the shock-compressed carbon (*18*) may well be muscovite, which is present as a minor contaminant in this sample.

We have described elsewhere (*12*) our observations on the glacier spherule material that was reported by Herr *et al.* (*19*) to contain carbynes. We examined two TEM mounts of this material provided by A. G. Whittaker. Two specific grains identified by Whittaker as the carbon polymorph carbon VIII were identified by us as talc, and we found many other sheet silicate grains on the same TEM mounts.

Our observations of the acid residue BK from the Allende meteorite have also been described in detail (*12*). This sample was reported to contain carbyne (*9*). We did not find any carbyne-like grains on a TEM mount of BK that we prepared. However, on a TEM mount provided by Whittaker we found 11 sheet silicate grains with d_{020} spacings that could cause them to be misidentified as carbynes. All grains that gave carbyne-type electron diffraction patterns were shown by EDS analysis to be silicate minerals. In an earlier study of an Allende residue (*11*) we found a small fraction of possible carbyne grains; subsequent EDS analyses showed that these are kaolinite (*12*).

In summary, it appears that these four published examples of carbynes do not withstand close scrutiny. In all cases the diffraction observations can be explained by the presence of minor quantities of sheet silicates, together with quartz in the case of the x-ray diffraction study of chaoite (*3*). It may appear surprising that a contaminant phase could have been misidentified as carbyne; however, it should be noted that in many of the reported electron diffraction studies (*1, 2, 9, 18*) crystalline carbyne grains appear to be a minor constituent of the whole sample. Also, up to 2.5 percent silicon by weight was found as an impurity in the carbyne sample described by Whittaker and Kintner (*5*). It is clear that in future searches for carbyne EDS analyses should be used to verify the chemistry of individual carbyne candidate grains.

Apart from diffraction observations, carbynes have been reported from negative-ion mass spectra obtained from an ion probe (*9, 19*). In this method the carbynes are recognized by their characteristic spectrum, in which the abundance of even-numbered carbon species is considered to reflect the tendency of a $-C\equiv C-C\equiv C-$ chain to cleave at the single bonds rather than at the triple bonds. Whittaker *et al.* (*9*) used reference spectra for graphite and the carbyne polymorphs to estimate the carbyne content of their sample; since the reference spectra have not been published it is difficult to comment on this work. However, the relative enrichment C_4^-/C_3^- of 2.1 to 3.0 reported by Herr *et al.* (*19*) and considered to be indicative of carbyne is close to the value of 2.0 obtained for amorphous carbon by the same technique (*20*) and less than the value of 4.1 reported for the thermal evaporation of graphite (*21*). Such enrichments of C_{2n}^- species in carbon vapors are in agreement with calculations of electron affinities based on molecular orbital theory (*22*) and can therefore be explained without the need for a carbyne phase. Pending the publication of further details concerning the reference spectra used in the identification of carbynes and the characterization of the reference standards (which must be based on electron diffraction and microanalysis), we consider that the negative-ion spectra do not provide compelling evidence for the existence of carbynes.

Doubts about the existence of carbynes have also been raised by Bundy (*23*), who questioned the reproducibility of Whittaker's phase equilibrium data (*6*), and by Jansta and Dousek (*24*), who questioned the thermodynamic stability of the proposed linear chain carbon structure. Another problem is the hexagonal, flakelike morphology reported for the carbynes (*25*), which suggests a sheet structure rather than the proposed structure of chains running parallel to the sixfold symmetry axis. In view of these concerns as well as the possibility of misidentifying sheet silicates as carbynes, we conclude that the evidence available at present is insufficient to establish the existence of the carbynes as new polymorphs of carbon.

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Geochronology of Type Uquian (Late Cenozoic) Land Mammal Age, Argentina

Abstract. *Mammal faunas collected from the Uquía Formation at Chucalezna and Esquina Blanca in Jujuy Province, northwest Argentina, are calibrated by potassium-argon age determinations and paleomagnetic polarity data. The sediments range in age from 2.5 million years old to perhaps as young as 1.5 million years, from late Pliocene through early Pleistocene, and correspond in time to late Blancan and early Irvingtonian land mammal age faunas in North America.*

In South America, as in North America, Cenozoic land mammal faunas from scattered localities are used by vertebrate paleontologists to subdivide geologic time. This practice has resulted in recognition of land mammal ages, which are based on aggregates of genera and species of fossil land mammals whose members are thought to have existed during a restricted interval of geologic time (*1*). A relative time scale for mammalian succession in South America is now agreed upon, and many beds and faunas have been partially calibrated by radioisotopic age determinations, magnetostratigraphic correlation with the magnetic polarity time scale, or both (*2, 3*). These geochronologic data are used to verify and refine the ages of the beds as inferred from composition and stage of evolution of the mammalian faunas.

Following establishment of the Panamanian land bridge about 3 million years ago, a reciprocal and apparently balanced interchange of the long-separated North and South American biotas occurred (*4*). The beginning of this interchange in South America is marked by the record of two mammalian genera (*5*) of North American origin in beds of Chapadmalalan (conventionally late Pliocene) age and about 20 mammalian genera (*5*) in beds of Uquian (conventionally early Pleistocene) age in Argentina (*6, 7*). Uquian faunas thus record the first major contingent of North American participants in the interchange.

We report radioisotopic age determinations and paleomagnetic data for faunas of Uquian age from the study of stratigraphic sections at Chucalezna and Esquina Blanca (about 4 km north of Chucalezna) in Jujuy Province, northwest Argentina (Fig. 1). Esquina Blanca,

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