

MATRICES OF CARBONACEOUS CHONDRITE METEORITES

*Peter R. Buseck and Xin Hua*¹

Departments of Geology and Chemistry, Arizona State University,
Tempe, Arizona 85287

KEY WORDS: transmission electron microscopy, matrix mineralogy, inter-
planetary dust, phyllosilicates

1. INTRODUCTION

Carbonaceous chondrite meteorites (CCs) are the most chemically primitive macroscopic solids in the solar system. They are nebular leftovers and are thus invaluable recorders of some of the oldest and best kept secrets regarding the formation and early history of the solar system. With a U/Pb age of 4.56×10^9 years, they are also the oldest known materials, 0.6 billion years older than the most ancient terrestrial rocks (Chen & Wasserburg 1981, Bowring et al 1990). They contain mineral grains that occurred in and even preceded the solar nebula. As relics of material that formed the sun and planets, they are a totally unique resource and have thus received intensive study. Yet, in spite of revealing many intimate secrets of solar system formation, they have, paradoxically, also proven remarkably intractable. Matrix is perhaps the least understood major component of CC meteorites.

Matrix is the background “sea” in which the chondrules, inclusions, and larger mineral grains occur. It is finely comminuted material that mainly consists of the anhydrous phases of meteorites, such as olivine, pyroxene, and Fe/Ni metal, together with lesser amounts of Fe oxides and sulfides, carbonates, sulfates, and a variety of other minerals that are generally present in only minor amounts. Some meteorites contain significant amounts of phyllosilicates, and these have been the focus of much

¹ Permanent address: China University of Geosciences (Wuhan), PR China

study and attention. The interplanetary dust particles (IDPs) are in some ways similar to the CC matrix in both mineralogy and composition, but the IDPs are even finer grained, which suggests that they are a related but distinct class of materials. The focus of this review is the matrix of the CCs.

There is much interest in matrix because (a) it contains a wealth of mineralogical and chemical information about the early history and subsequent development of the CCs (some of the minerals are intact from the time of the solar nebula, which is the earliest stage of the solar system that we can ever hope to understand in reasonable detail); (b) it forms a significant fraction of the highly important CCs; (c) it has long been difficult to study—a result of its extremely fine-grained, opaque character; and (d) it provides a model for studying alteration processes in the early solar system.

Much matrix appears to have developed from the primary anhydrous minerals olivine, pyroxene, and metal. It appears that accretion brought these minerals to a variety of meteorite parent bodies. It is probable that cometary debris and similar hydrated materials were included among the samples collected by the parent bodies and subsequently buried as other rocks rained onto the parent body surfaces. A variety of events, not all of which are known, then combined to produce alteration reactions. Regolith gardening, produced by the infall of other meteorites, resulted in collisional heating, fragmentation, and mixing of surficial rocks. These sources of energy, possibly combined with gentle heating from radioactive decay of unstable nuclides, provided the heat necessary for alteration.

Three features of CC matrices are of particular interest:

1. Tiny diamonds and crystals of SiC have recently been found in these meteorites (Lewis et al 1987, Tang & Anders 1988b, Bernatowicz et al 1987); their isotopic compositions indicate that they had their origin in circumstellar or interstellar space, outside of the solar system (Tang et al 1989, Zinner et al 1989, Lewis et al 1989, Huss & Lewis 1990). These are the first minerals about which it can be said with confidence that they are older than the materials of the solar system.
2. It has long been known that the bulk chemical composition of the CI meteorites closely matches that of the solar photosphere (Holweger 1977, Anders & Ebihara 1982), and yet recent work has shown that aqueous alteration is pervasive in at least some of these meteorites (Tomeoka & Buseck 1988, Zolensky & McSween 1988). It is apparent that the alteration must have occurred in a largely closed system so that it did not change the bulk composition significantly. Yet there are questions whether some of the alteration occurred prior to incorporation into a parent body. Paradoxically, the meteorite group that is

most primitive chemically (CI) is not the same as those that are physically most pristine (CO and CV). (The symbols for the meteorite types are defined in Section 3.)

3. The minerals of the matrix, because of their fine-grained, reactive character, provide a sensitive indicator of secondary processes such as heating, shock, and aqueous alteration. Unraveling these effects is required before a comprehensive understanding of the early solar system can be achieved.

Because much matrix appears to have developed as a result of alteration, or was profoundly affected by it, considerable emphasis in this review is placed on alteration minerals, processes, and mechanisms. Determining the temperatures, pressures, oxidation conditions, and durations of these alteration reactions is one of the challenging aspects of research on CC matrices. The resulting information provides insights into activities in the early solar system.

On a personal note, the senior author has long been both intrigued and frustrated regarding the character of CC matrix. Prior to the mid-1970s, the available mineralogical techniques were inadequate to provide much insight into the character of CC matrix. However, with the advent of the transmission electron microscope (TEM) as a viable mineralogical tool, especially through the use of high-resolution transmission electron microscopy (HRTEM), it became possible to image and study minerals as fine grained as those in the CC matrices (Buseck & Iijima 1974).

In order to achieve the goal of understanding the HRTEM images of the minerals in CC matrices, we embarked on a systematic series of studies to obtain the requisite knowledge and experience. Our investigations of pyroxene (Iijima & Buseck 1975, Buseck & Iijima 1975), micas (Iijima & Buseck 1978), serpentines (Veblen & Buseck 1979), and pyrrhotite (Pierce & Buseck 1974) were all part of that effort. Because of the problems of radiation damage, efforts to image clays (Mckee & Buseck 1978) of the types thought to occur in CCs had only limited success. However, in the late 1970s and early 1980s, several TEM studies of CC matrices appeared (Mackinnon & Buseck 1979; Barber 1981; Mackinnon 1982; Tomeoka & Buseck 1982a,b, 1983c). These and subsequent studies established the details of the secondary minerals that occur in the matrices.

It is now widely accepted that the TEM is a necessary tool for studying the details of matrix mineralogy, but only relatively few such studies have been completed (although the number is increasing steadily). As a result, the following discussion and generalizations are based disproportionately on those CC meteorites whose matrices have been studied using TEM techniques.

The main differences in the alteration products in matrix among different CC samples are (a) their amounts, (b) the phyllosilicates (generally either serpentine or saponite, a clay), and (c) the Fe-bearing phases (troilite, magnetite, maghemite, ferrihydrite, or a variety of poorly crystallized oxyhydroxides of uncertain character). Other alteration minerals that show differences in occurrence, abundance, and distribution include carbonates and sulfates.

Recent reviews that describe aspects of the matrices of the carbonaceous chondrites are by Scott et al (1988) on the matrix material itself, Barber (1985) on layer silicates within stony meteorites, Zolensky & McSween (1988) on the aqueous alteration, Grimm & McSween (1989) on the thermal evolution of carbonaceous chondritic parent bodies, and Tomeoka et al (1989) on alteration mineralogy of the CM meteorites.

2. MORPHOLOGY AND GENERAL CHARACTERISTICS

When viewed in hand specimen or at moderate magnifications using a conventional petrographic microscope, matrix is opaque, black, and relatively featureless—an appearance that visually distinguishes the CCs from other meteorites. The grain sizes of its constituent minerals range from $\sim 5 \mu\text{m}$ down to the limit of optical resolution. Using a TEM, it is evident that grains as small as a few nm in diameter can occur. Grain sizes vary with CC type (Scott et al 1988); they are smallest in the CRs (Zolensky 1991) and largest in the CVs. The minerals of matrix include typical CC anhydrous silicates such as olivine and pyroxene, as well as lesser oxides, carbonates, and sulfates. Also prominent are alteration products such as serpentines, other layer silicates, and hybrid phases such as tochilinite.

Definitions of matrix vary widely (see Scott et al 1988 for a review). For present purposes we include polyphasic material with grains smaller than $5 \mu\text{m}$ in diameter, in agreement with many others (Huss et al 1981, Nagahara 1984, Scott et al 1988, Brearley 1989); in many cases such material is interstitial to coarser crystals or crystal fragments, composite inclusions, or chondrules. By polyphasic we include regions where several grains are clustered and exclude small monophasic inclusions within larger crystals. The $5\text{-}\mu\text{m}$ size is arbitrary, and in specific cases the grains could be larger (e.g. Kallemeyn et al 1991). McSween & Richardson (1977) on the basis of their study of matrix compositions, redefined matrix as “all those low-temperature components which are genetically related and which, taken together, properly represent the composition of the primitive matter from which they formed.” While intriguing, this is a difficult definition to use because it presupposes we know which parts of the meteorite are pri-

mordial and also which parts are “genetically related.” Subsequently, McSween (1979a) defined matrix “operationally” as everything that is not recognizable petrographically as something else (i.e. chondrules, inclusions, lithic and mineral fragments, or opaque minerals).

Scott et al (1984) distinguished no fewer than seven types of matrix occurrences, ranging from lumps and clasts to rims of chondrules for the ordinary chondrites and the Vigarano (CV) meteorite. Clasts are common and can be of other types of meteorites than their hosts, giving rise to the interpretation that some CC meteorites were part of a regolith breccia (McSween & Richardson 1977, Bunch & Chang 1980), much like the surface of the moon. The clasts have typically been altered in whole or in part to phyllosilicate minerals, thereby complicating their recognition, although their outlines are retained. Bunch & Chang (1980) point out the common juxtapositions of altered and unaltered clasts, lending support to the mixing of fresh and altered material such as occurs on a parent body that is repeatedly impacted by falling bodies.

3. CLASSIFICATION

During the past three decades several versions of CC nomenclature have been used. For example, depending on when the paper was written, the Murchison meteorite is grouped with the type II, C2, or CM meteorites. Since these are all more or less equivalent, the terminology can be confusing. Therefore, in reviewing the literature of CCs it seems prudent to provide a brief summary of the terminology that is used so commonly for the CCs.

Based largely on the amounts of H₂O, S, and C, Wiik (1956) subdivided the CCs into types I, II, and III. In their “chemical-petrologic” classification of stony meteorites, Van Schmus & Wood (1967) retained Wiik’s groupings but changed their names to C1, C2, and C3, respectively, to be consistent with the other meteorite groups. The numerical designations reflect petrographic and mineralogical changes and extend to type 6. Type-3 meteorites are physically the most pristine, whereas types 2 and 1 contain increasing amounts of minerals typical of aqueous alteration. Types 4 to 6 show features that are compatible with progressively increasing intensities of thermal metamorphism. The C3 group was subsequently subdivided into C3(V) and C3(O) groups by Van Schmus (1969). That nomenclature was revised by Wasson (1974) to CI (for C1), CM (for C2), and CV and CO (for C3), where the second letters designate representative meteorites (Ivuna, Mighei, Vigarano, and Ornans, respectively). It is these last terms that are in current use. The several groups have distinctive mineralogical, chemical, and isotopic characteristics, although there is

Table 1 The classification of chondrites^a (a listing of some key taxonomic parameters)

GROUP	Al/Si	Mg/Si (normalized ratios)	Ni/Si	Zn/Si	FeO _x		
					FeO _x + MgO (mol%)	δ ¹⁷ O (‰)	δ ¹⁸ O (‰)
CV	1.34	1.00	0.85	0.25	35	-3	1
CO	1.07	0.97	0.87	0.21	33	-4	0
CM	1.10	0.97	0.92	0.48	43 ^b	1	7
CI	≅ 1.00	≅ 1.00	≅ 1.00	≅ 1.00	45 ^b	9	17

^a From *Philos. Trans. R. Soc. London Ser. A* 325: 535-44 (1988).

^b Estimated FeO_x/(FeO_x + MgO) for equilibrium assemblage.

overlap. Table 1 gives some salient chemical and isotopic characteristics for the major groups.

Recently, the CR (for Renazzo) and CK (for Karoonda) groups have been established for "anomalous" meteorites that do not comfortably fit into the above grouping. Their characteristics are given in Section 5.5. Both contain fewer meteorites than do the other CC groups, and so they have not received the extensive attention that the other major groups have had.

4. CHEMISTRY

4.1 *Inorganic Chemistry*

The chemical composition of the CCs, and the surprisingly similar abundances of their nonvolatile elements to those of the solar photosphere, is a major reason why the CCs are of such great interest and led to the conclusion that these meteorites are chemically primitive (Suess 1949, Suess & Urey 1956). Since the sun contains 99+ % of the mass of the solar system, its composition is considered representative of the solar system. The CCs contain the highest abundances of volatile elements of any meteorite group, an observation that is also supportive of their primitive origin since these elements tend to be depleted during geological processing. As a major component of CCs, matrix plays an important role in the search for pristine nebular materials and in understanding the early stages of the solar system. Other meteorites have experienced chemical fractionation such that their compositions deviate widely from that of the sun, as is also the case for all terrestrial rocks.

Although much has been written about the inorganic chemistry of the CCs, it is almost exclusively based on "whole-rock" analyses, and so it is

difficult to generalize about matrix composition using such data. Moreover, many CCs are brecciated and have a polymict character so that their compositions, while relatively homogeneous within a given clast, vary considerably from one clast to another. As a result, it is difficult to obtain reliable and representative matrix abundance data. However, *in situ* chemical analyses of CC matrices have been obtained by using broad-beam electron microprobe analysis (EMPA) (Fuchs et al 1973, Kerridge 1976, McSween & Richardson 1977, Rubin et al 1988, Scott et al 1988, Rubin & Kallemeyn 1990). Separated matrix has been analyzed by wet chemistry (Clarke et al 1970) and by instrumental neutron activation analysis (INAA) (Rubin & Wasson 1987, 1988).

The most thorough study of matrix compositions is by McSween & Richardson (1977), who analyzed 32 CCs using a defocussed beam with their electron microprobe. Although physical separation of matrix is not required with the microprobe, trace element abundances are not easily obtained. Rubin & Wasson (1987, 1988) determined the bulk matrix composition of CO3s and CV3s by INAA. However, their data differ significantly from the EMPA data of McSween & Richardson (1977). Rubin & Wasson indicate that these apparent discrepancies may arise from differences in methods of sampling and analysis, which points out a significant problem in the determination of average matrix compositions.

Larimer & Anders (1970) suggested that the CIs consist entirely of matrix, so their bulk analyses should provide direct matrix compositions. Compilations of CI elemental abundances are provided by Cameron (1982), Anders & Ebihara (1982), Wasson (1985), Anders & Grevesse (1989), and Wasson & Kallemeyn (1988); an evaluation of much prior work was made by Burnett et al (1989), who confirmed the previous abundance curves.

Figure 1 summarizes chemical data for the CC matrices. Since the water and organic contents within and among the several CC groups are variable, direct comparisons of matrix analyses are difficult. To minimize this problem, we adopt the method of McSween & Richardson (1977) by using Si-normalized weight ratios of the elements. The Na/Si ratios are depleted relative to the whole-rock analyses, with CI matrix the most depleted and CM the least. Na/Si ratios in CMs show much variation. Mg/Si ratios are unusual in being rather constant, with an average value of 0.822 ± 0.053 , similar to the value of ~ 0.910 from bulk analyses of CCs (McSween & Richardson 1977). Al/Si ratios show large variations, especially in the CM and CVs, and differ from the average Al/Si ratio of 0.083 in bulk analyses of CCs. K/Si ratios vary such that $CI > CM > CO, CV$. The K/Na ratios in the matrices are almost five times higher than those in the whole rock (Wiik 1956, Bunch & Chang 1980). Ti/Si, Cr/Si, and Mn/Si ratios are

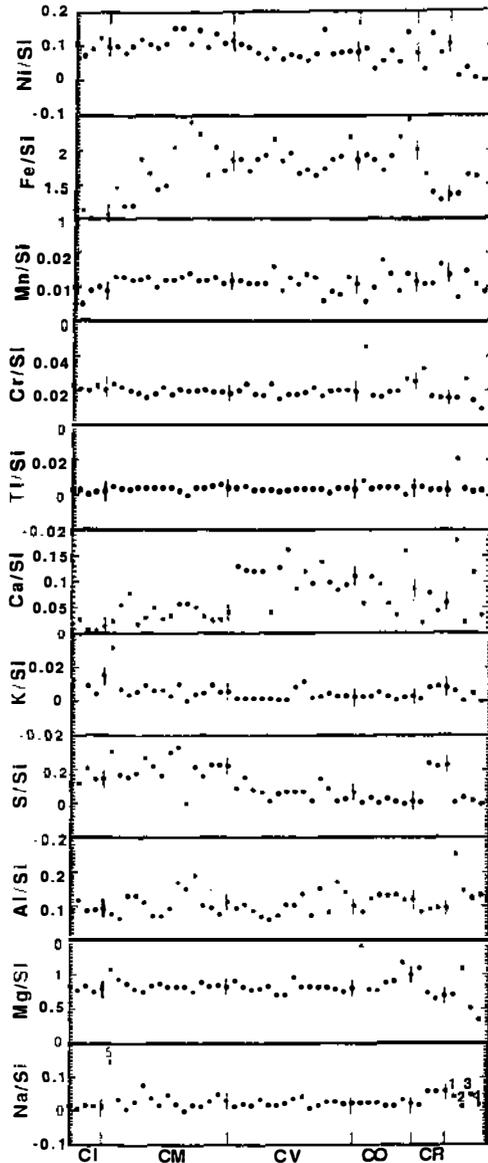


Figure 1 Compilation of chemical analyses of CC matrices, all normalized to Si. The average value for each subgroup is indicated with a bar. Meteorites that either do not belong to the indicated CC groups or that are of uncertain type are numbered: 1. Karoonda (CK); 2. Warrenton (CO?); 3. Ningqiang (CK?); 4. Lewis Cliff 85332; 5. Kakangari.

Sources of data are: 1. McSween & Richardson (1977, EMPA); 2. Kerridge (1976, EMPA); 3. Fuchs et al (1973, EMPA); 4. Clarke et al (1970, WCA); 5. Scott et al (1988, EMPA); 6. Rubin & Wasson (1988, INAA); 7. Rubin et al (1988, EMPA); and 8. Rubin & Kallemeyn (1990, EMPA). EMPA: electron microprobe analysis; WCA: wet chemistry analysis; INAA: instrumental neutron activation analysis.

nearly constant from group to group, but the low bulk concentrations of Ti and Mn make the Ti/Si and Mn/Si values uncertain. Ca/Si ratios vary in the sequence CI < CM < CO, CV. This sequence is explained in part by exclusion of minerals in veins from the CI matrix analyses. Fe/Si in CIs (1.04 ± 0.06) is distinctly lower than the 1.857 ± 0.297 of the CMs, CVs, and COs; Ni/Si is much higher in CMs than in CIs, COs, and CVs; S/Si varies in CMs. Both the Ni/Si and S/Si ratios in CMs suggest the existence of a Ni-, S-, Fe-bearing phase.

McSween & Richardson (1977) compared published bulk compositions of the CCs to their EMPA analyses of matrix and found a difference exists for the CIs. Moreover, the CI bulk compositions agree better with the solar abundances than does the matrix, which is strongly depleted in Na, Ca, S, and Fe relative to solar abundances and to the other CCs. This depletion presumably reflects the CI compositional heterogeneity that occurs on the scale of microscopic clasts plus the fact that McSween & Richardson assumed that magnetite, calcium sulfate, and carbonate vein-fillings are not matrix components and so avoided obtaining EMPA analyses in regions where they occur. The CM matrix compositions are, in fact, closer to solar values than those of the CIs. This difference results from a combination of the extensive aqueous alteration and consequent chemical fractionation of the CIs plus the selective EMPA analysis mentioned above. Clearly, bulk rather than matrix CI compositions must be considered when comparisons to solar abundances are made.

The major element abundances of matrix group into clusters that correspond to the CC types (McSween & Richardson 1977). The CIs show considerable compositional variations among the various clasts that comprise what are probably polymict regolith breccias. CV and CO matrices contain lower amounts of Mg, Al, Ca, Ti, and S than do CIs and CMs, presumably because these elements have not been as extensively mobilized into matrix from chondrules, inclusions, and sulfides. Even though McSween & Richardson found that the differences in matrix chemistry among the various CC types is significant, they concluded that, in general, the chemical variations are relatively small.

4.2 *Organic Chemistry*

The CC matrix is host to a large variety of organic matter—partly soluble material but mainly insoluble macromolecular carbon. A fascinating aspect of such compounds is that some may be precursors of life, thereby giving their study extra significance. Murchison is the most thoroughly studied meteorite for its organic chemistry, but Orgueil, Ivuna, Murray, Renazzo, Cold Bokkeveld, and Allende have also received attention.

Although discrete organic compounds in CCs occur in amounts less

than 1 wt%, they are widespread and sufficiently abundant to be analyzed in detail by current techniques. They are most concentrated in those meteorites and in those portions of the meteorites that experienced the most intense aqueous alteration (Cronin et al 1988, Bunch & Chang 1980). These are the CM and CI matrices, in which 70 wt% of the carbon occurs in extremely fine-grained (≤ 50 nm) acid-insoluble macromolecular matter containing H, N, O, S, and perhaps halogens (Chang & Bunch 1986), and 30% is in organic compounds that are soluble in nonpolar organic solvents like CCl_4 or polar solvents like CH_3OH and water (Hayes 1967). However, the polar solvents used for the extractions do not clearly separate organic compounds from inorganic salts, leading to an overestimate of the soluble fraction; thus, the actual insoluble to soluble ratio is probably greater than 7:3 (J. Cronin 1992, personal communication).

Significantly smaller amounts of carbonaceous matter occur in COs and CVs; much of the carbon in the Allende CV3 occurs in its elemental form as poorly ordered, turbostratic graphite (Lumpkin 1981, Smith & Buseck 1981). Smith & Buseck (1981) showed a TEM image (Figure 2) of carbon

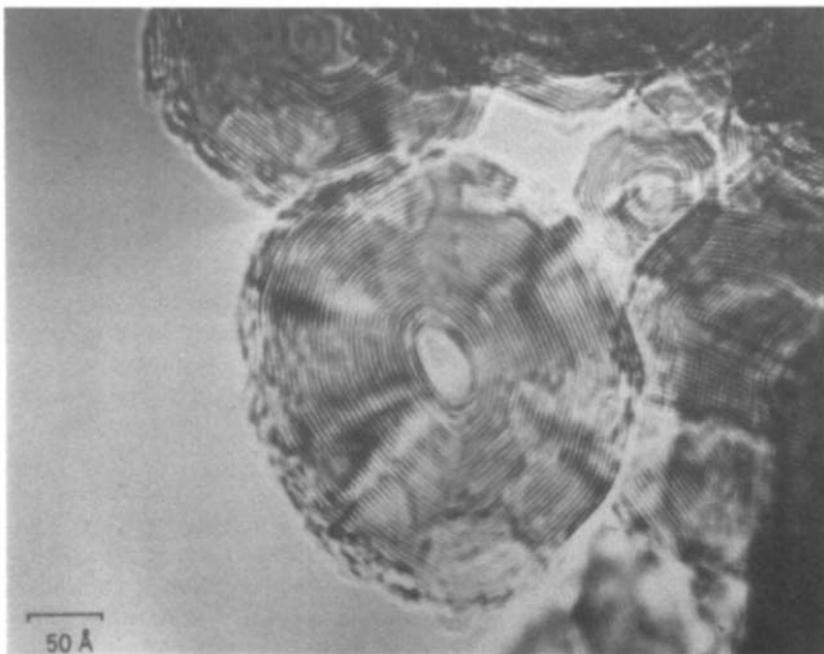


Figure 2 HRTEM image of round layered carbon, found in an acid-residue from Allende (Smith & Buseck 1981).

that resembles a hypothesized cross-section of the layered fullerenes that were recently proposed by Kroto et al (1985).

The macromolecular matter consists of both amorphous and poorly crystalline components including condensed aromatic, heteroaromatic, and hydroaromatic ring systems, cross-linked by short methylene chains, ethers, sulfides, and biphenyl groups (Hayatsu et al 1977, 1980; Cronin & Pizzarello 1986; Zenobi et al 1989; de Vries et al 1991). The soluble compounds include amino acids (Cronin et al 1988); aliphatic hydrocarbons (Cronin & Pizzarello 1990); aromatic hydrocarbons (Basile et al 1984); various carboxylic acids (Lawless et al 1974, Peltzer & Bada 1978, Yuen et al 1984); nitrogen heterocycles, amines, and amides (Hayatsu et al 1975, Jungclaus et al 1979); and alcohols and carbonyl compounds (Jungclaus et al 1976, Cronin et al 1988). Most data regarding the organic fraction of CCs have been obtained by analyses of bulk samples and are well reviewed by Cronin et al (1988) and Cronin & Chang (1992); a brief summary is given by Chang & Bunch (1986).

It would be desirable to know the exact location of the various organic compounds within different parts of the matrix. However, in situ studies of carbon and organic compounds are almost nonexistent—the result of the extreme challenge of analyzing the light elements in small sample regions. Two methods are currently available for such in situ analyses at high spatial resolution: (a) electron microscopy and (b) laser desorption combined with an analytical method such as mass spectrometry.

There is evidence from transmission electron microscopy that graphitic layers coat some mineral grains in Allende (Green et al 1971). However, currently the best hope for understanding in situ occurrences of organic materials in CCs are studies done by two-step, laser-desorption, mass spectrometry (L^2MS) (Hahn et al 1988, Zenobi et al 1989). This technique uses a CO_2 laser to volatilize neutral molecules intact from surfaces. After a 20- μs delay, a second laser (Nd:YAG) using the principle of resonance-enhanced multiphoton ionization (REMPI) selectively ionizes polycyclic aromatic hydrocarbons (PAHs) from among the vaporized desorbed species. These ions are passed into a time-of-flight mass spectrometer, which records species with masses up to ~ 1500 amu. The desorbing laser can be focused to a spot $\sim 40 \mu m$ in diameter, and the position of this spot can be monitored with an optical microscope with attached video camera. There is thus the possibility of selectively analyzing PAHs from specific places on the surface of a meteorite and correlating the results with mineralogical and textural observations, in effect giving rise to a microprobe for organic molecules. By using lasers having different wavelengths (or tunable lasers), it should be possible to analyze different types of organic species, especially if they are relatively volatile and ionizable.

L²MS studies indicate that a wide range of PAHs with extensively alkylated rings are heterogeneously distributed within the matrix of Allende. Major species include naphthalene, phenanthrene/anthracene, and their alkyl-substituted derivative, as well as a large range of heavier PAHs (Zenobi et al 1989). Specific correlations of particular organic species and inorganic minerals or structural features within the meteorites remain for the future.

Interstellar clouds, the solar nebula, and parent bodies within the solar system have each been proposed as locations where meteoritic organic matter formed (Miller 1955, Studier et al 1968, Khare & Sagan 1973, Hayatsu & Anders 1981, Greenberg 1984, Peltzer et al 1984). Based on the intriguing excess of deuterium in insoluble acid residues of meteorites, a relationship was suggested between meteoritic and interstellar organic matter (Kolodny et al 1980, Becker & Epstein 1982, Robert & Epstein 1982, Yang & Epstein 1983, Yuen et al 1984, Epstein et al 1987, Kerridge et al 1987). Some noble gases that have anomalous isotopic compositions are enriched in the acid-insoluble residues—an observation that also supports an interstellar origin (Anders 1981, Lewis & Anders 1981, Tang et al 1988). Shock & Schulte (1990) provide evidence that extraterrestrial amino acids and phyllosilicates formed in the same aqueous alteration events, presumably on the parent bodies of meteorites, as discussed in Sections 5 and 6. It seems clear that the formation of organic materials in the meteorites involved a combination of both interstellar and solar system abiogenic processes and environments.

δD and $\delta^{13}C$ values correlate with molecular species (Krishnamurthy et al 1991), whereas the macromolecular carbon is lighter and lies off the correlation line. The enrichment in deuterium implies an interstellar synthesis and suggests that at the radial distance of the asteroids (2–4 AU), in the approximate region where the primitive meteorites occur, the environment was not too harsh to preclude the survival of preexisting C-C and C-H bonded material. This material, which presumably predated the solar system, was then modified by the aqueous alteration that is so prominent in the CM and CI chondrites, consistent with the correlation of organic matter with extent of aqueous alteration (Cronin & Chang 1992).

4.3 *Isotope Chemistry*

During solar system formation and subsequent evolution, several processes took place that were recorded by the isotopic compositions of meteoritic material. As summarized by Clayton (1986), processes occurring at $T < 50$ K in a pre-solar molecular cloud caused isotopic variations of H, C, and N; evaporation caused by transient heating in the nebula and subsequent

recondensation led to large isotopic fractionation effects in Mg and Si and smaller effects in Ca and Ti; oxygen underwent large-scale isotopic exchange between solid and gaseous reservoirs. Continuous isotopic exchange of oxygen occurred within planetary bodies during melting and igneous differentiation, thermal metamorphism, and aqueous alteration. We focus on the isotopes of O, H, C, and N in the following section because they seem most likely to have recorded changes that occurred in the matrix. Isotopic data for organic species were discussed in Section 4.2.

Many isotopic measurements of CCs exist. Some are of particular fractions (e.g. magnetic, nonmagnetic, carbonates, acid-insoluble residues) while others are of unseparated pieces, producing “whole-rock” values. Certain measurements occur over a range of temperatures—the result of step-heating experiments. This potpourri of data is difficult to compare and summarize because the values are from different fractions or they were obtained under varied conditions. (For reviews of the implications of isotopic measurements in meteorites see Begemann 1980, Anders 1987, Clayton 1986, Grady et al 1988). Our Table 2 and Figure 3 indicate the ranges in $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and δD values by CC type. For details, we refer the reader to the references listed in the table. It is evident that the isotopic results are widely scattered and, not surprisingly, for a given CC type they are dispersed in proportion to the number of meteorites studied. It is difficult to be confident about trends from such a mixed set of measurements, but certain patterns can be discerned. In general, ^{17}O , ^{18}O , ^{15}N , and ^{13}C show the greatest enrichments among the meteorites that have most clearly been exposed to hydrous, low-temperature environments.

The whole-rock $\delta^{18}\text{O}$ measurements show the only clear trend. They indicate a progressive increase through the series CO, CV, CR, CM, and CI. The $\delta^{18}\text{O}$ trend for the carbonates, on the other hand, is weaker and somewhat different, going from CV, CO/CI, CM, and at the high end, CR. For the $\delta^{13}\text{C}$ whole-rock measurements, the corresponding trend is CO/CV, CI/CM, and CR. For the $\delta^{15}\text{N}$ whole-rock measurements, the trend is similar to that for $\delta^{13}\text{C}$: CO/CV, CI, CR, and CM; the last two types are interchanged. Finally, for the δD whole-rock measurements, the trend is CI/CV, CM, and CR. CM and CI values are interchanged for the acid-insoluble residues.

The isotope compositions can be used to provide information regarding the sources and subsequent events involved in the formation of CC matrices. Although the basis of their interpretation has been challenged by Thiemens (1988), Clayton & Mayeda (1984) proposed a widely accepted model of two oxygen reservoirs and two episodes of fluid-solid interaction for the origin of CMs. The reservoirs initially had different oxygen-isotope abundances, with the solid-phase reservoir enriched in ^{16}O , while the gas-

Table 2 Summary of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and δD measurements of carbonaceous chondrite matrices

Group	Meteorite	Fraction	$\delta^{18}\text{O}_{\text{SMOW}}$		$\delta^{13}\text{C}_{\text{PDB}}$		$\delta^{15}\text{N}_{\text{AIR}}$		$\delta\text{D}_{\text{SMOW}}$	
			(‰)	Refs	(‰)	Refs	(‰)	Refs	(‰)	Refs
CI	Alais	whole rock	*15.85/16.84 [3]	1	−6.6/−15.6 [1]	2, 3	31/52 [3]	4	44/223 [3]	4, 5
	Ivuna	carbonate	11.9/30.55 [3]	6	23.3/70.2 [3]	6, 7				
	Orgueil	non-magnetic	17.82 [1]	1						
CM	26 meteorites analyzed	magnetic	17.35/19.26 [1]	1						
		HF-HCl residues	−23.6/3.7 [1]	15	−19.4 [1]	3	27 [1]	3	950/1150 [1]	3
		bulk matrix	10.90/12.61 [3]	1	−0.4/−22.0 [15]	4	13/47† [11]	4	−176/990 [15]	4
		carbonate	19.2/35.3 [26]	6	1.9/80.7 [26]	6				
		HF-HCl residues			−13.0/−14.6 [3]	3	18/29 [3]	3	650/830 [3]	3
CR	Al-Rais	whole rock	1.5/6.8 [4]	13	−9.9/−11.8 [2]	4, 8	140/190 [2]	4, 3	520/1014 [2]	5, 9
	Renazzo	carbonate	23.1/33.8 [3]	6	54.3/65.4 [3]	6				
CV	Y 790112	HF-HCl residues			−21.0 [1]	3	150/175.6 [3]	3, 14	2500 [1]	3
	7 meteorites analyzed	bulk matrix	2.10/3.72 [1]	10, 11	−12.8/−21.6 [7]	4	−43/24 [7]	4, 12	−77/440 [7]	4
CO	5 meteorites analyzed	carbonate	12.3/18.9 [1]	6	−6.3/−7.4 [1]	6				
		whole rock	−2.3/0 [4]	13	−14.2/−19.3 [5]	4	−30/13 [5]	4	−147/2150 [5]	4
		carbonate	17.5/25.0 [3]	6	−16.9/5.2 [3]	6				

* The slash signifies a range; e.g. 15.85/16.84 indicates the smallest and largest values.

† The 335 value for $\delta^{15}\text{N}$ in Bells is far higher than any other CM meteorite and has not been included in the table.

[#] indicates the number of measured meteorites to which this range applies; in several cases multiple measurements were made.

References:

1. Clayton & Mayeda (1984); 2. Boato (1954); 3. Robert & Epstein (1982); 4. Kerridge (1985); 5. Yang & Epstein (1983); 6. Grady et al (1988); 7. Smith & Kaplan (1970); 8. Grady et al (1983); 9. McNaughton et al (1982); 10. Clayton et al (1976); 11. Clayton et al (1983); 12. Kung & Clayton (1978); 13. Clayton & Mayeda (1989); 14. Grady et al (1991); 15. Halbout et al (1986).

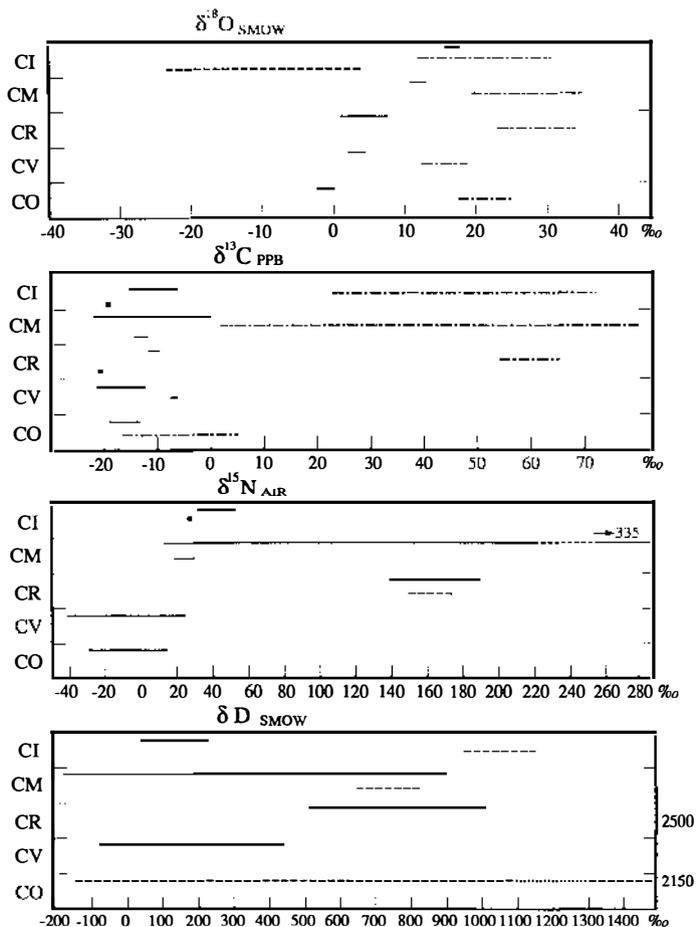


Figure 3 Summary of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and δD data for measurements on the whole rock or matrix, carbonates, and acid-insoluble residues of CCs. Solid line: data for whole rock or matrix; dashed line or the single dots: data for HF-HCl residues; dashed and dotted line: data for carbonates. The values are from Table 2.

phase reservoir, consisting principally of H_2O and CO , was depleted in ^{16}O . The two episodes were: 1. an incomplete exchange at high temperatures between solid (or melt) and gas to yield the oxygen isotope compositions of anhydrous silicates, and 2. alteration, much of which occurred at 20°C or less and that required at least 44% by volume of water to make the phyllosilicates and carbonates. In contrast, the CIs are more strongly depleted in ^{16}O than CMs, which suggests the alteration occurred in a

warmer, wetter environment, with temperatures ranging from 100 to 150°C. The CO and CV chondrites are relatively unaltered and therefore required only the high-temperature step.

Many assignments of Antarctic meteorites to specific groups based on oxygen isotope compositions differ from similar assignments based on mineralogy. These differences suggest an ambiguity in the distinction between CI and CM chondrites and a possible continuum of chemical, mineralogical, and isotopic features (Mayeda et al 1987). For example, Belgica-7904 is classified as a CM meteorite based on its mineralogy, but it is likely to be a CI meteorite according to its oxygen isotope composition; Yamato-82042 is just the reverse.

Unusually high D/H and $^{15}\text{N}/^{14}\text{N}$ ratios were found by Epstein et al (1987) in the amino acids and monocarboxylic acids extracted from the matrix of Murchison ($\delta\text{D} = 1370\text{‰}$, $\delta^{15}\text{N} = 90\text{‰}$). These values provide evidence for a relationship between the organic matter in CC matrix and interstellar clouds. As shown by Robert & Epstein (1982), D is extremely high (up to 3500‰) in acid residues. The D/H ratios of gases released on step heating vary with temperature above 400°C, which indicates that different hydrogen hosts in the acid residues have different isotopic compositions.

The meteoritic carbonates in CI, CM, and CR matrices are enriched in ^{13}C , with $\delta^{13}\text{C}$ ranging from 40 to 50‰ for CMs, 50 to 80‰ for CIs, and most values below 60‰ for CRs (Grady et al 1988). Carbonates are rare or absent in CV and CO meteorites. The carbonates in matrix are more ^{13}C -enriched than those derived from alteration of high-temperature inclusions, presumably because the ^{13}C -rich fluid could more easily percolate through the porous and fine-grained matrix than through the more indurated CAIs (Grady et al 1988).

Stepped combustion gives unusual isotopic results for C in the high-temperature fraction (above 650°C) of acid residues. These refractory carbonaceous materials have a $\delta^{13}\text{C}$ value of at least +1500‰ (Swart et al 1983, Yang & Epstein 1984), and in situ ion probe measurements show values as high as +7000‰ (Niederer et al 1985, Zinner et al 1986). These high values are presumably derived from refractory interstellar materials such as SiC and perhaps other carbides. The tiny diamond (2–10 nm) and larger SiC (0.1–1.0 μm) grains were found in acid residues from primitive meteorites (CCs, types 1 to 3 ordinary chondrites, and type 4 enstatite chondrites) (Huss et al 1981; Bernatowicz et al 1987; Tielens et al 1987; Tang & Anders 1988a,b; Huss 1990). Significantly, diamond and SiC as well as some amorphous carbon also show associated Ne and Xe anomalies and enrichment of heavy N, all of which point to an interstellar origin (Tang et al 1988, Anders et al 1988).

5. CC TYPE VS MATRIX MINERALOGY

5.1 *Matrix in CIs*

The CIs have the largest fraction of matrix among all known meteorites; they consist almost entirely of matrix, containing neither chondrules nor aggregates of anhydrous minerals. The rarity of CI meteorites may arise from the abundance of extremely fine-grained minerals, which leads to fragility and susceptibility to alteration. As a result, there have been relatively few detailed studies of their matrix mineralogy, although thorough studies exist for Orgueil, Ivuna, Alais, and Yamato-82162 (see Table 3 for references); the most carefully studied CI meteorite is Orgueil, which fell in 1864 in France.

Minerals occurring in CIs are summarized in Table 3. Phyllosilicates are major phases, but most are poorly crystalline and occur as extremely small crystals (see Table 4). Thus their identities are controversial. Using different techniques, a variety of conclusions have been reached, some of which conflict. For example, major phyllosilicates reportedly are serpentine and montmorillonite (Bass 1971—x-ray powder diffraction, Mackinnon 1985—analytical electron microscopy), smectite (Caillère & Rautureau 1974—electron diffraction, Fanale & Cannon 1974—adsorption measurements), Fe-rich chlorite or serpentine (Boström & Fredriksson 1966, Kerridge 1976—microprobe analyses), and chamosite (Zaikowski 1979—infrared spectroscopy).

A review of the papers describing matrix and alteration features in Orgueil is given by Tomeoka & Buseck (1988), who also did a HRTEM study of the matrix phases in an attempt to resolve questions regarding the matrix phyllosilicates and Fe-bearing phases. They found the major minerals to be Fe-bearing serpentine, saponite (a variety of trioctahedral smectite) (Figures 4 and 5), and ferrihydrite—a poorly crystallized S- and Ni-bearing ferric hydroxide of somewhat variable composition, together with lesser amounts of magnetite and sulfides (Figure 6). The serpentine and saponite occur in roughly equal molar proportions, are coherently intergrown, and occur in intimate association with the ferrihydrite, suggesting a related origin.

Ferrihydrite is dispersed in particles <8 nm in diameter; it contains ~60% of the Fe in matrix, which causes the superparamagnetic character of CIs (Wdowiak & Agresti 1984, Madsen et al 1986). Most remaining Fe is in the saponite, which accounts for 40% of the matrix Fe in CIs (Tomeoka & Buseck 1988).

The ferrihydrite is extremely fine grained, and it is probable that the high surface area acted as a “getter” for volatiles and minor elements, thereby contributing to its somewhat variable compositional and structural

Table 3 Matrix mineralogy of CCs

CC type	Major phases	Minor phases	Phyllosilicates	Meteorites represented	References
CU	olivine pyroxene	magnetite, Fe-Ni sulfides, enstatite, diopside, fassaite, andradite, chromite, spinel, anorthite, sodalite	montmorillonite*, saponite, Na-phlogopite*, margarite*, clintonite*	Allende, Kaba, Mokoia, Vigarano.	1 to 8
CO	olivine	Ca-rich & Ca-poor clinopyroxene, kamacite, taenite, magnetite, maghemite, ferrihydrite, ferroxhyte	serpentine	Lancé, Ormans, ALHA77307, Kainsaz, Warrenton, Isna; inclusions in Murchison, Isna.	5, 10, 11
CM	phyllosilicate tochilinite	olivine, pyroxene, pentlandite, pyrrhotite, magnetite, calcite, aragonite, dolomite spinel, brucite, iron-hydroxide, alkali- halides (NaCl, KCl), carbonaceous matter	cronstedtite, greenalite, antigorite, chrysotile	Murchison, Cold Bokkeveld, Nawapali, Cochabamba, Mighei, Murray, Yamato 82042, Yamato 86720, ALH84034, Nogoya; xenoliths in Jodzie	3, 9, 12 to 26
C1	phyllosilicate	magnetite, olivine, pyroxene, ferrihydrite, pentlandite, pyrrhotite, troilite, cubanite, dolomite, ankerite, aragonite, vaterite, ferroan magnesite, gypsum, hexahydrite, blödite, epsomite, carbonaceous matter	serpentine, montmorillonite, smectite, chlorite, chamosite, saponite	Orgueil, Ivuna, Alais, Yamato-82162	25, 28 to 51
CB	olivine pyroxene	plagioclase, metal, sulfides	saponite, serpentine	Renazzo, EET87770, Essebi, MAC87300	49

* Minerals occur in CAIs. We include them here for comparison.

character. The ferrihydrite adsorbed much S and Ni onto its surfaces, which helps explain the high content of S in CI matrix (Boström & Fredriksson 1966) and the correlation of S and Ni (Kerridge 1977, McSween & Richardson 1977). It has an approximate formula of $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ (Chukhrov et al 1973).

Relatively minor phases include magnetite and vein fillings of Mg and Ca sulfates (mainly epsomite and gypsum), together with dolomite, breunnerite, and magnesite as the carbonate phases (DuFresne & Anders 1962, Boström & Fredriksson 1966, Richardson 1978). Magnetite in CIs displays a variety of morphologies; it occurs in framboids, spherulites, plaquettes, and a variety of miscellaneous shapes (Jedwab 1971, Kerridge et al 1979, Tomeoka et al 1989). Isolated carbonates and sulfates provide strong evidence of aqueous alteration on the parent bodies (Boström & Fredriksson 1966, Nagy 1975, Fredriksson & Kerridge 1988).

5.2 *Matrix in CMs*

CMs contain between 57 and 85 vol% matrix (McSween 1979a), with the remainder consisting of chondrules, CAIs, and isolated mineral fragments. CM matrix is a complex assemblage consisting mainly of phyllosilicates and PCP (see definition below), with lesser amounts of carbonates, sulfides, oxides, hydroxides, silicates, alkali halides, and organic matter (Table 3). The most detailed observations on CM matrix are of Murchison, but Cold Bokkeveld, Nawapali, Cochabamba, Mighei, Murray, Yamato-82042, Yamato-86720, Nogoya, ALH-84034, and CM-like xenoliths in Jodzie have also received careful attention (see Table 3 for references).

Products of aqueous alteration (Table 4) are ubiquitous in CMs and in

References:

1. Tomeoka & Buseck (1982a); 2. Cohen et al (1983); 3. Tomeoka & Buseck (1985); 4. Tomeoka & Buseck (1990); 5. Keller & Buseck (1990a,b); 6. Zolensky et al (1989); 7. Keller & Buseck (1991); 8. Zolensky & McSween (1988); 9. Liorca & Brearley (1992); 10. McSween (1977); 11. Wood (1967); 12. Johnson & Prinz (1991); 13. Barber (1977); 14. Barber (1981); 15. Barber et al (1983); 16. Mckee & Moore (1979); 17. Mackinnon & Buseck (1979); 18. Akai (1980); 19. Mackinnon (1980); 20. Mackinnon (1982); 21. Bunch & Chang (1980); 22. Fuchs et al (1973); 23. Ramdohr (1973); 24. Tomeoka & Buseck (1983a,b); 25. McSween & Richardson (1977); 26. Bunch et al (1979); 27. Mackinnon & Zolensky (1984); 28. Bass (1971); 29. Caillière & Rautureau (1974); 30. Fanale & Cannon (1974); 31. Boström & Fredriksson (1966); 32. Kerridge (1976); 33. Zaikowski (1979); 34. Mackinnon (1985); 35. Tomeoka & Buseck (1988); 36. Tomeoka (1990); 37. Chukhrov et al (1973); 38. Herr & Skerra (1969); 39. Wdowiak & Agresti (1984); 40. Madsen et al (1986); 41. Nagy (1975); 42. Fredriksson et al (1980); 43. Richardson (1978); 44. Fredriksson & Kerridge (1988); 45. Jedwab (1971); 46. Tomeoka et al (1989); 47. Kerridge et al (1979); 48. Lewis & Anders (1975); 49. Zolensky (1991); 50. Kerridge (1977); 51. Brearley (1992).

Table 4 Secondary minerals in CC matrix

Group name	Mineral name	Basal spacing (nm)	CC type	Meteorites represented	Morphology	M/Si + Al	References
●Phyllosilicate	Serpentine	ferroan serpentine (Mg,Fe) ₃ Si ₂ O ₅ (OH) ₄	0.7–0.73	CO CR	Lance Renazzo	platy, ribbon-like tubes,	1 8
		cronstedtite (Fe ⁺² ,Fe ⁺³) ₃ (Si,Fe ⁺³)O ₅ (OH) ₄	0.7–0.73	CM	Cochabamba	fibers, flat &	1.5
		greenalite (Fe ⁺² ,Fe ⁺³) ₂₋₃ Si ₂ O ₅ (OH) ₄	0.7–0.73	CM	Cold Bokkeveld	corrugated	1–1.5
		ferroan antigorite (Mg,Fe,Mn) ₃ (Si,Al)O ₅ (OH) ₄	0.7–0.73	CM CI	Murchison Orgueil	sheets, cones	1.5
		chrysotile Mg ₃ Si ₂ O ₅ (OH) ₄	0.7–0.73	CM		tubes, fibers, flat & corrugated	1.5
Smectite	montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ n(H ₂ O)	1.0–1.4	CV CI	Allende	sheets	0.83
	saponite	(Ca _{0.5} Na) _{0.3} (Mg,Fe ⁺²) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·4H ₂ O	1.0–1.5	CV CI	Allende, Mokoia		0.83
	sobotkite	(Ca _{0.5} K) _{0.3} (Mg ₂ ,Al)(Si ₃ ,Al)O ₁₀ (OH) ₂ ·5H ₂ O		CR CV	Renazzo		
		Na-phlogopite	(Na,K)(Mg,Al,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂	1.0	CV	Mokoia	sheets
Mica*	margarite	Ca(Mg _{0.2} ,Al _{1.7})(Si _{1.8} ,Al _{2.2})O ₁₀ (OH) ₂	2.0	CV	Allende		0.73 19
	clintonite	Ca(Mg _{2.5} ,Al _{0.5})(Si _{1.6} ,Al _{2.4})O ₁₀ (OH) ₂	1.9	CV	Allende		0.95 19
Chlorite	chamosite (Fe ⁺² ,Mg,Fe ⁺³) ₅ Al(Si ₃ ,Al)O ₁₀ (OH) ₈	1.4	CI		sheets	1.5	15, 20

●Tochilinite	tochilinite $\sim \text{Fe}_{1.3}\text{Ni}_{0.1}\text{SO}_{1.4} \cdot \text{Mg}(\text{OH})_2?$	1.07– 1.13, 0.54	CM	Murchison	massive, tubes	4, 5, 11, 17, 21 to 30
	haapalaite $4(\text{Fe},\text{Ni})\text{S} \cdot 3(\text{Mg},\text{Fe}^{+2})(\text{OH})_2$		CM		fibers, flat & corrugated sheets	33
●Hydroxide	brucite $\text{Mg}(\text{OH})_2$	0.5	CM		sheets & filled tubes	5, 26, 28, 30, 37
	ferrihydrite $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$		CM CI			1, 20, 23, 31, 32, 34 to 36 20, 38 to 40
●Carbonate	calcite & aragonite (CaCO_3)		CM, CI	Orgueil		33
	dolomite $\text{Ca}(\text{Mg},\text{Fe}^{+2},\text{Mn})(\text{CO}_3)_2$		CM, CI			33
	ankerite $\text{Ca}(\text{Fe}^{+2},\text{Mg},\text{Mn})(\text{CO}_3)_2$		CI			33
	vaterite CaCO_3		CI			33
	ferroan magnesite $(\text{Mg},\text{Fe}^{+2})\text{CO}_3$		CI			33
●Sulfate	epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$		CI			33
	hexahydrate $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$					33
	gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$					33
	blödite $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$					33

* The micas may be primary; see text.

References:

- Keller & Buseck (1990a);
- Müller et al (1979);
- Barber (1977);
- Barber (1981);
- Mackinnon (1980);
- Tomeoka & Buseck (1988);
- Zolensky (1991);
- Tomeoka & Buseck (1982);
- Cohen et al (1983);
- Tomeoka & Buseck (1982);
- Tomeoka & Buseck (1985);
- Tomeoka & Buseck (1990);
- Bass (1971);
- Mackinnon (1985);
- Tomeoka (1990);
- Zolensky et al (1989);
- Bunch & Chang (1980);
- Zaikowski (1979);
- Keller & Buseck (1991);
- Boström & Fredriksson (1966);
- Fuchs et al (1973);
- Ramdohr (1973);
- McSween & Richardson (1977);
- Bunch et al (1979);
- Barber et al (1983);
- Mackinnon & Buseck (1979);
- Tomeoka & Buseck (1983a,b);
- Akai (1980);
- Mackinnon & Zolensky (1984);
- Mackinnon (1982);
- Chukhrov et al (1973);
- Kerridge (1977);
- Zolensky & McSween (1988);
- Herr & Skerra (1969);
- Wdowiak & Agresti (1984);
- Madsen et al (1986);
- Mckee & Moore (1979);
- Nagy (1975);
- Fredriksson & Kerridge (1988);
- DuFresne & Anders (1962).

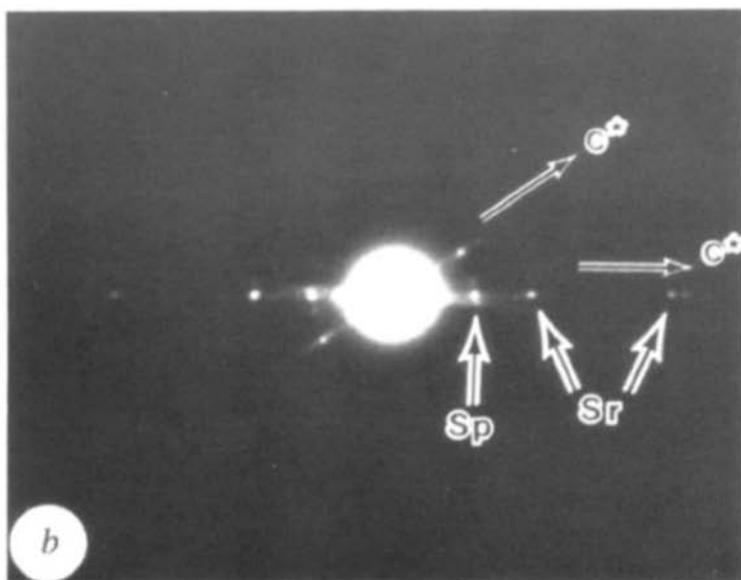
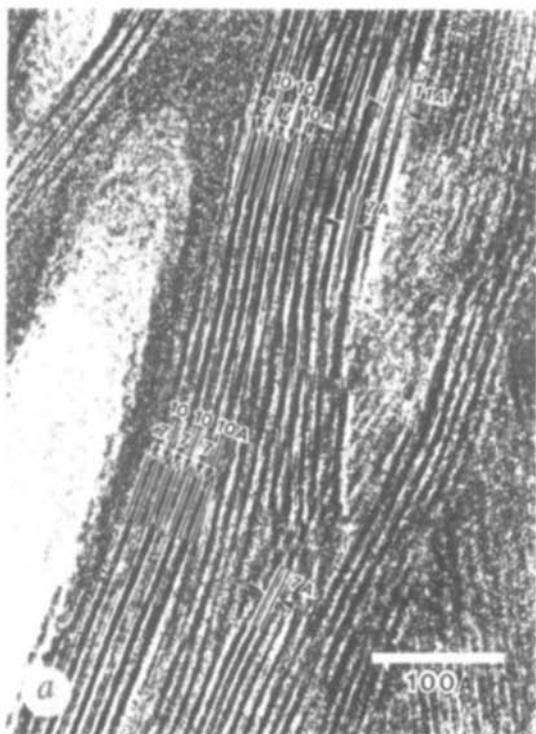
amounts far greater than those in CVs and COs. Relative to CIs, CMs lack saponite and ferrihydrite; instead, Fe-rich layer silicates such as cronstedtite, ferroan antigorite, and greenalite are the dominant fine-grained phases (Tomeoka & Buseck 1985a). TEM observations show a wide variety of morphologies (Figure 7).

Fuchs et al (1973), as a result of a careful examination of CM matrices, introduced two terms: "PCP" and "spinach." Both have been widely used. "Spinach," a semi-transparent, green, hydrated silicate within chondrules and commonly associated with anhydrous silicates in CMs, is an intergrowth of Fe-rich serpentines (Bunch & Chang 1980, Tomeoka & Buseck 1985a). If it occurs in matrix at all, it does so as a minor component. The situation for PCP, which is the second most abundant material in CM matrix, is more complex.

Identification of the mineral constituents of PCP has a complicated history. It was originally defined by Fuchs et al (1973) as *Poorly Characterized Phase* because its character could not be determined by the then standard methods of mineralogy. Bunch et al (1979) and Bunch & Chang (1980) identified three forms of PCP and suggested that it consists of an Fe-rich serpentine and an Fe-Ni-S-C-rich phase. A series of TEM studies sheds considerable light on its constituent minerals as well as on its origin and development (Mackinnon & Buseck 1979; Mackinnon 1980, 1982; Tomeoka & Buseck 1983a,b,c; Tomeoka & Buseck 1985a). As a result of those studies, Tomeoka & Buseck (1985a) redefined PCP as *Partly Characterized Phases*.

The mineralogical character of PCP was problematical both because of its fine-grained nature and its unusual mineralogy. It now seems widely accepted that it consists of an intimate intergrowth of cronstedtite and tochilinite (see Table 4 for their compositions), both of which are rare terrestrially. Tochilinite, a composite mineral consisting of alternating layers of mackinawite-like sulfide and brucite (Organova et al 1971), was recognized as the identity of a PCP constituent by Mackinnon & Zolensky (1984). Prior to that time, Mackinnon & Buseck (1979) had used transmission electron microscopy to identify alternating layers in PCP from the Murchison CM meteorite; the layers have spacings (~ 7 and 5 \AA) that they thought belonged to serpentine- and brucite-type minerals (Figure 8A). Tomeoka & Buseck (1983a,b,c) provided more detail regarding the struc-

Figure 4 Serpentine (Sr, 7-\AA layers)—saponite (Sp, 10-\AA to 11-\AA layers) intergrowths. (a) TEM image showing coherent but disordered intergrowths of the two silicates. (b) Selected-area electron-diffraction pattern showing diffuse streaks along [001], with intensity maxima corresponding to $\sim 7 \text{ \AA}$ (Sr) and $\sim 12 \text{ \AA}$ (Sp) spacings. [From Orgueil CI (Tomeoka & Buseck 1988).]



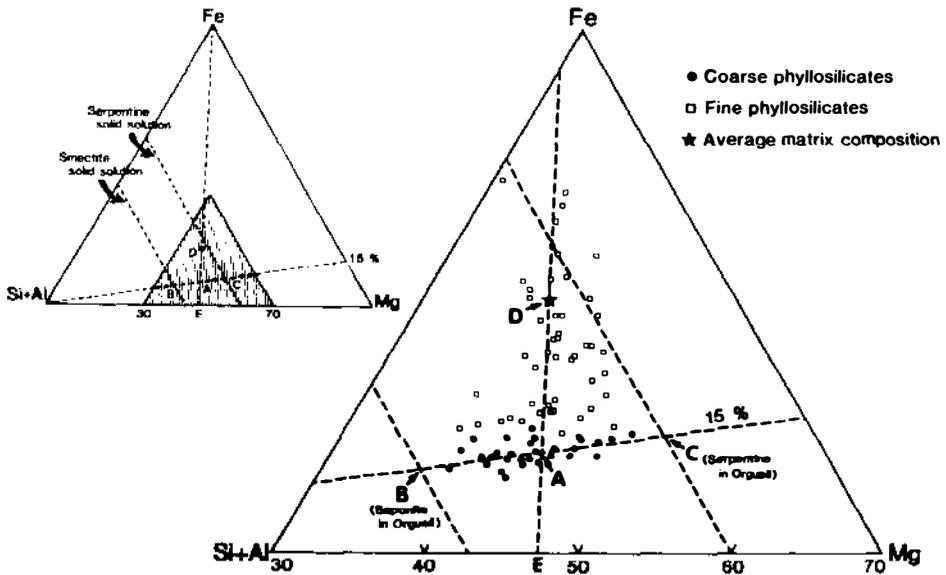


Figure 5 The ideal Mg-Fe composition lines for serpentine and smectite solid solutions. The shaded triangle is enlarged at the right. Line BC represents $\text{Fe}/(\text{Mg} + \text{Fe}) = 15$ atomic%, D represents the average matrix composition, and A shows the average composition of the matrix phyllosilicates in Orgueil. [From Orgueil CI (Tomeoka & Buseck 1988).]

tures and intergrowths of the two layer types; they also recognized the importance of sulfur in one set of layers. Barber et al (1983) found that PCP has an Fe/S atomic ratio of 1.4 and O/S ratio of 1.3.

A striking characteristic of the tochilinite in PCP is the wide variety of complex and beautiful forms it assumes (Figures 8A-F). Its undulatory character and its curved or even circular lattice fringes result from the misfit between the sulfide and hydroxide layers (Tomeoka & Buseck 1983b, Mackinnon & Zolensky 1984).

The origin and development of PCP was studied by Tomeoka & Buseck (1985a), who observed two major types. Type I occurs in chondrules and aggregates and consists largely of an Fe-Ni-S-O phase, presumably tochilinite; type II, in platelet and acicular fiber shapes, occurs in matrix and consists of tochilinite and cronstedtite. Microprobe analyses show variable S and Si contents, trace Cr and P, and low summations. It forms in cylindrical, corrugated, wavy, and ribbon structures in both ordered and disordered intergrowths. Most common is the ordered sequence with a ~ 17.8 -Å spacing (Tomeoka & Buseck 1985a), with 5.4-, 5.4-, and 7.0-

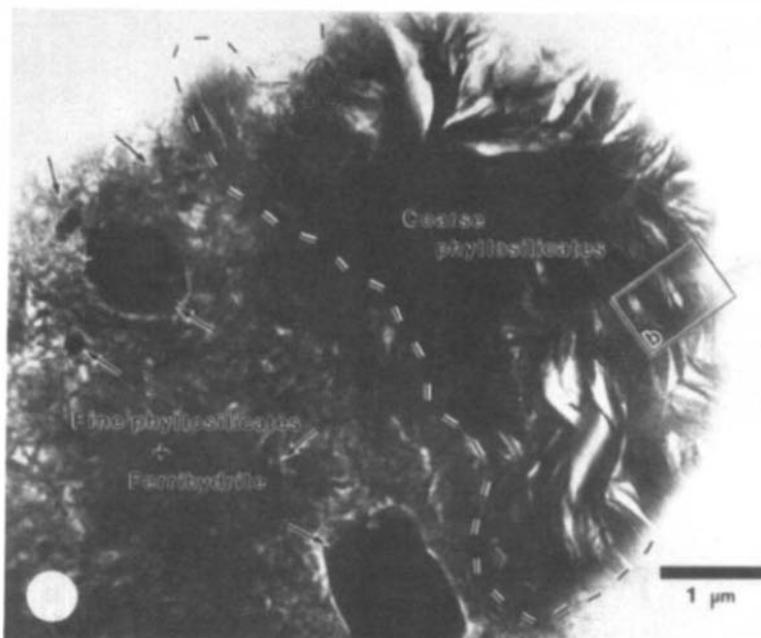


Figure 6 TEM image of ferrihydrite and adjacent phyllosilicates. Large ferrihydrite aggregates (*arrows*) occur together with fine phyllosilicates (left), whereas the coarse phyllosilicates (right) appear free of ferrihydrite. [From Orgueil CI (Tomeoka & Buseck 1988).]

Å spacings, which resembles the SBB sequence of Mackinnon & Buseck (1979; Figure 8A). We believe that further work on tochilinite is warranted.

Olsen et al (1988) described several xenoliths (inclusions having characteristics and perhaps sources that differ from their hosts) from the Murchison CM meteorite. These xenoliths have the mineralogical characteristics of other CC types. For example, their xenolith MX1 has alteration minerals (prominent among which is berthierine, a 1:1 Fe-rich layer silicate that is a member of the serpentine-kaolinite group) that bear a close resemblance to those of Lancé (Keller & Buseck 1990a), a CO3 meteorite.

5.3 *Matrix in CVs*

CV meteorites contain abundant chondrules, fragments of olivine and pyroxene, and refractory inclusions. Consequently they contain less matrix than CIs or CMs (35–50 vol%) (McSween 1979a). Typical matrix minerals such as phyllosilicates occur in at least small amounts in most CVs, and they provide important insights into alteration histories. In Allende most phyllosilicates occur in the Ca-, Al-rich inclusions (CAIs) and in some

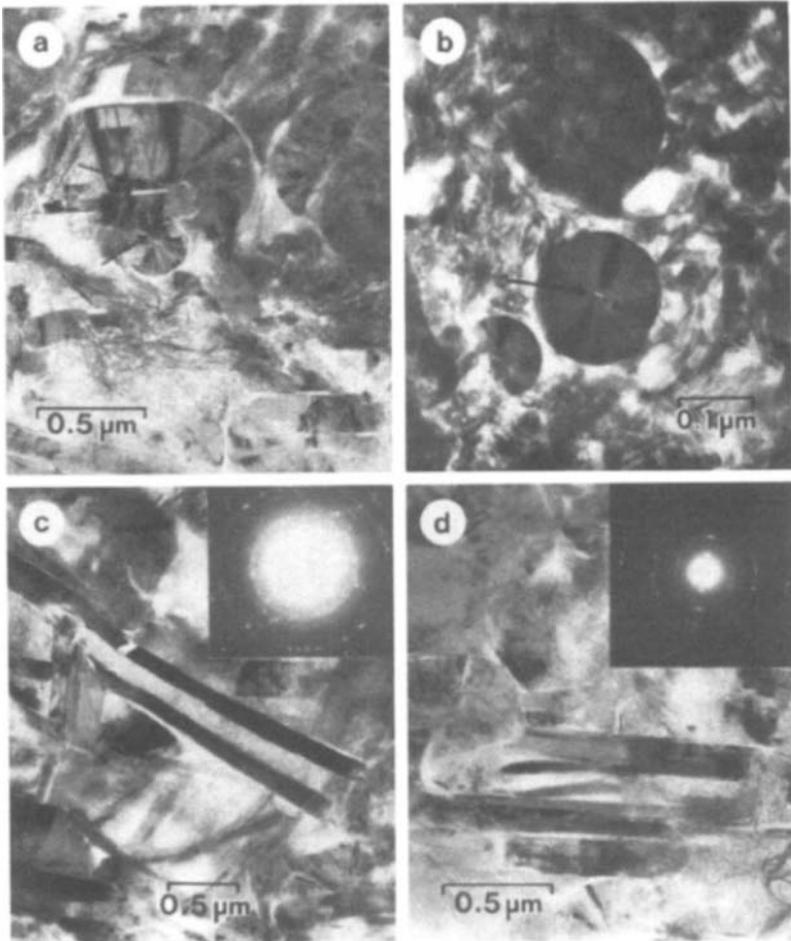
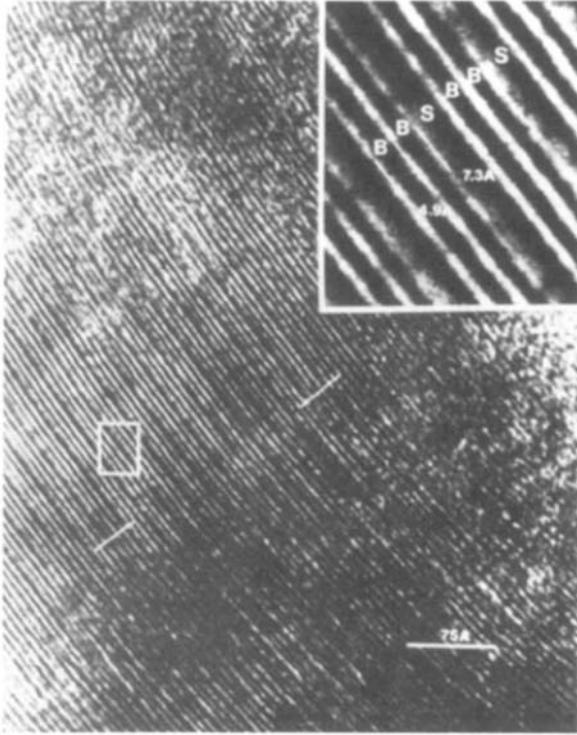


Figure 7 Varied morphologies of Fe-rich serpentines in CMs. (a) Spherulites and sectored crystals on platelike nuclei (arrow); Nawapali. (b) Tubular chrysotile fibers showing a central void (arrow); Cochabamba. (c) Platy crystals separated by “spongy” material containing small chrysotile-like fibers; Nawapali. (d) Boundary between massive partly-spherulitic material (left) and “spongy” material containing small tubular fibers (right); Nawapali. (From Barber 1981.)

chondrules, but in the vast majority of CVs the phyllosilicates also occur in the matrix (Tomeoka & Buseck 1982a, Cohen et al 1983, Fegley & Post 1985, Tomeoka & Buseck 1986, Hashimoto & Grossman 1987, Keller & Thomas 1991). Published observations on CV matrix are from Allende, Bali, Grosnaja, Kaba, Mokoia, and Vigarano (see Table 3 for references).



(A)

Figure 8 The varied appearances of tochilinite and its intergrowths in PCP, as viewed by transmission electron microscopy. As discussed in the text, prior to its recognition as tochilinite, this component in PCP was variously called SBB, FESON, or by its major elements. These terms and labels appear in some of the following figures.

(A) Ten ordered "SBB" units occur between the arrows. The white rectangle is enlarged in the inset. See text for explanation. [From Murchison CM (Mackinnon & Buseck 1979b).]

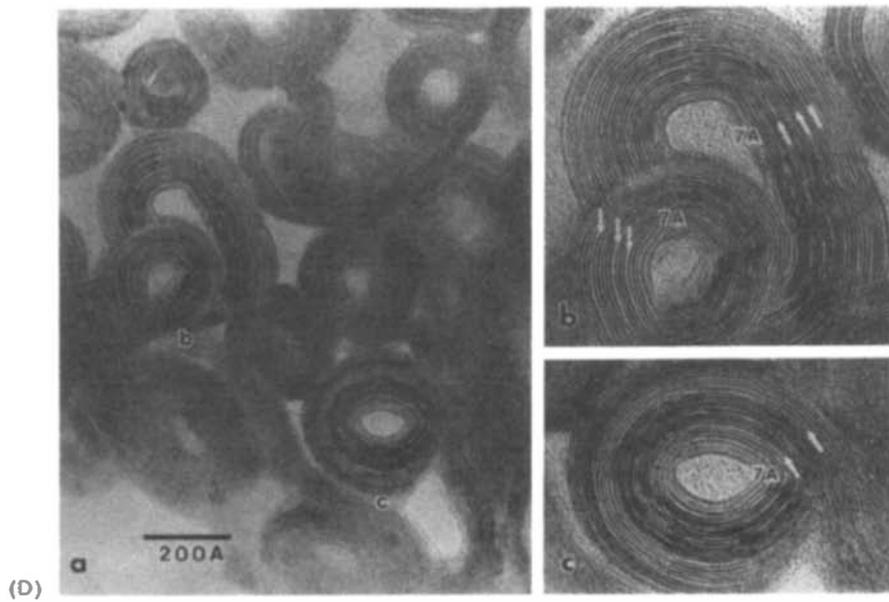
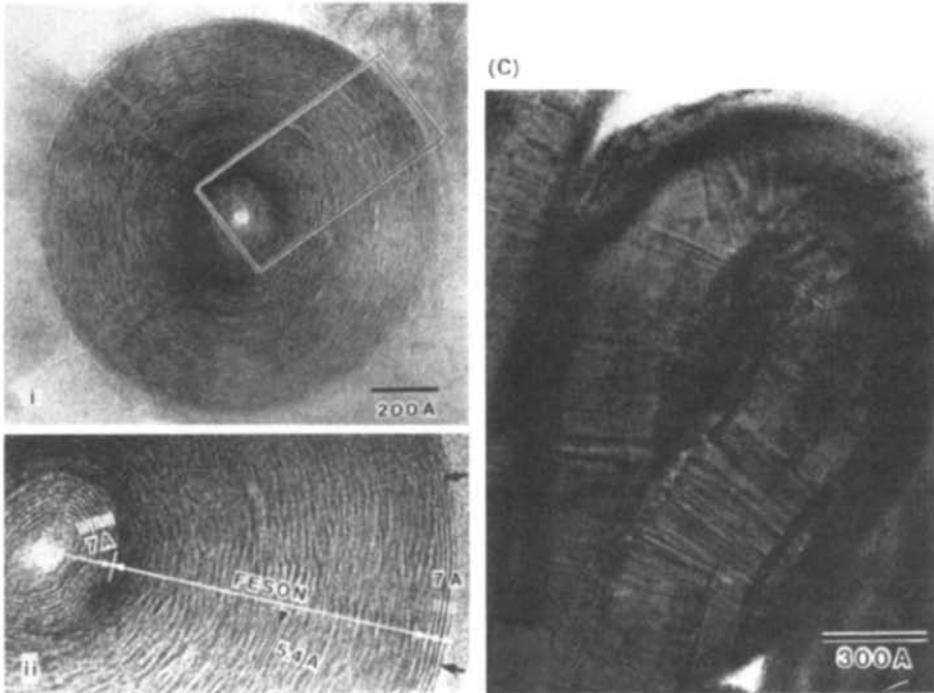
(B) Presumed tochilinite tube, viewed end-on. (i) The concentric layers and cylindrical structure are evident; (ii) enlargement of the framed area in (i), with the black arrows indicating areas where layers are bent (cf "Povlen" chrysotile). [From Murchison (Tomeoka & Buseck 1985a).]

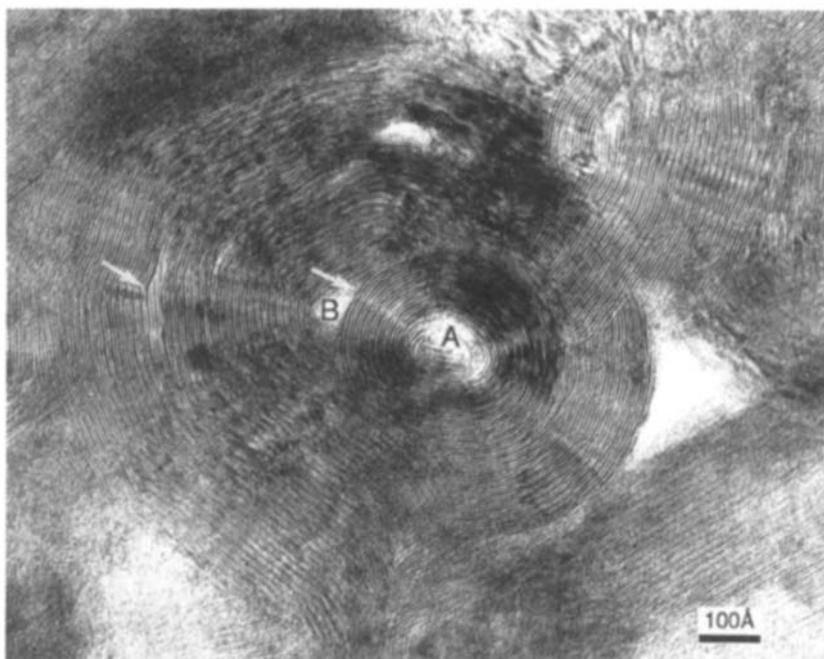
(C) Image showing undulations in the structure and a reversal in the direction of the curvature. Scale bar = 300 Å. [From Murray (Tomeoka & Buseck 1983b).]

(D) (a) Set of tubes viewed end-on. (b), (c) Enlargements of the tubes indicated in (a); they consist of alternating intergrowths of 5.4- and 7-Å layers. The centers consist of 7-Å layers. [From Murchison (Tomeoka & Buseck 1983a).]

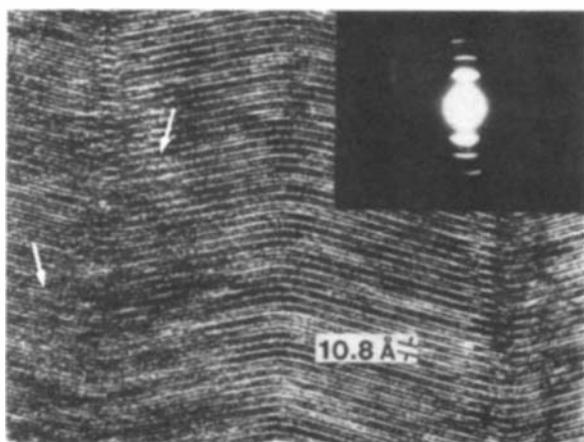
(E) Terminations and discontinuities (arrows) of the layers in a PCP spherule in an olivine chondrule. [From Mighei (Tomeoka & Buseck 1983b).]

(F) 500-kV image of undulations, 7.7-Å transverse spacings (arrows), and the corresponding electron-diffraction pattern. [From Murchison (Barber et al 1983).]





(E)



(F)

Mokoia CV matrix has been the topic of a recent study by Tomeoka & Buseck (1990). The main matrix phase is olivine, which is characterized by a wide compositional range (Peck 1983, Tomeoka & Buseck 1990) and so indicates a lack of internal equilibration and consequent homogenization. Additional matrix phases include magnetite, FeNi sulfides, pyroxenes (enstatite, diopside, and fassaite), andradite, and chromite together with lesser spinel, anorthite, and sodalite.

Phyllosilicates are interspersed among these minerals, although they appear to be mainly associated with the olivine. The major phyllosilicate is saponite, similar to that in Orgueil. In places the Mokoia smectite is associated with ferrihydrite, as it also is in Orgueil. However, because in Mokoia the alteration is far less advanced, and so olivine is still present, there is direct observational evidence that the saponite developed from the olivine (Figure 9). It grew along crystal edges as well as interiors, especially along planar defects (Figure 10). Since the metal/Si ratio of olivine (2.0) is appreciably closer to that of serpentine (1.5) than to saponite (0.83, Table 4), it is surprising that saponite is the alteration phase. Tomeoka & Buseck (1990) proposed that the planar features may represent Fe-rich precipitates that segregated from olivine, making the original olivine cation-deficient near these precipitates and thereby promoting saponite development.

The phyllosilicate described in the previous paragraph had been called "LAP" (for *Low-Al Phyllosilicate*; Cohen et al 1983. Cohen also described "HAP" (*High-Al Phyllosilicate*) in CAIs (Table 5). Tomeoka & Buseck (1990) identified it as an intimate intergrowth of serpentine and Na-rich phlogopite and found it in chondrule interstices and mesostasis glass. Although the serpentine-phlogopite intergrowths are not concentrated in matrix, their occurrence raises the possibility that they might be an early stage of matrix formation since they could well be precursors to the components that ultimately comprise much matrix.

Kaba, another CV3 CC, also contains phyllosilicates, although in relatively low abundance (McSween & Richardson 1977, Peck 1984). However, they occur in matrix, CAIs, and altered chondrules (Keller & Buseck 1990b). The phyllosilicates in Kaba matrix occur in coarse- and fine-grained clusters, in isolated packets between olivine grains, and as lamellar replacements of olivine. Only the clusters are large enough for energy-dispersive spectrometry (EDS) analysis; they have the composition of saponite, similar to that in Mokoia, Orgueil, and Yamato-82162 (Zolensky & McSween 1988, Tomeoka et al 1989).

Based on fringe spacings and analytical electron microscopy (AEM) analyses, Keller & Buseck (1990b) assumed that Fe-bearing saponite is the widespread, albeit minor, phyllosilicate that occurs throughout Kaba.

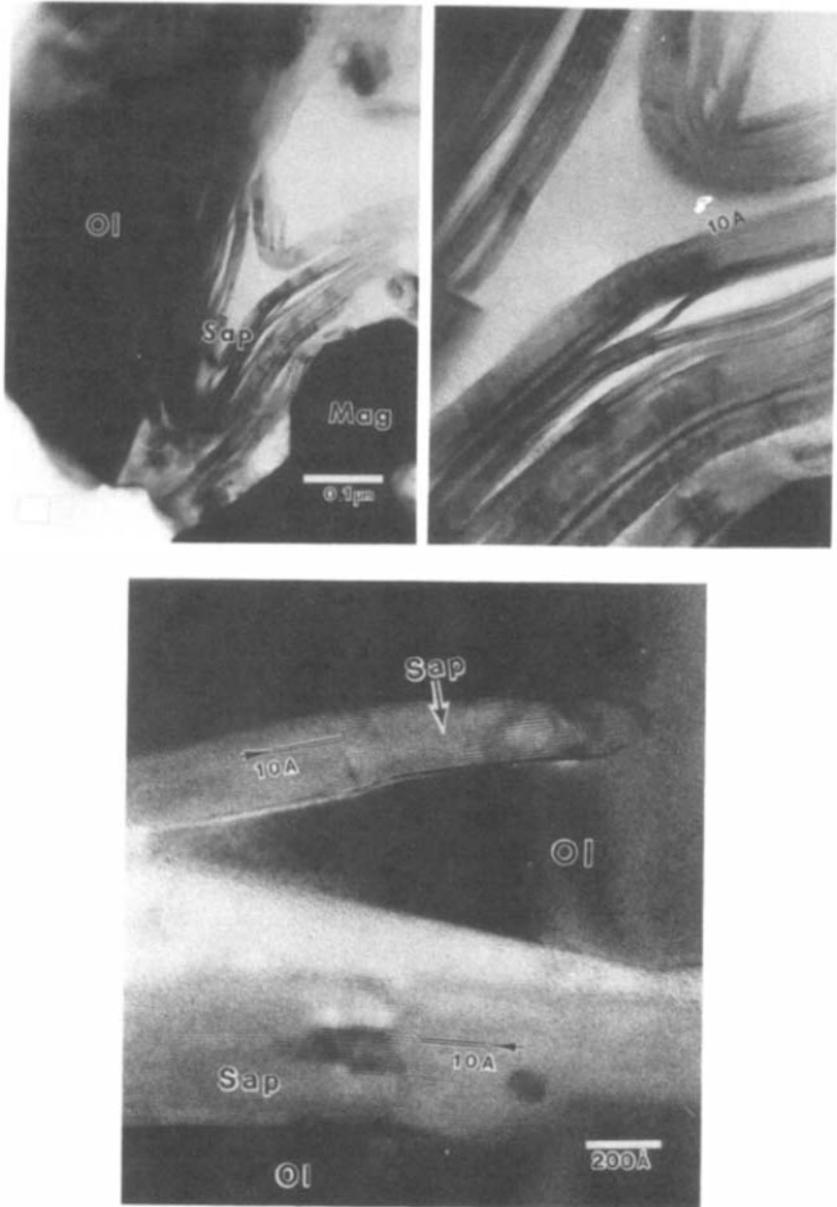


Figure 9 Saponite replacing olivine. (*Top*) The saponite (Sap) layers developed adjacent to the olivine (Ol), close to a large grain of magnetite (mag). (*Bottom*) Saponite layers intruding and presumably replacing the interior of an olivine crystal. [From Mokoia (Tomeoka & Buseck 1990).]

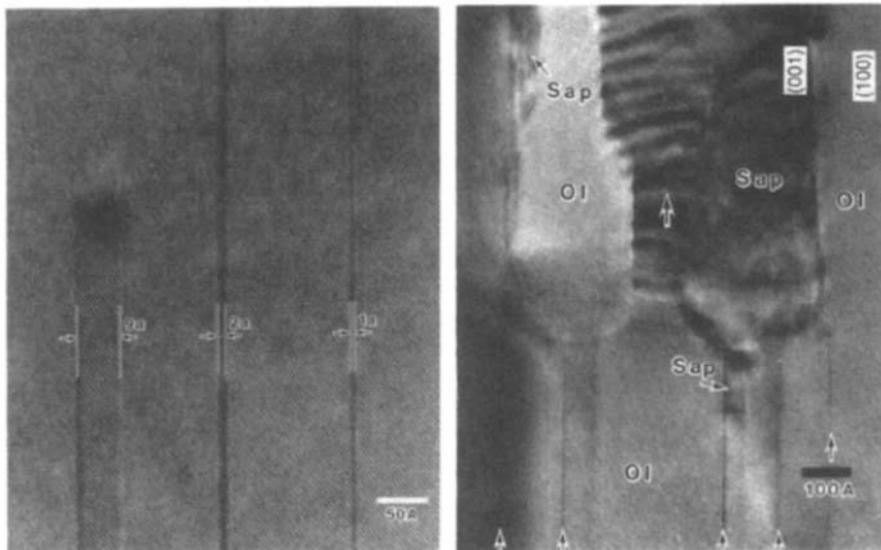
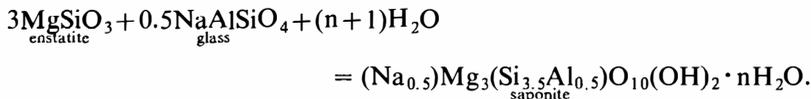


Figure 10 Planar zones of various thicknesses within olivine. (Left) From right to left the planes correspond to widths equaling 1, 2, and 9 unit cells along the a crystallographic dimension of olivine. (Right) Saponite (Sap) with its (001) planes parallel to olivine (Ol) (100). The arrow indicates Moiré fringes, presumably arising from overlapping saponite and olivine crystals. [From Mokoia (Tomeoka & Buseck 1990).]

They concluded that it formed on the parent body, consistent with the general calculations of Prinn & Fegley (1989). The saponite developed from both olivine and enstatite, but it seems to have preferentially attacked the pyroxene in chondrules. The minor amounts of Na, Al, and Si that were needed for the reaction were presumably derived from the mesostasis glass:



As shown by Keller & Buseck (1990b, and Figure 11), the development of saponite from enstatite requires relatively little structural rearrangement, and the diffusion required to introduce the necessary elements was over short paths. The structural rearrangement to alter olivine is more complex, which is perhaps why such alteration is less well developed. The reaction temperature inferred by Keller & Buseck is $< 100^\circ\text{C}$, which may be another reason why olivine alteration was inhibited.

The alteration phases in Kaba resemble those in Mokoia (Tomeoka &

Table 5 Acronyms in the literature related to CC matrix

Acronym	Meaning	Possible minerals or materials	References
LAP	Low Aluminum Phyllosilicate	Trioctahedra Ca-Mg smectite	2
HAP	High Aluminum Phyllosilicate	Al-serpentine with mixed layers of Na-, K-rich, phyllosilicates	2
		Al-rich smectite	3
		Coherent intergrowth of Na-rich phlogopite and serpentine	4
PCP	Poorly Characterized Phase	A group of Fe-S-Ni-O- and Fe-S-Ni-Si-O-rich phases	5
	Partially Characterized Phases	Tochilinite and an unnamed mineral consisting of coherently interstratified serpentine and tochilinite	6, 7, 8, 9, 10, 11
		Complex intergrowth of tochilinite, cronstedtite, and submicron particles of magnetite, chromite and a mineral containing Fe, Ni, Cr, and P	12, 13
PAHs	Polycyclic Aromatic Hydrocarbons	Phenanthrene, anthracene, naphthalene, pyrene, fluoranthrene, etc	1, 14

References:

1. Zenobi et al (1989); 2. Cohen et al (1983); 3. Zolensky & McSween (1988); 4. Tomeoka & Buseck (1990); 5. Fuchs et al (1973); 6. Mackinnon & Zolensky (1984); 7. Zolensky et al (1987); 8. Barber et al (1983); 9. Mackinnon (1980); 10. Mackinnon (1982); 11. Mackinnon & Buseck (1979); 12. Tomeoka & Buseck (1983a,b); 13. Tomeoka & Buseck (1985); 14. Wing & Bada (1991).

Buseck 1990), although there are differences in the nature and distribution of the Fe oxides. Also, Fe sulfides are more abundant in Kaba. Alteration in both of these CV3s was in a relatively oxidizing environment, but that in Kaba was perhaps slightly more reducing. Kaba contains neither the Na-phlogopite that occurs in Mokoia nor the mica in Allende (Hashimoto & Grossman 1987, Keller & Buseck 1990b).

The saponite in Kaba is similar in composition to that in the Orgueil and Yamato-82162 CIs (Tomeoka & Buseck 1988, Zolensky et al 1989). However, Kaba is far less altered than any CI, and the saponite is not intergrown with serpentine in the way it is in Orgueil. In Yamato-82162, Zolensky et al (1989) described saponite-ferrihydrite intergrowths similar to those observed in Kaba. The Bali, Vigarano, and Grosnaja CVs contain saponites and Fe-bearing serpentine in the matrices, although they are not as altered as Kaba and Mokoia (Keller & Thomas 1991, Graham & Lee 1992).

5.4 Matrix in COs

Like the CVs, the matrices of most CO chondrites show little evidence of alteration. The main anhydrous matrix minerals are olivine and pyroxene.

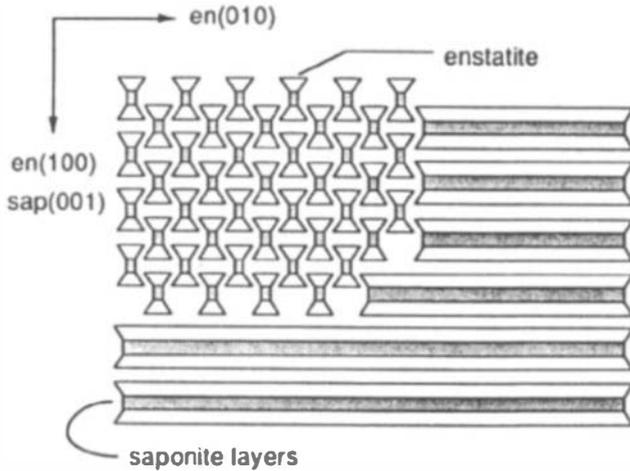
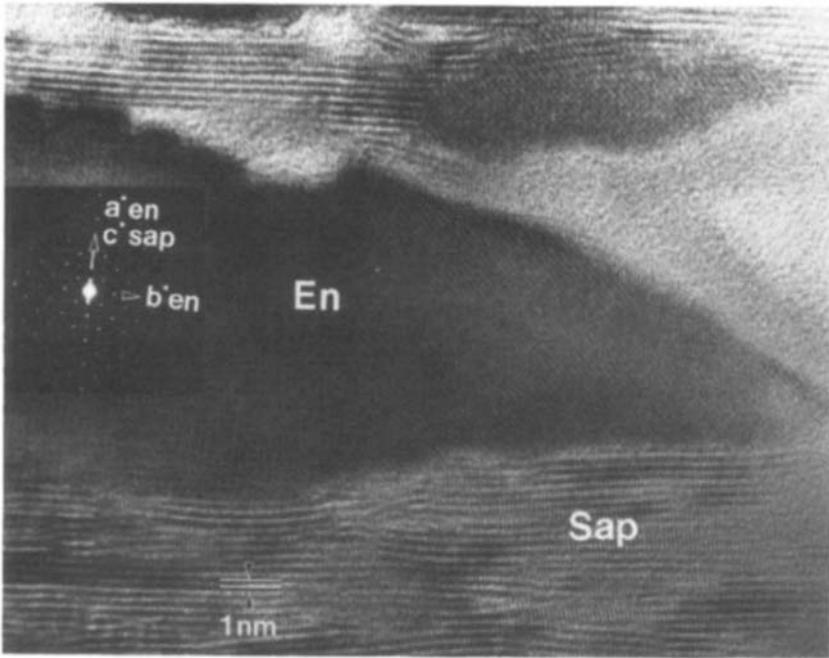


Figure 11 (Top) HRTEM image of a saponite-enstatite intergrowth. (Bottom) Sketch of an oriented enstatite-saponite intergrowth showing pyroxene I-beams abutting saponite sheets. [From Kaba (Keller & Buseck 1990b).]

Keller & Buseck (1990a) studied three of the 13 known CO falls: Lancé, Warrenton, and Kainsaz. Of these, only Lancé shows evidence of significant matrix alteration, and the data suggest that the maximum post-accretional temperature to which it might have been subjected is 450°C. ALH A-77307, one of the least equilibrated CO3 chondrites, has a rather different matrix mineralogy from other CO3 meteorites; notable is the relatively abundant Si-, Fe-rich amorphous material (Brearley 1990).

The Lancé matrix consists mainly of fragmented Fe-rich olivine, lesser phyllosilicates, poorly crystalline Fe oxides and hydroxyoxides, Ca-rich and Ca-poor clinopyroxenes, metal, and oxides (Keller & Buseck 1990a). An unusual feature of the olivine is that it contains periodically arranged pits a few nanometers in dimension on some of its surfaces (Figure 12); because they are seen in TEM images, which are 2-dimensional, the possibility that these are actually grooves cannot be excluded. Keller & Buseck speculated that these features subsequently formed channels within the

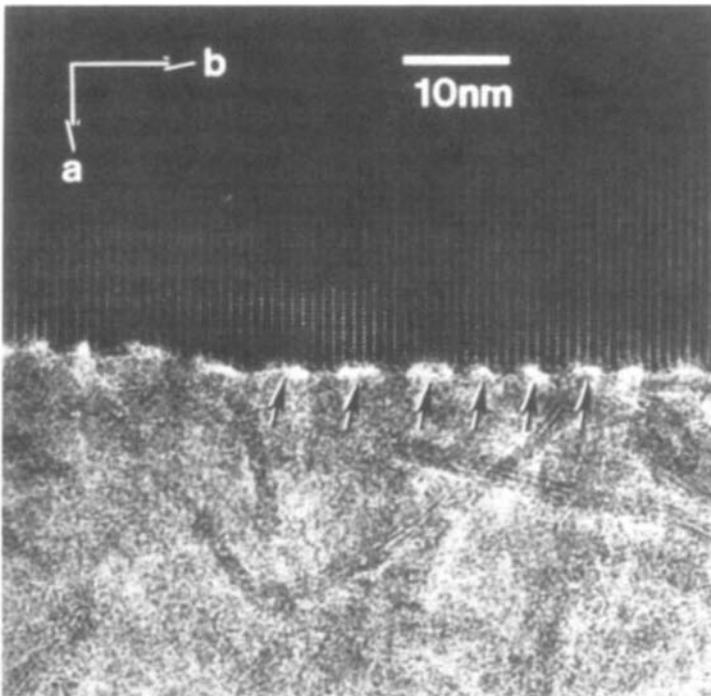


Figure 12 Pits (or grooves; periodic white spots at the crystal margins indicated by arrows) in euhedral matrix olivine. Note the serpentine packets in matrix. [From Lancé (Keller & Buseck 1990b).]

olivine, and these, in turn, were sites for both attack by phyllosilicate alteration minerals and fracture during regolith gardening.

The phyllosilicates are either draped around the olivine or parallel to (100) planes of olivine, which suggests limited crystallographic control. Keller & Buseck (1990a) estimated the phyllosilicate composition as $(\text{Mg}_{2.2}\text{Fe}_{0.8})\text{Si}_2\text{O}_5(\text{OH})_4$, a variety of serpentine that forms through a hydration reaction with olivine. The Fe released in the process formed the fine-grained Fe oxide, which is either ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) or ferroxhyte ($\delta\text{-FeOOH}$).

The morphologies of these Fe minerals differ among the few meteorites in which they have been studied in detail. In Lancé (CO3) they occur as finely dispersed, poorly crystalline grains that pervade the sample. In Orgueil they occur in granular masses that appear to be pseudomorphic after framboidal magnetite (Tomeoka & Buseck 1988), and in Kakangari (a unique chondrite) they occur in featherlike masses as well as in rims around troilite (Brearley 1989).

The Kainsaz and Warrenton CO3s are among the least altered CO meteorites, and their anhydrous (unaltered) matrix minerals are essentially the same as those in Lancé. However, in Kainsaz, Keller & Buseck (1990a) observed kamacite, which is one of the first phases to be attacked and consumed during alteration, and sparse graphite.

The anhydrous minerals in CV3 and CO3 chondrites are similar, and it is probable that their prealteration mineralogy differed little from one another. However, as shown by the contrast between Kaba and Lancé (Keller & Buseck 1990a,b), their alteration products differ even though the degree of reaction in both was relatively slight. Lancé contains serpentine and Fe oxides that suggest alteration at higher temperature and more oxidizing conditions; their sparser distribution also suggests less water was available for Lancé alteration.

The matrix mineralogy of Mokoia (CV3) and Lancé (CO3) are similar (Keller & Buseck 1990a). However, the main alteration product of Mokoia olivine is saponite and Fe oxides while in Lancé it is serpentine, presumably reflecting a higher alteration temperature. The phyllosilicates in Kaba resemble those in Mokoia rather than those in Lancé.

5.5 *Matrices in CRs and CKs*

The proportions of Mg, Fe, and Si to one another in the matrices of the CRs are similar to those in the CM, CO, and CV meteorites, but S is significantly higher than in CVs and COs. Olivine is the dominant phase in the CR matrix. Metal, sulfides, saponite and serpentine are abundant, and the two layer silicates are locally intergrown.

The phyllosilicates and carbonates in CRs differ from those in other

meteorite groups (Weisberg & Prinz 1991). Some chlorite-like phases are highly aluminous (10 to 15 wt% Al_2O_3), whereas the serpentines and saponites are not as magnesian as those in CI, CM, and CV chondrites. In distinction to CIs and CMs, the CR carbonates have compositions ranging from pure CaCO_3 to containing up to 7.3 wt% FeO, 3.1 wt% MgO, and 1.9 wt% MnO. Unique to the CRs, CaCO_3 also occurs as rims surrounding curved, unbroken surfaces of chondrules. Weisberg et al (1991) showed that dark inclusions in CR2 chondrites have textures, compositions, and oxygen isotope ratios similar to the CR matrices, which they interpret as indicating that at least some matrix existed as lithified material prior to the aggregation of CR chondrites.

The phyllosilicates in CR meteorites are significantly finer grained than those in CIs. That, together with the abundant olivine, suggests that aqueous alteration was not pervasive. The lack of tochilinite suggests that the CRs experienced a maximum alteration temperature of $\sim 150^\circ\text{C}$. Their mineralogy resembles that of many saponite-class IDPs (Zolensky 1991).

The compositional, textural, and oxygen-isotope data of the CKs are closely related to the CVs and COs, except that all CKs have been significantly metamorphosed, with petrographic grades from 4 to 6; some contain shock features (Kallemeyn et al 1991). Their matrix consists of two types of materials. 90 vol% consists of olivine (50–200 μm), plagioclase (20–100 μm), magnetite and sulfides (several micrometers across)—the olivine grains are unzoned, contain significant (~ 0.5 wt%) NiO, and are appreciably larger than in matrix of the other CC types, as defined in Section 2. 10 vol% consists of fine-grained augite (< 2 μm), low-Ca pyroxene (< 5 μm , $\sim \text{Fs}_{27}$), anhedral olivine (< 2 μm , $\sim \text{Fa}_{29}$), and subhedral magnetite (< 1 μm , containing $\sim 2\%$ Cr, $\sim 1\%$ Al) (Brearley et al 1987, Kallemeyn et al 1991).

5.6 *Comparison to Interplanetary Dust Particles*

Several studies have suggested a relationship between the CCs and the IDPs (e.g. Tomeoka & Buseck 1985b, Rietmeijer & Mackinnon 1985, Bradley & Brownlee 1986). Although most IDPs differ from CCs in the details of their mineralogy and textures, two recent papers provide convincing evidence of a relationship between CCs and certain IDPs. Keller et al (1992) show that IDP number W7013F5 contains Mg-Fe carbonates as well as coherent intergrowths of Mg-Fe serpentine and Fe-bearing saponite on a unit-cell scale, similar to what is observed in CIs. There is also compositional overlap of phyllosilicates, carbonates, and sulfides in W7013F5 with those in the CIs. Bradley & Brownlee (1991) show that the minerals in IDP RB12A44 resemble those in the matrix of certain CMs. It contains tochilinite and, moreover, the tochilinite is intergrown with

cronstedtite. The minor phases in RB12A44 also resemble those in CM matrix. Some IDPs are thought to be derived from comets; McSween & Weisman (1989) discussed the possibility that cometary nuclei may be similar in many aspects to CC parent bodies.

6. ALTERATION

6.1 *Alteration Processes and Phases*

6.1.1 GENERAL. In spite of their primitive composition, it has long been perceived that CCs experienced aqueous alteration. The effects of such alteration were first noted by DuFresne & Anders (1962) on the basis of veins containing hydrous sulfates and carbonates. Similar early petrographic observations were made by Nagy et al (1963) and by Boström and Fredriksson (1966). Petrography combined with electron microprobe analyses allowed Richardson (1978), McSween (1979b), and Bunch & Chang (1980) to elaborate on this alteration. Details were provided by subsequent TEM studies (see references in Sections 1 and 5). In the case of CI chondrites, their mineralogy is almost totally the result of such secondary processes, and the matrix is the main repository of these secondary products. Indeed, matrix mineralogy cannot be properly understood without considering alteration. During the past decade much work has provided details, primarily by use of TEM to identify the alteration minerals and, to a lesser extent, also to detail the mechanisms whereby the alteration occurred.

We will explore the alteration by considering matrix in the CCs that are physically most primitive (least altered) and then consider the more heavily altered types. In general, the sequence is CV, CO, CM, and CI, although there are significant variations within each group. It is worth noting that alteration reactions occurred at many temperatures. Thus, there is an extensive literature regarding reactions experienced by minerals in inclusions formed at high ($> \sim 1200$ K) temperatures. These minerals do not, however, form in matrix, and therefore we restrict this discussion to hydrated minerals. Micas are included in Table 4 because they are hydrated and are mineralogically related to the other minerals in the table, although it is probable that they formed before matrix developed (Keller & Buseck 1991).

A thorough electron microprobe study of alteration phases in CM meteorites was provided by Bunch & Chang (1980). Based on compositional and textural evidence, they concluded that alteration was extensive and that it occurred in situ on parent bodies at low temperatures (< 400 K). Their indications of alteration—pseudomorphic replacements, cross-cutting veins, colloform textures, hydrated minerals—have been

confirmed by subsequent TEM studies that allowed observation of more details of the minerals and their replacement relations (Tomeoka & Buseck 1985a, Tomeoka et al 1989).

McSween (1979a), as a result of detailed electron microprobe studies of a suite of CMs and CIs, observed that the volume percent of matrix is proportional to the extent of alteration. He therefore concluded that much matrix is secondary, having resulted from the comminution of coarser material. The comminution was produced by regolith gardening, which resulted from impact of other meteorites onto the CC parent bodies. He provides estimates of the amount of matrix in various CCs, and from that it is possible to estimate the degree of processing that occurred to produce a given CC. However, the details of the alteration were not known, although they could potentially provide information about development of matrix and conditions on the parent body.

A series of five alteration steps for CMs were outlined by Tomeoka & Buseck (1985a) and Tomeoka et al (1989) and are illustrated in Figure 13. It is assumed that the initial meteorite contained mainly anhydrous silicates such as olivine and pyroxene and lesser amounts of metal and sulfide, primarily kamacite and troilite. A small amount of carbon was present, but it did not significantly influence the alteration reactions.

- *Step I*: This first low-temperature alteration stage occurred when a S-bearing fluid, presumably generated by decomposing some of the sulfides, attacked the kamacite to produce tochilinite. The presumed presence of hydroxyl reflects the widespread assumption that the fluid contained water.
- *Step II*: More extensive aqueous alteration occurred together with regolith gardening, resulting in greater comminution plus extensive alteration of olivine to phyllosilicates such as serpentine and the development of "spinach" from mesostasis glass. Richardson & McSween (1978) suggested that this alteration greatly weakened the meteorites, thereby facilitating disaggregation (and even breakup). This disaggregation helped produce mixing of the *step-II* products into the matrix.
- *Step III*: Si, released during the alteration of olivine and pyroxene, reacted with the tochilinite to produce magnesian cronstedtite. The result was intimate intergrowths and intercalations of the two phases. This mixture has long been called PCP, and it is widespread in many partly altered CM meteorites.
- *Step IV*: Cronstedtite became the dominant alteration mineral. It formed both by consuming tochilinite and by scavenging Fe from ferroan serpentine, thereby becoming more Fe-rich and resulting in a more magnesian serpentine. The effects of continued regolith gardening were to repeatedly stir the surface of the host parent body, exposing fresh PCP and serpentine as well as olivine and pyroxene to reaction and thus producing more

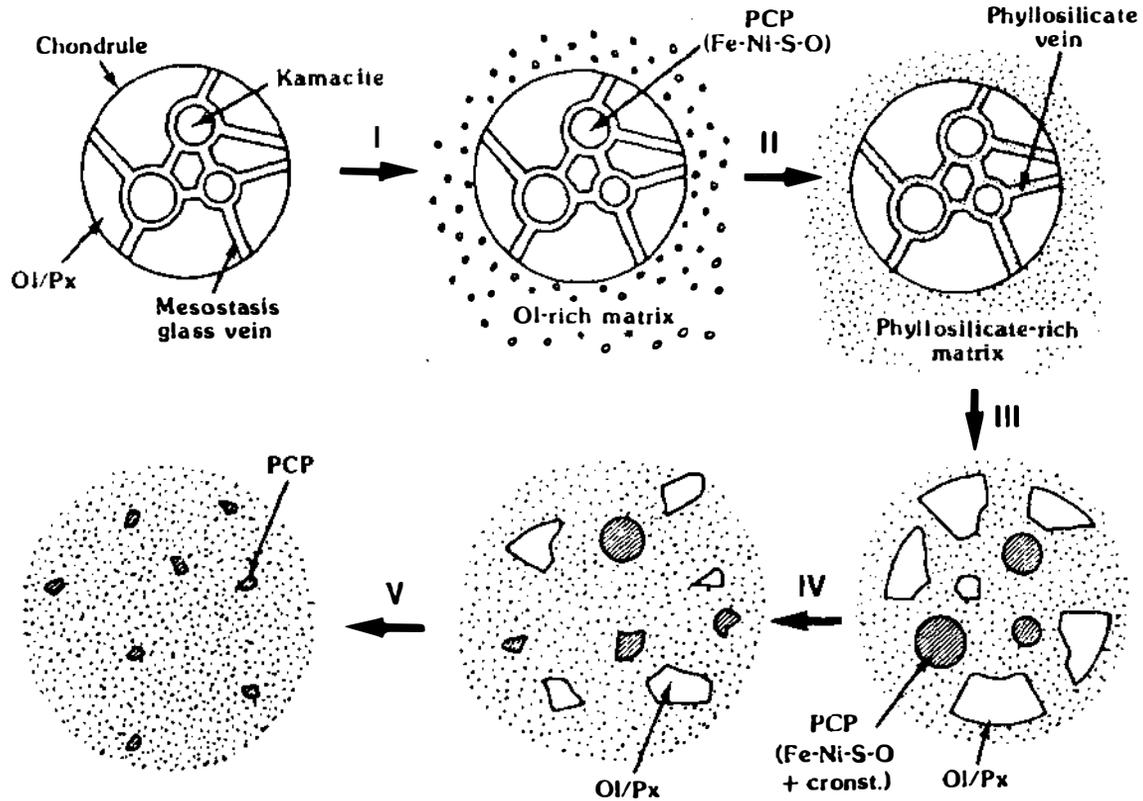


Figure 13 Schematic illustration of the aqueous alteration process that probably occurred in the regolith of the CM parent body. The alteration converted chondrules and fine-grained, olivine-rich matrix to phyllosilicate-rich matrix (modified from Tomeoka & Buseck 1985b).

cronstedtite. The bulk composition of the matrix became richer in Mg. Fe released during this process produced the fine-grained magnetite (perhaps including the framboidal aggregates first described by Kerridge et al 1979) and the Fe-Ni sulfides that contribute to the opaque character of matrix.

● *Step V*: Repeated bombardment and continued comminution combined with alteration resulted in an almost uniformly fine-grained matrix that consists mainly of layer silicates and few, if any, residual coarse-grained fragments.

Some mineral and lithic clasts in polymict achondrites resemble CC matrix material. Brearley & Prinz (1992) propose that, based on oxygen isotopic composition, mineralogy, and bulk chemistry, certain clasts in the Nilpena ureilite are closely related to CIs; they are less altered than is Orgueil and so may serve as the starting material for the aqueous alteration of CI parent bodies. They essentially support the alteration model proposed by Tomeoka & Buseck (1988). Bourcier & Zolensky (1992) used computer models to try to reproduce the mineralogy produced during aqueous alteration. While their models do not work too well for the COs and CVs, the results for the CIs and CMs are encouraging.

6.1.2 MINERALOGICAL AND CHEMICAL CHANGES DURING ALTERATION

Since matrix is a major product of alteration, it follows that both its composition and mineralogy change during the alteration process. Based on broad-beam electron microprobe analyses, McSween (1979a) showed that the Mg content of CM matrix correlates with the amount of matrix (and perhaps with the degree of alteration). The destruction of the refractory anhydrous silicates that presumably resided in the unaltered CCs produced a net transfer of Mg into the matrix, thereby increasing the Mg/Si ratio. The Fe/Si ratio, on the other hand, decreased as the amount of matrix increased, presumably because of the development of iron oxides and sulfides, which McSween excludes from matrix. The combination produces an increase in Mg/Fe in the bulk matrix. The progressive development of tochilinite, serpentine, and cronstedtite as major alteration species is consistent with these trends. Ca was also progressively leached from the matrix and formed carbonate veins in the CIs. McSween (1987) did mass balance calculations from which he inferred the changes in relative proportions of minerals as alteration progressed.

6.2 *Water in CCs*

The original classification of the CCs was founded in part on their H₂O contents, with average values of 20.1 wt% for type I, 13.4 wt% for type II, and 0.99 wt% for type III CCs (Wiik 1956). These numbers can be compared with the average volume percentages of matrix determined by

McSween (1979a): 99% for CIs, 57–85% for CMs, and 35–50% for COs and CVs. The correlation is evident and is consistent with an increase in water content with degree of alteration. Also, the amount of matrix can be used as an indicator of the extent of alteration.

In spite of this widely accepted relationship, there are no published H₂O measurements on matrix alone (except for CIs, which are essentially only matrix). Many measurements were made by determining total H₂O content, and Van Schmus & Hayes (1974) point out the potentially severe problem of terrestrial contamination, the extent of which is hard to assess. By using H as a variable with Ar in plots of H/(10²Si) vs ³⁶Ar/(10¹⁰Si), they were able to separate the CO from CV meteorites.

It seems curious that the amount of H does not increase with degree of alteration within the CM group (McSween 1979a), since many of the presumed alteration phases are hydrated. Moreover, the source of the H₂O that produced the alteration is a major unresolved question. Kerridge & Bunch (1979) discussed possible sources of the H₂O that produced the alteration and speculated that it was one of the earliest recognizable events in the solar system. There are numerous possibilities, none of which have been confirmed. The H₂O may have accreted as ice together with lithic material at the time of parent-body formation. Alternatively, it may have come from cometary ices deposited during impacts, and then later released as the result of heating through the decay of short-lived radionuclides or magnetic induction resulting from interaction with a strong solar plasma (Grimm & McSween 1989) or from impacts onto the surface of the parent body (Lange et al 1985). McSween noted that the amount of retained H₂O seems to have remained approximately constant within CMs, independent of the extent of alteration. He suggests degradation of amino acids in matrix as a possible explanation, in which the H freed by destruction of the amino acids during alteration would be converted to H₂O. Such reactions would presumably produce an increase in the H/C ratio, and there is a suggestion that this does occur. Cronin (1989) noted a correlation between the amino acid content and the amount of PCP in five CMs, which strongly suggests that amino acid synthesis was related to an early stage of aqueous alteration on the parent body.

7. CLOSING THOUGHTS; FUTURE RESEARCH DIRECTIONS

Matrix provides a unique window to the most distant past of our solar system. It is an important component of all chondrites, and it is especially prominent in the CCs; the CIs consist essentially of only matrix. Although an integral and well-studied part of the meteorites, in many ways CC

matrix remains enigmatic, primarily because of its fine-grain sizes and intimately mixed nonmatrix materials. For these reasons, study of either individual grains or of bulk matrix presents formidable difficulties. Nonetheless, as shown in the previous sections, significant progress has been made in understanding matrix and the processes that contributed to its development.

It was long thought that matrix is pristine, but it is now widely recognized that it contains a strong imprint of aqueous alteration. The evidence is both chemical and mineralogical. The anhydrous silicates and simple oxides are presumably primary minerals, but there is a possibility that they have been cycled through previous geological or cosmochemical events. The alteration products are among the intriguing and characteristic features of matrix and have been the focus of extensive TEM studies.

The problem of *where* the alteration occurred remains one in which the most likely site—in situ on a parent body rather than in the nebula, prior to incorporation—seems reasonable. However, most evidence to date is textural and thus permissive rather than compelling and so cannot easily be used to disprove alternative sites. The calculations of Prinn & Fegley (1989) indicate that silicate hydration in the nebula would have been kinetically inhibited and therefore improbable.

A contrary view is suggested by Metzler et al (1991, 1992), Metzler & Bischoff (1991), and Graham & Kurat (1991), who reported accretionary dust mantles coating alteration products such as serpentine, tochilinite, calcite, and magnetite. They assume these mantles formed within the solar nebula by adhesion of dusty material onto surfaces of coarse chondritic components and thus conclude that the alteration minerals must have formed in the solar nebula or on small planetesimals.

A plausible question might be whether any matrix is pristine, but this question was answered definitively by the discovery, within the matrix, of minerals having interstellar origins. As discussed in Section 4.3, diamond and SiC have isotopic compositions that point convincingly toward sources outside the solar system. The D/H ratios of amino acids and monocarboxylic acids extracted from CMs also show interstellar sources.

While isotopic data would be especially helpful for resolving questions regarding the origin and development of matrix, the difficulty of separating “clean” matrix for isotopic analysis is a limiting factor. The ion probe is an important instrument for isotopic analyses of the larger ($> 2 \mu\text{m}$) matrix grains, but most of the meteorite matrix is still too fine grained for current instruments.

The origin of organic material has long been an important problem in understanding CCs. One approach is to determine exactly where in the matrix they reside. A potential solution to determining their spatial dis-

tribution has appeared within the last few years. The development of L²MS as a high-spatial-resolution analytical technique for large molecules (several hundred amu; Section 4.2) holds promise that in the future precise correlations will be possible between organic species and specific components of CC matrix.

Finally, there is the curious apparent anomaly that the CIs, the meteorites that are chemically the most similar to solar composition, are also the most highly altered. It would appear that alteration occurred in a closed system, but such a supposition is not supported by the depletion of at least some elements such as Na and Ca. The mismatch between the pristine character of CCs as based on chemical vs physical characteristics is intriguing. It is evident that important questions regarding matrix and their host meteorites remain to be solved.

In this review, we have tried to show the wealth of information stored within the fine-grained melange called matrix. It contains secreted within it some of the oldest and most remote known materials, but their study is still difficult and extremely challenging. It is certain that additional research will uncover further clues to this most fascinating and ancient material. Answering questions such as which fraction of matrix is primary and which is the product of alteration and when and where the alteration occurred awaits the development of yet more precise analytical techniques and procedures than exist today.

ACKNOWLEDGMENTS

We thank Drs. H. Y. McSween Jr., A. J. Brearley, R. N. Clayton, J. R. Cronin, and L. Keller for helpful comments on the manuscript and Drs. K. Tomeoka, D. J. Barber, and L. Keller for sending us copies of their figures. This work was supported by NASA grant NAG 9-59.

Literature Cited

- Akai, J. 1980. Tubular form of interstratified mineral consisting of a serpentine-like layer plus two brucite-like sheets newly found in the Murchison (C2) meteorite. *Mem. Natl Inst. Polar Res., Spec. Issue* 17: 299-310
- Anders, E. 1981. Noble gases in meteorites: evidence for presolar matter and super-heavy elements. *Proc. R. Soc. London Ser. A* 374: 207-38
- Anders, E. 1987. Local and exotic components of primitive meteorites, and their origin. *Philos. Trans. R. Soc. London Ser. A* 323: 287-304
- Anders, E., Ebihara, M., 1982. Solar-system abundances of the elements. *Geochim. Cosmochim. Acta* 46: 2363-80
- Anders, E., Grevesse, N., 1989. Abundances of the elements: meteoritic and solar. *Geochim. Cosmochim. Acta* 53: 197-214
- Anders, E., Lewis, R. S., Tang, M., Zinner, E. 1988. *Interstellar grains in meteorites: diamond and silicon carbide*. Presented at Interstellar Dust: IAU Symp. 135, NASA-Ames Res. Ctr., Santa Clara, CA
- Barber, D. J. 1977. The matrix of C2 and C3 carbonaceous chondrites. *Meteoritics* 12: 172-73
- Barber, D. J. 1981. Martix phyllosilicates and associated minerals in C2M car-

- bonaceous chondrites. *Geochim. Cosmochim. Acta* 45: 945–70
- Barber, D. J. 1985. Phyllosilicates and other layer-structured materials in stony meteorites. *Clay Minerals* 20: 415–54
- Barber, D. J., Bourdillon, A., Freeman, L. A. 1983. Fe-Ni-S-O layer phase in C2M carbonaceous chondrites—a hydrous sulphide? *Nature* 305: 295–97
- Basile, B. P., Middleditch, B. S., Oro, J. 1984. Polycyclic aromatic hydrocarbons in the Murchison meteorite. *Org. Geochem.* 5: 211–16
- Bass, M. N. 1971. Montmorillonite and serpentine in Orgueil meteorite. *Geochim. Cosmochim. Acta* 35: 139–47
- Becker, R., H. Epstein, S. 1982. Carbon, hydrogen and nitrogen isotopes in solvent-extractable organic matter from carbonaceous chondrites. *Geochim. Cosmochim. Acta* 46: 97–103
- Begemann, F. 1980. Isotopic anomalies in meteorites. *Rep. Prog. Phys.* 43: 1309–56
- Bernatowicz, T., Fraundorf, G., Tang, M., Anders, E., Wopenka, B., et al. 1987. Evidence for interstellar SiC in the Murray carbonaceous meteorite. *Nature* 330: 728–30
- Boato, G. 1954. The isotopic composition of hydrogen and carbon in the carbonaceous chondrites. *Geochim. Cosmochim. Acta* 6: 209–20
- Boström, K., Fredriksson, K. 1966. Surface compositions of the Orgueil meteorite parent body as indicated by mineral associations. *Smithson. Misc. Collect.* 151: 1–39
- Bourcier, W. L., Zolensky, M. E. 1992. Computer modeling of aqueous alteration on carbonaceous chondrite parent bodies. *Lunar Planet. Sci. XXXIII*, pp. 143–44. Houston: Lunar Planet. Inst.
- Bowring, S. A., Housh, T. B., Isachser, E. E. 1990. The Acasta gneisses: remnant of Earth's early crust. In *Origin of the Earth*, ed. H. E. Newsom, J. H. Jones, pp. 319–40. Oxford: Oxford Univ. Press
- Bradley, J. P., Brownlee, D. E. 1986. Cometary particles: thin sectioning and electron beam analysis. *Science* 231: 1542–44
- Bradley, J. P., Brownlee, D. E. 1991. An interplanetary dust particle linked directly to type CM meteorites and an asteroidal origin. *Science* 251: 549–52
- Brearley, A. J. 1989. Nature and origin of matrix in the unique chondrite, Kakangari. *Geochim. Cosmochim. Acta* 53: 2395–2411
- Brearley, A. J. 1990. Matrix mineralogy of the unequilibrated CO3 chondrite ALH A77307: evidence for disequilibrium condensation processes and implications for the origin of chondrite matrices. *Lunar Planet. Sci. XXI*, pp. 125–26. Houston: Lunar Planet. Inst.
- Brearley, A. J. 1992. Mineralogy of fine-grained matrix in the Ivuna CI carbonaceous chondrite. *Lunar Planet. Sci. XXXIII*, pp. 153–54. Houston: Lunar Planet. Inst.
- Brearley, A. J., Prinz, M. 1992. CI chondrite-like clasts in the Nilpena polymict ureillite: implications for aqueous alteration processes in CI chondrites. *Geochim. Cosmochim. Acta* 56: 1373–86
- Brearley, A. J., Scott, E. R. D., Mackinnon, I. D. R. 1987. Electron petrography of fine-grained matrix in the Karoonda C4 carbonaceous chondrite. *Meteoritics* 22: 339–40
- Bunch, T. E., Chang, S. 1980. Carbonaceous chondrites-II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* 44: 1543–77
- Bunch, T. E., Chang, S., Frick, U., Neil, J., Moreland, G. 1979. Characterization and significance of carbonaceous chondrite (CM2) xenoliths in the Jodzie howardite. *Geochim. Cosmochim. Acta* 43: 1727–42
- Burnett, D. S., Woolum, D. S., Benjamin, T. M., Rogers, P. S. Z., Duffy, C. J., Maggiore, C. 1989. A test of the smoothness of the elemental abundances of carbonaceous chondrites. *Geochim. Cosmochim. Acta* 53: 471–81
- Buseck, P. R., Iijima, S. 1974. High resolution electron microscopy of silicates. *Am. Mineral.* 59: 1–21
- Buseck, P. R., Iijima, S. 1975. High resolution electron microscopy of enstatite II: geological application. *Am. Mineral.* 60: 771–80
- Caillère, S., Rautureau, M. M. 1974. Détermination des silicates phylliteux des météorites carbonées par microscopie et microdiffraction électroniques. *C. R. Acad. Sci. Ser. D* 279: 539–42
- Cameron, A. G. W. 1982. Elemental and nuclidic abundances in the solar system. In *Essays in Nuclear Astrophysics*, ed. C. A. Barnes, D. D. Clayton, D. N. Schramm, pp. 23–43. Cambridge: Cambridge Univ. Press
- Chang, S., Bunch, T. B. 1986. Clays and organic matter in meteorites. In *Clays Minerals and the Origin of Life*, ed. A. G. Cairns-Smith, H. Hartman, pp. 116–29. Cambridge: Cambridge Univ. Press
- Chen, J. H., Wasserburg, G. J. 1981. The isotopic compositions of uranium and lead in Allende inclusions and meteoritic phosphates. *Earth Planet. Sci. Lett.* 52: 1–15
- Chukhrov, F. V., Zöyagin, B. B., Gorshkov, A. I., Yermilova, L. P., Balashova, V. V.

1973. O ferrigidrite (ferrihydrite). *Int. Geol. Rev.* 16: 1131-43
- Clarke, R. S., Jarosewich, E. Jr., Mason, B., Nelen, J., Gomez, M., Hyde, J. R. 1970. The Allende, Mexico, meteorite shower. *Smithson. Contrib. Earth Sci.* No. 5, 53 pp.
- Clayton, R. N. 1986. High temperature isotope effects in the early solar system. In *Stable Isotopes in High Temperature Geological Processes*, vol. 16, ed. J. W. Valley, H. P. Taylor Jr., J. R. O'Neil, pp. 129-40
- Clayton, R. N., Mayeda, T. K. 1984. The oxygen isotope record in Murchison and other carbonaceous chondrites. *Earth Planet. Sci. Lett.* 67: 151-61
- Clayton, R. N., Mayeda, T. K. 1989. Oxygen isotope classification of carbonaceous chondrites. *Lunar Planet. Sci. XX*, pp. 169-70. Houston: Lunar Planet. Inst.
- Clayton, R. N., Onuma, N., Grossman, L., Mayeda, T. K. 1976. A classification of meteorites based on oxygen isotopes. *Earth Planet. Sci. Lett.* 30: 10-18
- Clayton, R. N., Onuma, N., Ikeda, Y., Mayeda, T. K., Hutcheon, I. D., et al. 1983. Oxygen isotopic compositions of chondrules in Allende and ordinary chondrites. In *Chondrules and Their Origins*, ed. E. A. King, pp. 37-43. Houston: Lunar Planet. Inst.
- Cohen, R. E., Kornacki, A. S., Wood, J. A. 1983. Mineralogy and petrology of chondrules and inclusions in the Mokoia CV3 chondrite. *Geochim. Cosmochim. Acta* 47: 1739-57
- Cronin, J. R. 1989. Origin of organic compounds in carbonaceous chondrites. *Adv. Space Res.* 9(2): 59-64
- Cronin, J. R., Chang, S. 1992. The organic matter of the Murchison meteorite: molecular and isotopic analyses. In *The Chemistry of Life's Origins*, ed. J. M. Greenberg, V. Pironello. In preparation
- Cronin, J. R., Pizzarello, S. 1986. Amino acids of the Murchison meteorite. III. Seven carbon acyclic primary α -amino alkanolic acids. *Geochim. Cosmochim. Acta* 50: 2419-27
- Cronin, J. R., Pizzarello, S. 1990. Aliphatic hydrocarbons of the Murchison meteorite. *Geochim. Cosmochim. Acta* 54: 2859-68
- Cronin, J. R., Pizzarello, S., Cruikshank, D. P. 1988. Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets. See Kerridge & Matthews 1988, pp. 819-57
- de Vries, M. S., Wendt, H. R., Hunziker, H. 1991. Search for high molecular weight polycyclic aromatic hydrocarbons and fullerenes in carbonaceous meteorites. *Lunar Planet. Sci. XXII*, pp. 315-16.
- Houston: Lunar Planet. Inst.
- DuFresne, E. R., Anders, E. 1962. On the chemical evolution of the carbonaceous chondrites. *Geochim. Cosmochim. Acta* 26: 1085-1114
- Epstein, S., Krishnamurthy, R. V., Cronin, J. R., Pizzarello, S., Yuen, G. U. 1987. Unusual stable isotope ratios in amino acid and carboxylic acid extracts from the Murchison meteorite. *Nature* 326: 477-79
- Fanale, F. P., Cannon, W. A. 1974. Surface properties of the Orgueil meteorite: implications for the early history of solar system volatiles. *Geochim. Cosmochim. Acta* 88: 453-70
- Fegley, B., Post, J. E. 1985. A refractory inclusion in the Kaba CV3 chondrite: some implications for the origin of spinel-rich objects in chondrites. *Earth Planet. Sci. Lett.* 75: 297-310
- Fredriksson, K., Kerridge, J. F. 1988. Carbonates and sulfates in CI chondrites: formation by aqueous activity on the parent body. *Meteoritics* 23: 35-44
- Fredriksson, K., Jarosewich, E., Beauchamp, R., Kerridge, J. 1980. Sulfate veins, carbonates, limonite and magnetite: evidence on the late geochemistry of the C-1 regoliths. *Meteoritics* 15: 291-92
- Fuchs, L. H., Olsen, E., Jensen, K. J. 1973. Mineralogy, mineral-chemistry, and composition of the Murchison (C2) meteorite. *Smithson. Contrib. Earth Sci.* 10: 1-39
- Grady, M. M., Wright, I. P., Fallick, A. E., Pillinger, C. T. 1983. The stable isotopic composition of carbon, nitrogen, and hydrogen in some Yamato meteorites. *Proc. 8th Symp. Antarctic Meteorites*, ed. T. Nagata. Tokyo: Natl. Inst. Polar Res. 30: 292-305
- Grady, M. M., Wright, I. P., Awart, P. K., Pillinger, C. T. 1988. The carbon and oxygen isotopic composition of meteoritic carbonates. *Geochim. Cosmochim. Acta* 52: 2855-66
- Grady, M. M., Wright, I. P., Pillinger, C. T. 1991. Comparisons between Antarctic and non-Antarctic meteorites based on carbon isotope geochemistry. *Geochim. Cosmochim. Acta* 55: 49-58
- Graham, A. L., Kurat, G. 1991. Phyllosilicates in the Yamato-82042 carbonaceous chondrite—primitive or not? *Lunar Planet. Sci. XXII*, pp. 475. Houston: Lunar Planet. Inst.
- Graham, A. L., Lee, M. 1992. The matrix mineralogy of the Vigarano (CV3) chondrite. *Lunar Planet. Sci. XXIII*, pp. 435. Houston: Lunar Planet. Inst.
- Green, H. W., Radcliffe, S. V., Heuer, A. H. 1971. Allende meteorite: a high-voltage electron petrographic study. *Science* 172: 936-39

- Greenberg, J. M. 1984. Chemical evolution in space. *Origins of Life* 14: 25–35
- Grimm, R. E., McSween, H. Y. Jr. 1989. Water and the thermal evolution of carbonaceous chondrite parent bodies. *Icarus* 82: 244–80
- Hahn, J. H., Zenobi, R., Bada, J. L., Zare, R. N. 1988. Application of two-step laser mass spectrometry to cosmochemistry: direct analysis of meteorites. *Science* 239: 1523–25
- Halbout, J., Robert, F., Javoy, M. 1986. Oxygen and hydrogen isotope relations in water and acid residues of carbonaceous chondrites. *Geochim. Cosmochim. Acta* 50: 1599–1609
- Hashimoto, A., Grossman, L. 1987. Alteration of Al-rich inclusions inside amoeboid olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta* 51: 1685–1704
- Hayatsu, R., Anders, E. 1981. Organic compounds in meteorites and their origins. In *Cosmo- and Geochemistry*, vol. 99, *Topics in Current Chemistry*, pp. 1–37. Berlin: Springer-Verlag
- Hayatsu, R., Matsuoka, S., Scott, R. G., Studier, M., Anders, E. 1977. Origin of organic matter in the early solar system—VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta* 41: 1325–39
- Hayatsu, R., Studier, M. H., Moore, L. P., Anders, E. 1975. Purines and triazines in the Murchison meteorite. *Geochim. Cosmochim. Acta* 39: 471–88
- Hayatsu, R., Winans, R. E., Scott, R. G., McBeth, R. L., Moore, L. P., Studier, M. H. 1980. Phenolic ethers in the organic polymer of the Murchison meteorite. *Science* 207: 1202–4
- Hayes, J. M. 1967. Organic constituents of meteorites: a review. *Geochim. Cosmochim. Acta* 31: 1395–440
- Herr, W., Skerza, B. 1969. Mössbauer spectroscopy applied to the classification of stony meteorites. In *Meteorite Research*, ed. P. M. Millman, pp. 106–22. Dordrecht: Reidel
- Holweger, H. 1977. The solar Na/Ca and S/Ca ratios: a close comparison with carbonaceous chondrites. *Earth Planet. Sci. Lett.* 34: 152–54
- Huss, G. R. 1990. Ubiquitous interstellar diamond and SiC in primitive chondrites: abundances reflect metamorphism. *Nature* 347: 159–62
- Huss, G. R., Keil, K., Taylor, G. J. 1981. The matrices of unequilibrated ordinary chondrites: implications for the origin and history of chondrites. *Geochim. Cosmochim. Acta* 45: 33–51
- Huss, G. R., Lewis, R. S. 1990. Interstellar diamonds and silicon carbide in enstatite chondrites. *Lunar Planet. Sci. XXI*, pp. 542–43. Houston: Lunar Planet. Inst.
- Iijima, S., Buseck, P. R. 1975. High resolution electron microscopy of enstatite I: Twinning, polymorphism, and polytypism. *Am. Mineral.* 60: 758–70
- Iijima, S., Buseck, P. R. 1978. Experimental study of disordered mica structures by high resolution electron microscopy. *Acta Cryst.* A34: 709–19
- Jedwab, J. 1971. La magétite de la météorite d'Orgueil vue au microscope électronique à Balayage. *Icarus* 35: 319–40
- Johnson, C. A., Prinz, M. 1991. Carbonate compositions in CM and CI chondrites and Mg-Fe-Mn partitioning during aqueous alteration. *Lunar Planet. Sci. XXI*, pp. 643–44. Houston: Lunar Planet. Inst.
- Jungclauss, G. A., Cronin, J. R., Moore, C. B., Yuen, G. U. 1979. Aliphatic amines in the Murchison meteorite. *Nature* 261: 126–28
- Jungclauss, G. A., Yuen, G. U., Moore, C. B., Lawless, J. G. 1976. Evidence for the presence of low molecular weight alcohols and carbonyl compounds in the Murchison meteorite. *Meteoritics* 11: 231–37
- Kallemeyn, G. W., Rubin, A. E., Wasson, J. T. 1991. The compositional classification of chondrites: V. The Karoonda (CK) group of carbonaceous chondrites. *Geochim. Cosmochim. Acta* 55: 881–92
- Keller, L. P., Buseck P. R. 1990a. Matrix mineralogy of the Lancé CO3 carbonaceous chondrite. *Geochim. Cosmochim. Acta* 54: 1155–63
- Keller, L. P., Buseck, P. R. 1990b. Aqueous alteration of the Kaba CV3 carbonaceous chondrite. *Geochim. Cosmochim. Acta* 54: 2113–20
- Keller, L. P., Buseck, P. R. 1991. Calcic micas in the Allende meteorite: evidence for hydration reactions in the early solar nebula. *Science* 252: 946–49
- Keller, L. P., Thomas, K. L. 1991. Matrix mineralogy of the Bali CV3 carbonaceous chondrite. *Lunar Planet. Sci. XXII*, pp. 705–6. Houston: Lunar Planet. Inst.
- Keller, L. P., Thomas, K. L., McKay, D. S. 1992. An interplanetary dust particle with links to CI chondrites. *Geochim. Cosmochim. Acta* 56: 1409–12
- Kerridge, J. F. 1976. Major element compositions of phyllosilicates in the Orgueil carbonaceous meteorite. *Earth Planet. Sci. Lett.* 29: 194–200
- Kerridge, J. F. 1977. Correlation between nickel and sulfur abundances in Orgueil phyllosilicates. *Geochim. Cosmochim. Acta* 41: 1163–64
- Kerridge, J. F. 1985. Carbon, hydrogen and nitrogen in carbonaceous chondrites:

- abundances and isotopic compositions. *Geochim. Cosmochim. Acta* 49: 1707-14
- Kerridge, J. F., Bunch, T. E. 1979. Aqueous activity on asteroids: evidence from carbonaceous meteorites. In *Asteroids*, ed. R. P. Binzel, T. Gehrels, M. S. Matthews, pp. 745-64. Tucson: Univ. Ariz. Press
- Kerridge, J. F., Chang, S., Shipp, R. 1987. Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* 51: 2527-40
- Kerridge, J. F., Mackay, A. L., Boynton, W. V. 1979. Magnetite in CI carbonaceous meteorites: origin by aqueous activity on a planetesimal surface. *Science* 205: 395-97
- Kerridge, J. F., Matthews, M. S., eds. 1988. *Meteorites and the Early Solar System*. Tucson: Univ. Ariz. Press. 1269 pp.
- Khare, B. N., Sagan, C. 1973. Red clouds in reducing atmospheres. *Icarus* 20: 311-21
- Kolodny, Y., Kerridge, J. F., Kaplan, I. R. 1980. Deuterium in carbonaceous chondrites. *Earth Planet. Sci. Lett.* 46: 149-58
- Krishnamurthy, R. V., Epstein, S., Pizzarello, S., Cronin, J. R., Yuen, G. U. 1991. Stable hydrogen and carbon isotope ratios of extractable hydrocarbons in the Murchison meteorite. *Lunar Planet. Sci. XXII*, pp. 757-58. Houston: Lunar Planet. Inst.
- Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., Smalley, R. E. 1985. C₆₀: Buckminsterfullerene. *Nature* 318: 162-63
- Kung, C. C., Clayton, R. N. 1978. Nitrogen abundances and isotopic compositions in stony meteorites. *Earth Planet. Sci. Lett.* 38: 421-35
- Lange, M. A., Lambert, P., Ahrens, T. J. 1985. Shock effects on hydrous minerals and implications for carbonaceous chondrites. *Geochim. Cosmochim. Acta* 49: 1715-26
- Lanimer, J. W., Anders, E. 1970. Chemical fractionations in meteorites—III. Major element fractionations in chondrites. *Geochim. Cosmochim. Acta* 34: 367-87
- Lawless, J. G., Zeitman, B., Pereira, W. E., Summons, R. E., Duffield, A. M. 1974. Dicarboxylic acids in the Murchison meteorite. *Nature* 251: 40-41
- Lewis, R. S., Anders, E. 1975. Condensation time of the solar nebula from extinct ¹²⁹I in primitive meteorites. *Proc. Natl. Acad. Sci. USA* 72: 268-73
- Lewis, R. S., Anders, E. 1981. Isotopically anomalous xenon in meteorites: a new clue to its origin. *Astrophys. J.* 247: 1122-24
- Lewis, R. S., Anders, E., Draine, B. T. 1989. Properties, detectability and origin of interstellar diamonds in meteorites. *Nature* 339: 117-21
- Lewis, R. S., Tang, M., Wacker, J. F., Anders, E. 1987. Interstellar diamonds in meteorites. *Nature* 326: 160-62
- Llorca, J., Brearley, A. J. 1992. Alteration of chondrules in ALH84034, an unusual CM2 carbonaceous chondrite. *Lunar Planet. Sci. XXII*, pp. 793-94. Houston: Lunar Planet. Inst.
- Lumpkin, G. R. 1981. Electron microscopy of carbonaceous matter in Allende acid residues. *Proc. Lunar Planet. Sci. Conf. 12B*, pp. 1153-66. Houston: Lunar Planet. Inst.
- Mackinnon, I. D. R. 1980. Structures and textures of the Murchison and Mighei carbonaceous chondrite matrices. *Proc. Lunar Planet. Sci. Conf. 11th*, pp. 839-52. Houston: Lunar Planet. Inst.
- Mackinnon, I. D. R. 1982. Ordered mixed-layer structures in the Mighei carbonaceous chondrite matrix. *Geochim. Cosmochim. Acta* 46: 479-89
- Mackinnon, I. D. R. 1985. Fine-grained phases in carbonaceous chondrites: Alais and Leoville. *Meteoritics* 20: 702-3
- Mackinnon, I. D. R., Buseck, P. R. 1979. New phyllosilicate types in a carbonaceous chondrite matrix. *Nature* 280: 219-20
- Mackinnon, I. D. R., Zolensky, M. 1984. Proposed structures for poorly characterized phases in C2M carbonaceous chondrite meteorites. *Nature* 309: 240-42
- Madsen, M. B., Morup, S., Costa, T. V. V., Knudsen, J. M., Olsen, M. 1986. Superparamagnetic component in the Orgueil meteorite and Mössbauer spectroscopy studies in applied magnetic fields. *Nature* 321: 501-3
- Mayeda, T. K., Clayton, R. N., Yanai, K. 1987. Oxygen isotopic compositions of several Antarctic meteorites. *Proc. 11th Symp. Antarctic Meteorites*, ed. K. Yanai, 46: 144-50. Tokyo: Natl. Inst. Polar Res.
- McKee, T. R., Buseck, P. R. 1978. HRTEM observation of stacking and ordered interstratification in rectorite. *Ninth Int. Congr. Electr. Microsc.*, 1: 272-73. Toronto: Microsc. Soc. Can.
- McKee, T. R., Moore, C. B. 1979. Characterization of submicron matrix phyllosilicates from Murray and Nogoya carbonaceous chondrites. *Proc. Lunar Planet. Sci. Conf. 10th*, pp. 921-36. New York: Pergamon
- McNaughton, N. J., Hinton, R. W., Pillinger, C. T., Fallick, A. E. 1982. D/H ratios of some ordinary and carbonaceous chondrites. *Meteoritics* 17: 252
- McSween, H. Y. Jr. 1977. Chemical and petrographic constraints on the origin of chondrules and inclusions in car-

- bonaceous chondrites. *Geochim. Cosmochim. Acta* 41: 1843–60
- McSween, H. Y. Jr. 1979a. Alteration in CM carbonaceous chondrites inferred from modal and chemical variations in matrix. *Geochim. Cosmochim. Acta* 43: 1761–70
- McSween, H. Y. Jr. 1979b. Are carbonaceous chondrites primitive or processed? A review. *Rev. Geophys. Space Phys.* 17: 1059–78
- McSween, H. Y. Jr. 1987. Aqueous alteration in carbonaceous chondrites: mass balance constraints on matrix mineralogy. *Geochim. Cosmochim. Acta* 51: 2469–77
- McSween, H. Y. Jr., Richardson, S. M. 1977. The composition of carbonaceous chondrite matrix. *Geochim. Cosmochim. Acta* 41: 1145–61
- McSween, H. Y. Jr., Weissman, P. R. 1989. Cosmochemical implications of the physical processing of cometary nuclei. *Geochim. Cosmochim. Acta* 53: 3263–71
- Metzler, K., Bischoff, A. 1991. Evidence for aqueous alteration prior to parent body formation: petrographic observations in CM-chondrites. *Lunar Planet. Sci. XXII*, pp. 893–94. Houston: Lunar Planet. Inst.
- Metzler, K., Bischoff, A., Morfill, G. 1991. Accretionary dust mantles in CM chondrites: chemical variations and calculated time scales of formation. *Meteoritics* 26: 372
- Metzler, K., Bischoff, A., Stöffer, D. 1992. Accretionary dust mantles in CM chondrites: evidence for solar nebula processes. *Geochim. Cosmochim. Acta* 56: 2873–97
- Miller, S. L. 1955. Production of some organic compounds under possible primitive Earth conditions. *J. Am. Chem. Soc.* 77: 2351–61
- Müller, W. F., Kurat, G., Kracher, A. 1979. Chemical and crystallographic study of cronstedtite in the matrix of the Cochabamba (CM2) carbonaceous chondrite. *Tschermaks Mineral. Petrogr. Mitt.* 26: 293–304
- Nagahara, H. 1984. Matrices of type 3 ordinary chondrites—primitive nebular records. *Geochim. Cosmochim. Acta* 46: 2581–95
- Nagy, B. 1975. *Carbonaceous Meteorites*. New York: Elsevier. 747 pp.
- Nagy, B., Meinschein, W. G., Hennessy, D. J. 1963. Aqueous low temperature environment of the Orgueil meteorite parent body. *Ann. N. Y. Acad. Sci.* 108: 534–52
- Niederer, F. R., Eberhardt, P., Geiss, J. 1985. Carbon isotope abundances in Murchison residue 2C10c. *Meteoritics* 20: 716–18
- Olsen, E. J., Davis, A. M., Hutcheon, I. D., Clayton, R. N., Mayeda, T. K., Grossman, L. 1988. Murchison xenoliths. *Geochim. Cosmochim. Acta* 52: 1615–26
- Organova, N. I., Genkin, A. D., Drits, V. A., Dmitrik, A. L., Kuzmina, O. V. 1971. Tochilinite: a new sulfide hydroxide of iron and magnesium. *Zap. Vses. Mineral. O.* 4: 477–87
- Peck, J. A. 1983. An SEM petrographic study of C3(V) meteorite matrix. *Lunar Planet. Sci. XIV*, pp. 598–99. Houston: Lunar Planet. Inst.
- Peck, J. A. 1984. Origin of the variation in properties of CV3 meteorite matrix and matrix clasts. *Lunar Planet. Sci. XV*, pp. 635–36. Houston, Lunar Planet. Inst.
- Peltzer, E. T., Bada, J. L. 1978. α -Hydroxycarboxylic acids in the Murchison meteorite. *Nature* 272: 443–44
- Peltzer, E. T., Bada, J. L., Schlesinger, G., Miller, S. L. 1984. The chemical conditions on the parent body of the Murchison meteorite: some conclusions based on amino, hydroxy and dicarboxylic acids. *Adv. Space Res.* 4: 69–74
- Pierce, L., Buseck, P. R. 1974. Electron imaging of pyrrhotite superstructures. *Science* 186: 1209–12
- Prinn, R. G., Fegley, B. 1989. Solar nebula chemistry: origin of planetary satellite, and cometary volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. Atreya, J. Pollack, M. S. Matthews, pp. 78–136. Tucson: Univ. Ariz. Press
- Ramdohr, P. 1973. *The Opaque Minerals in Stony Meteorites*. New York: Elsevier. 245 pp.
- Richardson, S. M. 1978. Vein formation in the CI carbonaceous chondrites. *Meteoritics* 13: 141–59
- Richardson, S. M., McSween, H. Y. Jr. 1978. Textural evidence bearing on the origin of isolated olivine crystals in C2 carbonaceous chondrites. *Earth Planet. Sci. Lett.* 37: 485–91
- Rietmeijer, F. J. M., Mackinnon, I. D. R. 1985. Layer silicates in a chondritic porous interplanetary dust particle. *Proc. Lunar Planet. Sci. Conf.*, 15th, *J. Geophys. Res.* 90: D149–55
- Robert, F., Epstein, S. 1982. The concentration and isotopic composition of hydrogen, carbon and nitrogen in carbonaceous meteorites. *Geochim. Cosmochim. Acta* 46: 81–95
- Rubin, A. E., Kallemeyn, W. G. 1990. Lewis Cliff 85332: a unique carbonaceous chondrite. *Meteoritics* 25: 215–25
- Rubin, A. E., Wang, D., Kallemeyn, G. W., Wasson, J. T. 1988. The Ningqiang meteorite: classification and petrology of an anomalous CV chondrite. *Meteoritics* 23: 13–23
- Rubin, A. E., Wasson, J. T. 1987. Chondrules, matrix and coarse-grained chon-

- drule rims in the Allende meteorite: origin, interrelationships and possible precursor components. *Geochim. Cosmochim. Acta* 51: 1923–37
- Rubin, A. E., Wasson, J. T. 1988. Chondrules and matrix in the Ormans CO3 meteorite: possible precursor components. *Geochim. Cosmochim. Acta* 52: 425–32
- Scott, E. R. D., Barber, D. J., Alexander, C. M., Hutchison, R., Peck, J. A. 1988. Primitive material surviving in chondrites: Matrix. See Kerridge & Matthews 1988, pp. 718–45
- Scott, E. R. D., Rubin, A. E., Taylor, G. J., Keil, K. 1984. Matrix material in type 3 chondrites—occurrence, heterogeneity and relationship with chondrules. *Geochim. Cosmochim. Acta* 48: 1741–57
- Shock, E. L., Schulte, M. D. 1990. Summary and implications of reported amino acid concentrations in the Murchison meteorite. *Geochim. Cosmochim. Acta* 54: 3159–73
- Smith, J. W., Kaplan, I. R. 1970. Endogenous carbon in carbonaceous meteorites. *Science* 167: 1367–70
- Smith, P. P. K., Buseck, P. R. 1981. Graphitic carbon in the Allende meteorite: a microstructural study. *Science* 212: 322–24
- Studier, M. H., Hayatsu, R., Anders, E. 1968. Origin of organic matter in the early solar system—I. Hydrocarbons. *Geochim. Cosmochim. Acta* 32: 151–73
- Suess, H. E. 1949. Zur Chemie der Planeten- und Meteoritenbildung. *Z. Elektrochem.* 53: 237–41
- Suess, H. E., Urey, H. C. 1956. Abundances of the elements. *Rev. Mod. Phys.* 28(1): 53–74
- Swart, P. K., Grady, M. M., Pillinger, C. T., Lewis, R. S., Anders, E. 1983. Interstellar carbon in meteorites. *Science* 220: 406–10
- Tang, M., Anders, E. 1988a. Isotopic anomalies of Ne, Xe, and C in meteorites. II. Interstellar diamond and SiC: carriers of exotic noble gases. *Geochim. Cosmochim. Acta* 52: 1235–44
- Tang, M., Anders, E. 1988b. Interstellar silicon carbide: How much older than the solar system? *Astrophys. J. Lett.* 335: L31–34
- Tang, M., Anders, E., Hoppe, P., Zinner, E. 1989. Meteoritic silicon carbide and its stellar sources for galactic chemical evolution. *Nature* 339: 351–54
- Tang, M., Lewis, R. S., Anders, E., Grady, M. M., Wright, I. P., Pillinger, C. T. 1988. Isotopic anomalies of Ne, Xe, and C in meteorites. I. Separation of carriers by density and chemical resistance. *Geochim. Cosmochim. Acta* 52: 1221–34
- Thiemens, M. H. 1988. Heterogeneity in the nebula: evidence from stable isotopes. See Kerridge & Matthews 1988, pp. 899–923
- Tielens, A. G., Seab, D. J., Hollenbach, D. J., McKee, C. F. 1987. Shock processing of interstellar dust: diamonds in the sky. *Astrophys. J.* 319: L109–13
- Tomeoka, K. 1990. Phyllosilicate veins in a CI meteorite: evidence for aqueous alteration on the parent body. *Nature* 345: 138–40
- Tomeoka, K., Buseck, P. R. 1982a. Intergrown mica and montmorillonite in the Allende carbonaceous chondrite. *Nature* 299: 326–27
- Tomeoka, K., Buseck, P. R. 1982b. High-resolution transmission electron microscopy observations of “Poorly characterized phase” in the Mighei C2M carbonaceous chondrite. *Meteoritics* 17: 289–90
- Tomeoka, K., Buseck, P. R. 1983a. An exotic Fe-Ni-S-O layered mineral: an improved characterization of the “Poorly Characterized Phase” in C2M carbonaceous chondrites. *Lunar Planet. Sci. XIV*, pp. 789–90. Houston: Lunar Planet. Inst.
- Tomeoka, K., Buseck, P. R. 1983b. Unusual microstructures in the C2 carbonaceous chondrites. 41st *Annu. Electr. Microsc. Soc. Am.*, pp. 188–89. San Francisco: San Francisco Press
- Tomeoka, K., Buseck, P. R. 1983c. A new layered mineral from the Mighei carbonaceous chondrite. *Nature* 306: 354–56
- Tomeoka, K., Buseck, P. R. 1985a. Indicators of aqueous alteration in CM carbonaceous chondrites: microtextures of a layered mineral containing Fe, S, O, and Ni. *Geochim. Cosmochim. Acta* 49: 2149–63
- Tomeoka, K., Buseck, P. R. 1985b. Hydrated interplanetary dust particle linked with carbonaceous chondrites? *Nature* 314: 338–40
- Tomeoka, K., Buseck, P. R. 1986. Phyllosilicates in the Mokoia CV3 carbonaceous chondrite: petrographic and transmission electron microscope observations. *Lunar Planet. Sci. XVII*, pp. 899–900. Houston: Lunar Planet. Inst.
- Tomeoka, K., Buseck, P. R. 1988. Matrix mineralogy of the Orgeuil CI carbonaceous chondrite. *Geochim. Cosmochim. Acta* 52: 1627–40
- Tomeoka, K., Buseck, P. R. 1990. Phyllosilicates in the Mokoia CV carbonaceous chondrite: evidence for aqueous alteration in an oxidizing condition. *Geochim. Cosmochim. Acta* 54: 1745–54
- Tomeoka, K., McSween, H. Y. Jr., Buseck, P. R. 1989. Mineralogical alteration of CM carbonaceous chondrites: a review. *Proc., NIPR. Symp. Antarctic Meteorites* 2: 221–34
- Tomeoka, K., Kojima, H., Yanai, K. 1989. Yamato-82162: a new kind of CI carbonaceous chondrite found in Antarctica.

- Proc., NIPR. Symp. Antarctic Meteorites* 2: 36-54
- Van Schmus, W. R. 1969. Mineralogy, petrology and classification of types 3 and 4 carbonaceous chondrite. In *Meteorite Research*, ed. P. M. Millman, pp. 480-91. Dordrecht: Reidel
- Van Schmus, W. R., Hayes, J. M. 1974. Chemical and petrographic correlations among carbonaceous chondrites. *Geochim. Cosmochim. Acta* 38: 47-64
- Van Schmus, W. R., Wood, J. A. 1967. A chemical-petrologic classification for the chondritic meteorites. *Geochim. Cosmochim. Acta* 31: 737-65
- Veblen, D. R., Buseck, P. R. 1979. Serpentine minerals: intergrowths and new combination structures. *Science* 206(4425): 1398-400
- Wasson, J. T. 1974. *Meteorites: Classification and Properties*. New York: Springer-Verlag. 316 pp.
- Wasson, J. T. 1985. *Meteorites—Their Record of Early Solar-System History*. New York: Freeman. 267 pp.
- Wasson, J. T., Kallemeyn, G. W. 1988. Compositions of chondrites. *Philos. Trans. R. Soc. London Ser. A* 325: 535-44
- Wdowiak, T. J., Agresti, D. G. 1984. Presence of a superparamagnetic component in the Orgueil meteorite. *Nature* 311: 140-42
- Weisberg, M. K., Prinz, M. 1991. Aqueous alteration in CR2 chondrites. *Lunar Planet. Sci. XXII*, pp. 1483-84. Houston: Lunar Planet. Inst.
- Weisberg, M. K., Prinz, M., Chatterjee, N., Clayton, R. N., Mayeda, T. K. 1991. Dark inclusions in CR2 Chondrites. *Meteoritics* 26: 407
- Wiik, H. B. 1956. The chemical composition of some stony meteorites. *Geochim. Cosmochim. Acta* 9: 279-89
- Wing, M. R., Bada, J. L. 1991. Geochromatography on the parent body of the carbonaceous chondrite Ivuna. *Geochim. Cosmochim. Acta* 55: 2937-42
- Wood, J. A. 1967. Chondrites: their metallic minerals, thermal histories, and parent planet. *Icarus* 6: 1-49
- Yang, J., S. Epstein. 1983. Interstellar organic matter in meteorites. *Geochim. Cosmochim. Acta* 47: 2199-2216
- Yang, J., Epstein, S. 1984. Relic interstellar grains in meteorites. *Nature* 311: 544-47
- Yuen, G., Blair, N., Des Marais, D. J., Chang, S. 1984. Carbon isotope composition of low molecular weight hydrocarbons and monocarboxylic acids from Murchison meteorite. *Nature* 307: 252-54
- Zaikowski, A. 1979. Infrared spectra of the Orgueil (C-1) chondrite and serpentine minerals. *Geochim. Cosmochim. Acta* 43: 943-45
- Zenobi, R., Philippoz, J. M., Buseck, P. R., Zare, R. N. 1989. Spatially resolved organic analysis of the Allende meteorite. *Science* 246: 1026-29
- Zinner, E., Fahey, A., McKeegan, K. 1986. Ion probe isotopic measurements of refractory phases from CM and CV meteorites. *Terra Cognita* 6: 129
- Zinner, E., Tang, M., Anders, E. 1989. Interstellar SiC in the Murchison and Murray meteorites: isotopic composition of Ne, Xe, Si, C, and N. *Geochim. Cosmochim. Acta* 53: 3273-90
- Zolensky, M. E. 1991. Mineralogy and matrix composition of "CR" chondrites Renazzo and EET 87770, and ungrouped chondrites Essebi and MAC 87300. *Meteoritics* 26: 414
- Zolensky, M. E., Gooding, J. L., Barrett, R. A. 1987. Mineralogical variations within the matrices of CM carbonaceous chondrites. *Meteoritics* 22: 544-45
- Zolensky, M. E., McSween, H. Y. Jr. 1988. Aqueous alteration. See Kerridge & Matthews 1988, pp. 114-43
- Zolensky, M. E., Barret, R. A., Prinz, M. 1989. Petrography, mineralogy and matrix composition of Yamato-82162, a new C12 chondrite. *Lunar Planet. Sci. XX*, pp. 1253-54. Houston: Lunar Planet. Inst.