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Carbonates in Vigarano: Terrestrial, preterrestrial, or both?

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Abstract–Studies of two separate stones of the CV3 chondrite Vigarano have revealed the presence of previously unreported occurrences of calcite. In the first stone, calcite occurs as thin veins in a type B CAI. In contrast, observations of the second stone, which was recovered one month after its fall, show three calcite occurrences: networks of veins, vesicle fillings in the fusion crust, and pseudomorphic replacement of augite associated with a porphyritic olivine chondrule. The most common occurrence is as veins ranging in thickness from <1 μm to 25 μm and extending for more than several hundred μm. Some veins crosscut the fusion crust and are connected to a carbonate coating on the exterior of the meteorite. Extensive minor element zoning occurs in carbonate masses, indicating variations in the fluid composition and/or redox potential during carbonate growth. Based on the textural evidence and a comparative study with carbonate veins in the CV3 chondrite Leoville, we conclude that the veins are terrestrial in origin. We propose a model for rapid carbonate formation in which calcite precipitation is driven by hydrolysis and oxidation in the meteorite interior that move the fluid composition to alkaline values. In addition, both stones also contain minor occurrences of carbonate that are not readily explained by terrestrial alteration. Minor carbonate in a type B CAI occurs in the first stone and calcite occurs as pseudomorphic replacement of augite in the second stone. Both of these occurrences appear to be preterrestrial, probably asteroidal in origin.

INTRODUCTION

The CV carbonaceous chondrites are a diverse group of meteorites that show a wide range in their degree of oxidation, textural characteristics, and metamorphism (e.g., McSween 1977; Krot et al. 1995), pointing to a complex evolutionary history. McSween (1977) made the important observation that the CV chondrites could be divided into oxidized and reduced subgroups. The oxidized group is characterized by the presence of magnetite and high-Ni metal, taenite, whereas the reduced group contains kamacite. Vigarano, the type CV3 chondrite, belongs to the reduced subgroup of the CV chondrites, but it is a breccia that contains both reduced and oxidized material (McSween 1977). Although Vigarano appears to be relatively unmetamorphosed, it has experienced limited aqueous alteration, as indicated by the presence of small amounts of ferrihydrite and smectite in its matrix (Lee et al. 1996).

Vigarano was observed to fall on the evening of January 22, 1910 in Vigarano Pieve, a farming community west of the city of Ferrara, Italy. It consists of two stones weighing 11.5 kg and 4.5 kg, respectively. The first stone was collected from a snow-covered field within hours of its fall (Rosati 1910a). The second, smaller stone was recovered a month after the first, approximately 700 m from the Saracca farm, where the first stone was observed to fall (Rosati 1910b). Both Vigarano stones have a polished, dark fusion crust. However, when the second stone was first examined, it already showed evidence of terrestrial weathering indicated by metallic rust visible to the unaided eye (Rosati 1910b). These alteration products were attributed to the second stone's longer residence in the fine-textured, clay-rich, fluvial sediments characteristic of the Ferrara region.

As part of a study to investigate the distribution of carbonaceous material in the matrices of CV chondrites, we have studied Vigarano in order to compare it with our observations on Allende (Brearley 1999). During preliminary scanning electron microscopy (SEM) studies of thin sections from the University of New Mexico (UNM) collection, we encountered ubiquitous and previously unreported occurrences of calcium carbonate that typically occur in crosscutting veins. This work is the first detailed description of carbonates in Vigarano, although they have been reported previously in CAIs by several workers (Mao et al. 1990; Davis et al. 1991; Sylvester et al. 1993). We describe the detailed occurrences of carbonates in Vigarano and compare them with the results of a study of terrestrial carbonates in the Leoville CV3 find. These observations are used to place constraints on the possible conditions and environments of carbonate formation in Vigarano.

SAMPLE AND EXPERIMENTAL METHODS

Several thin sections of Vigarano from each of the Vigarano stones were examined. The thin sections from the second stone are from the UNM collection, section numbers UNM610 and UNM873 and a transmission electron microscopy (TEM) section without an identification number. The first two sections crosscut the fusion crust, whereas the third section does not. We also studied several thin sections that were prepared from a chip of the first Vigarano stone. This sample was kindly provided by Dr. Monica Grady of the Natural History Museum, London, England. Finally, we have also studied a thin section of the reduced CV3 chondrite Leoville from the UNM collection, UNM674.

The petrographic thin sections were examined using backscattered electron (BSE) imaging on a JEOL 5800LV scanning electron microscope. The X-ray mapping was performed on this instrument using an Oxford Instrument ISIS 200 X-ray analysis system linked to a Pentafet ultra-thin window (UTW) energy dispersive spectroscopy (EDS) detector. The SEM was operated in the high-vacuum mode at an accelerating voltage of 20 kV. The qualitative EDS analyses were used to identify calcium carbonates. The cathodoluminescence (CL) imaging was also performed on the JEOL 5800LV, utilizing an Oxford Instruments cathodoluminescence system with a dwell time per pixel of 1600 μsec. The quantitative chemical data were obtained using a JEOL JXA-733 Superprobe equipped with five wavelength dispersive spectrometers (WDS). The microprobe analyses were carried out at an accelerating voltage of 15 kV and a probe current of 20 nA using an electron probe diameter of 1 μm. The standards used for the analyses were calcite (Ca), dolomite (Mg), siderite (Fe), celestite (Sr), and spessartine (Mn), all from the Smithsonian Institution (Jarosewich and Macintyre 1983). Full ZAF corrections were applied to the data. Under the analytical conditions used for the calcite analyses, the detection limits for the minor elements are as follows: MgO = 0.012 wt%, FeO = 0.010 wt%, MnO = 0.010 wt%, and SrO = 0.014 wt%.

Transmission electron microscopy of carbonate was carried out using a JEOL 2010 HRTEM operating at 200 kV. Electron diffraction pattern analysis was carried out on TEM plates and by fast fourier transform analysis of digital high resolution TEM images using GATAN Digital Microscopy Suite software.

Geochemist's Workbench software tools version 3.2.2, developed at the University of Illinois, was used to calculate the phase diagrams for the altering solutions responsible for the formation of the carbonate.

RESULTS

Second Vigarano Stone

Calcium carbonate occurs most commonly as veins in the UNM Vigarano thin sections. Using BSE imaging (Figs. 1a and 2b), we identified systems of veins ranging in thickness from <1 μm to 25 μm that extend several hundred μm through the thin sections. The carbonate veins form a network that crosscuts the Vigarano matrix with individual veins sometimes following the interfaces between the matrix and chondrules. The veins also occur crosscutting chondrules and CAIs, as shown in Fig. 1c.

The interface between the veins and the host meteorite is sharp and no alteration of material adjacent to the veins is evident, indicating that the veins may have formed along existing fractures in the meteorite. Carbonate may fill part or all of the fracture (Fig. 1d). In section UNM873, some of the veins crosscut the fusion crust and connect to a carbonate-rich layer associated with very fine-grained, reddish-brown material, tentatively identified as Fe oxyhydroxide, that occurs adhering locally to the fusion crust (Fig. 1e). Based on TEM studies of Vigarano matrix (Lee et al. 1996; Brearley and Abreu 2001), it is highly probable that this Fe oxyhydroxide is ferrihydrite. Several carbonate veins originate from the carbonate layer on the meteorite exterior and extend into the interior of the stone, as shown in Fig. 1e. Carbonate is also present filling vesicles in the fusion crust.

To identify the carbonate, we removed a small amount of material from the calcrete layer of the stone and examined carbonate fragments dispersed on a holey carbon film using TEM. Several zone axis electron diffraction patterns (e.g., Fig. 1f) of the carbonate were obtained in the TEM that could be indexed unequivocally as calcite rather than aragonite. We were not, however, able to remove actual vein material from the interior of the stone because of the very small size of the veins and their rarity.

The veins are up to 25 μm in thickness at the fusion crust and become progressively thinner over less than 1 cm into the interior of the meteorite. Occasionally, thick calcite veins subdivide into a series of small, interconnected channels. The third UNM section that appears to be part of an interior region of the Vigarano stone also contains a complex system of carbonate veins. In this section, the abundance of veins appears to be independent of the distance from the fusion crust.

BSE imaging of most carbonate veins did not reveal any evidence of compositional zoning on the fine scale. Electron microprobe analyses show that this vein-filling material is calcite, sometimes with variable concentrations of MgO (0.17–4.2 wt%) and FeO (0.3–5.5 wt%). SrO is present in trace amounts (up to 0.58 wt%) and MnO is always below detection limits. Representative electron microprobe analyses of calcite are reported in Table 1. However, in one particularly

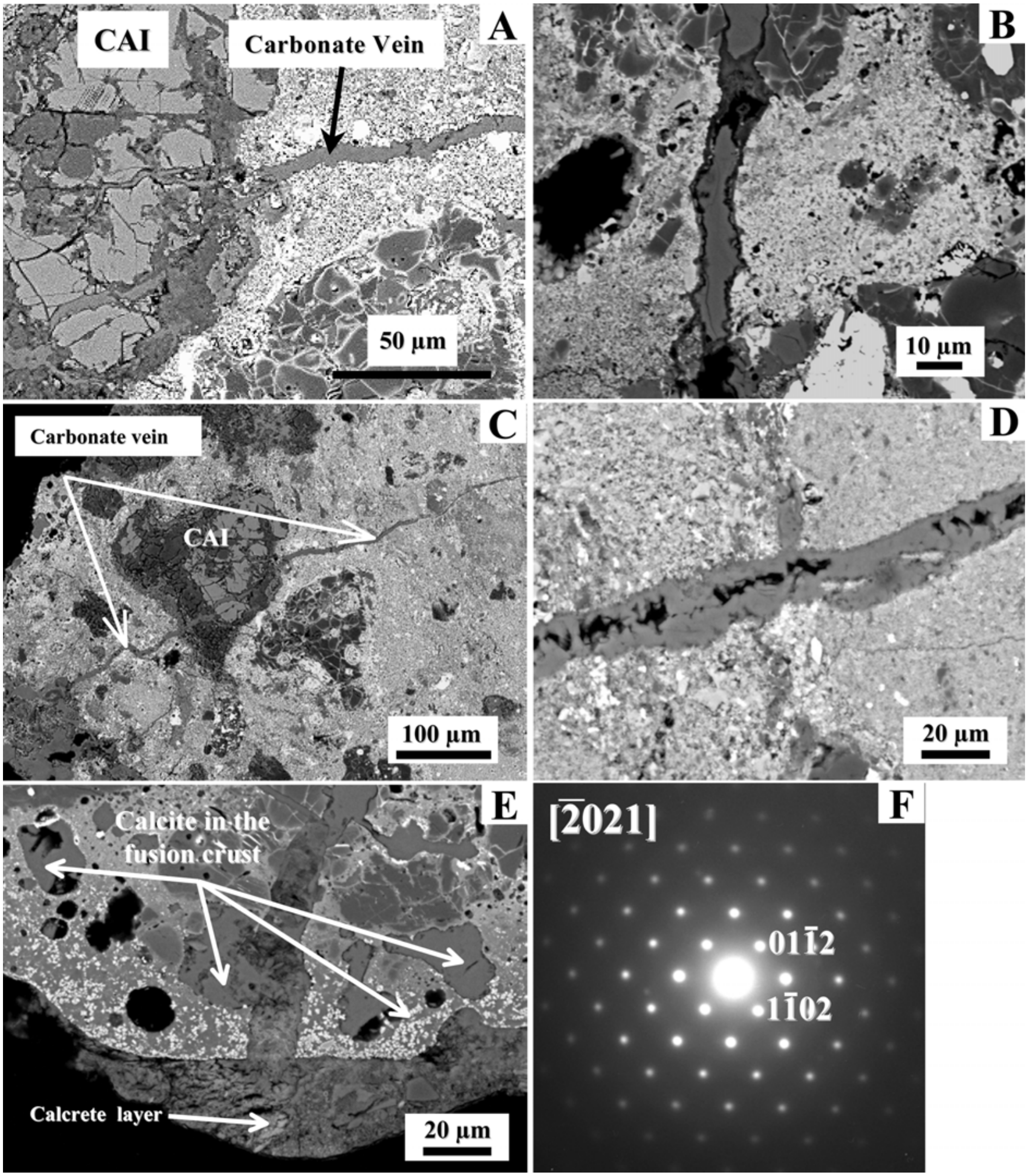

Fig. 1. BSE images of calcite veins in the second Vigarano stone. a) An image of a region of Vigarano showing extensive development of carbonate veins (arrowed). These veins range in thickness from <1 to >25 µm and can be traced for several hundreds of µm across the thin section. b) A BSE image of a segment of a carbonate vein from a sample of the second Vigarano stone. Note the detachment of the calcrete material from the host meteorite walls. Veins generally have sharp but irregular interfaces, which suggests that these formed within fractures rather than by replacement. c) A BSE image of a carbonate vein cross-cutting a region of Vigarano clastic matrix. This vein extends from a region close to the fusion crust, and crosscuts a fine-grained rim, before entering a CAI. Veins often form a complex network through the matrix and follow interfaces between the matrix and larger objects. However, they are also found crosscutting CAIs and chondrules. d) A BSE image showing a partially-filled vein in Vigarano. This clearly indicates that precipitation occurred in fractures and that fluid movement occurred within the veins. e) A BSE image of a calcrete layer associated with Fe oxide that occurs locally adhering to the fusion crust in the second Vigarano stone. The material can be traced surrounding and filling voids in the fusion crust. The carbonate veins extend from this layer into the interior of the chondrite. Veins in Vigarano are thicker close to the fusion crust and then branch into a complex array of secondary veins along their path. f) [$\bar{2}$021] zone axis electron diffraction pattern of carbonate obtained by transmission electron microscopy from the calcrete layer on the surface of the second Vigarano stone, positively identifying the carbonate as calcite.

Table 1. Representative electron microprobe analyses of calcite from veins in the second Vigarano stone.

Wt% oxide					
CaO	55.25	54.81	53.45	51.89	55.77
MgO	0.51	0.83	1.71	0.75	0.84
FeO	1.05	0.43	0.57	0.62	0.30
SrO	–	0.06	–	–	–
Total	56.80	56.12	55.73	56.17	56.91

"–" indicates below detection limit.

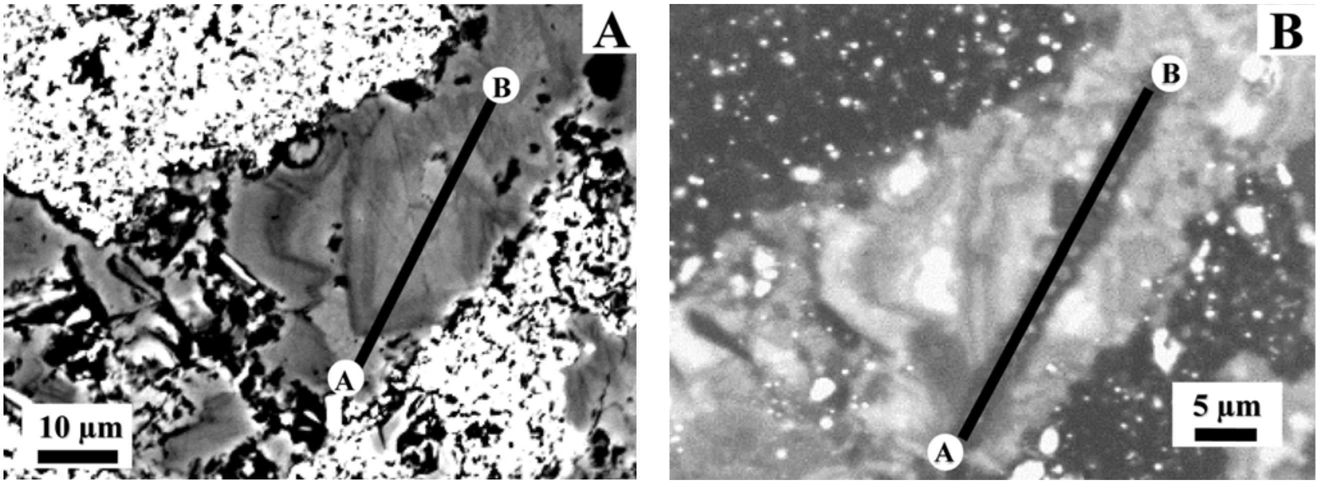

Fig. 2. BSE and CL images of carbonate occurrences in Vigarano. a) A BSE image of a large carbonate mass in Vigarano that shows complex oscillatory zoning. The points marked as A and B correspond to the start and end of the zoning profile in Figs. 2c and 2d. Compositional data from the electron probe traverse from A to B are shown in Figs. 2c and 2d. b) An image corresponding to the region studied by electron microprobe analysis. Cathodoluminescence image showing complex zoning in the carbonate mass. Dark line is a region of beam damage produced during the electron microprobe measurements. Note that the intensity profiles shown in Figs. 2c and 2d are only qualitative estimates and are not related to the wavelength of cathodoluminescence emission.

large carbonate mass in thin section UNM610, complex oscillatory zoning was observed in both BSE and CL images (Figs. 2a and 2b). Three electron microprobe traverses were measured on this grain normal to the zoning. Data for one traverse are shown in Figs. 2c and 2d, superimposed on a CL intensity profile of the grain. The CL image shown in Fig. 2b was obtained after the electron microprobe analyses were carried out. The major element (Ca) and minor element (Fe and Mg) compositions of calcite in the zoned mass and unzoned veins are compared in Fig. 3. $MgCO_3$ and $CaCO_3$ show a strong negative correlation (Fig. 3a), indicating that the dominant substitution in the calcite involves solid solution toward Mg calcite. The different profiles show slightly different trends suggesting that they may represent different periods of carbonate growth. Zoning profile 3 in particular contains a cluster of analyses that lie off the major compositional trend, although like the other profiles, this profile was also measured normal to the zoning. These analyses represent a group of carbonate analyses that have relatively high $FeCO_3$ contents (Fig. 3b). The data show no clear compositional relationships between other minor elements. For example, $MgCO_3$ appears to vary entirely independently of $FeCO_3$ (Fig. 3a) and $SrCO_3$ (not shown). Compositional data for the unzoned carbonate veins (vein data) fall within the compositional fields defined by the zoned carbonate mass.

Due to the significant beam damage to the carbonate during the microprobe analyses, exact spatial correlation between the CL intensity and the minor element contents of the calcite is not possible. The comparison of the minor element data in the zoning profiles with CL intensity was therefore carried out on parallel profiles approximately 10 µm apart. CL images (e.g., Fig. 2b) illustrate the extremely complex nature of the zoning that is present in these regions. Finger-like structures with high CL intensity are intercalated with regions of very low CL. As noted above and as confirmed by the microprobe traverses, the concentrations of $FeCO_3$, $MgCO_3$, $MnCO_3$, and $SrCO_3$ are quite variable through this carbonate mass. In general, there is only a mild correlation between the zones of high CL intensity and the areas where the $FeCO_3$, $MgCO_3$, $MnCO_3$, and $SrCO_3$ contents in the calcite are elevated. Certainly, there is no evidence of a clear correlation of high CL with Mn content, which is one of the main known activators of CL in carbonates (Machel et al. 1991). The lack of any obvious correlation may result from the limited registry between the CL and microprobe data or that some other element(s) is the key CL activator (see later discussion).

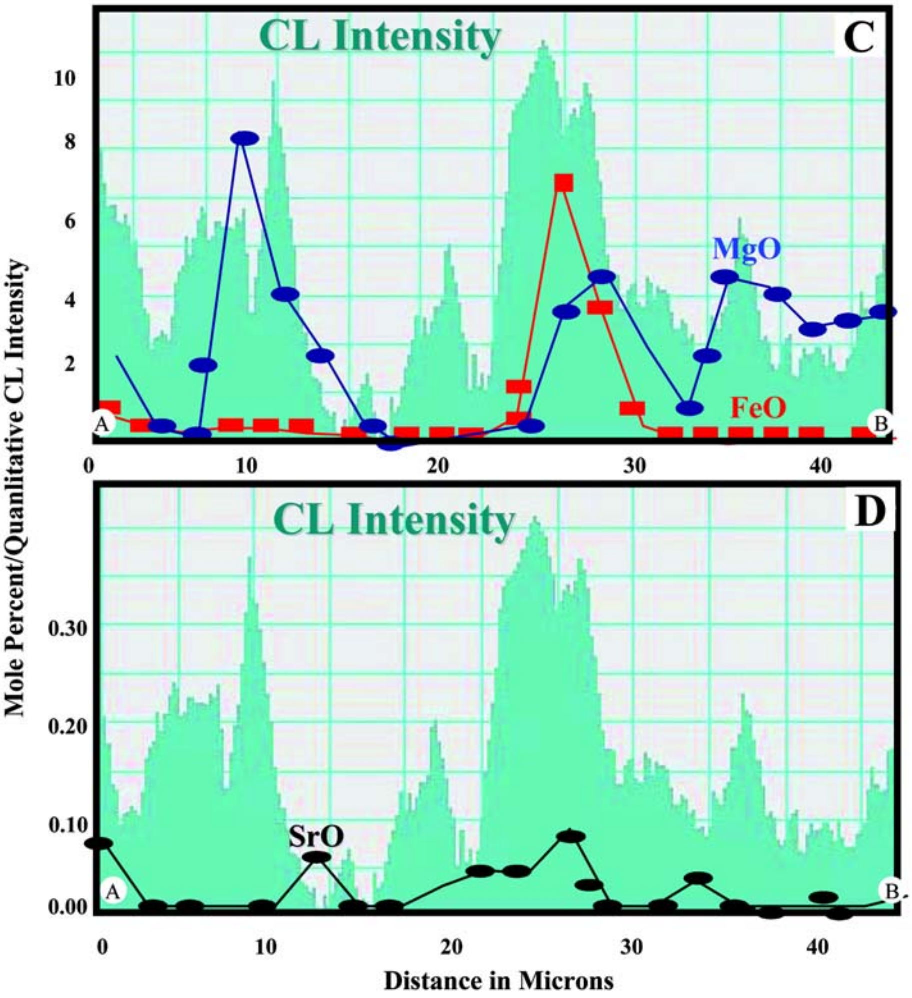

Fig. 2. *Continued.* BSE and CL images of carbonate occurrences in Vigarano. c) Electron microprobe zoning profile showing complex MgO and FeO variations across the grain along the traverse shown from A to B in Fig. 2a superimposed on a CL intensity profile and d) electron microprobe zoning profile showing complex SrO variations across the grain. MnO remains consistently below the electron probe detection limits. Variations in the minor elements show only a mild correlation with variations in CL intensity.

In addition to the carbonate veins, we have observed one occurrence of a calcite vein associated with clinopyroxene. In thin section UNM873, calcite veins are juxtaposed against diopside grains. In this case, the diopside grains are <10 µm in size and show no evidence of replacement by carbonate (Fig. 4).

In the unnumbered TEM thin section, several augite grains are present that have been partially to completely replaced by calcite on the exterior of an olivine-rich porphyritic chondrule (Figs. 5a and 5b). Representative augite compositions determined by electron microprobe are reported in Table 2. No additional alteration phases are present in the pseudomorphs. The calcite crystals are euhedral to subhedral in morphology and perfectly pseudomorph the augite crystals, although the degree of replacement is variable from one grain to another. In some pseudomorphs, irregularly shaped, corroded, relict augite grains are present in the core regions of the calcite. The adjacent chondrule olivine and low-Ca pyroxene phenocrysts show no evidence of alteration, but carbonate does occur in altered opaque assemblages within the chondrule. Matrix surrounding the different augite and calcite crystals also appears to be unaffected. Despite an extensive search of several thin sections for similar replacement textures, this is the only example of this texture we have found.

First Vigarano Stone

To help constrain the origins of the carbonates in the second Vigarano stone, we examined several thin sections that come from the stone recovered immediately after its fall. These thin sections were prepared for TEM study and have no specific number. The sample comes from the interior of the stone, away from the fusion crust. Thus, in this respect, the

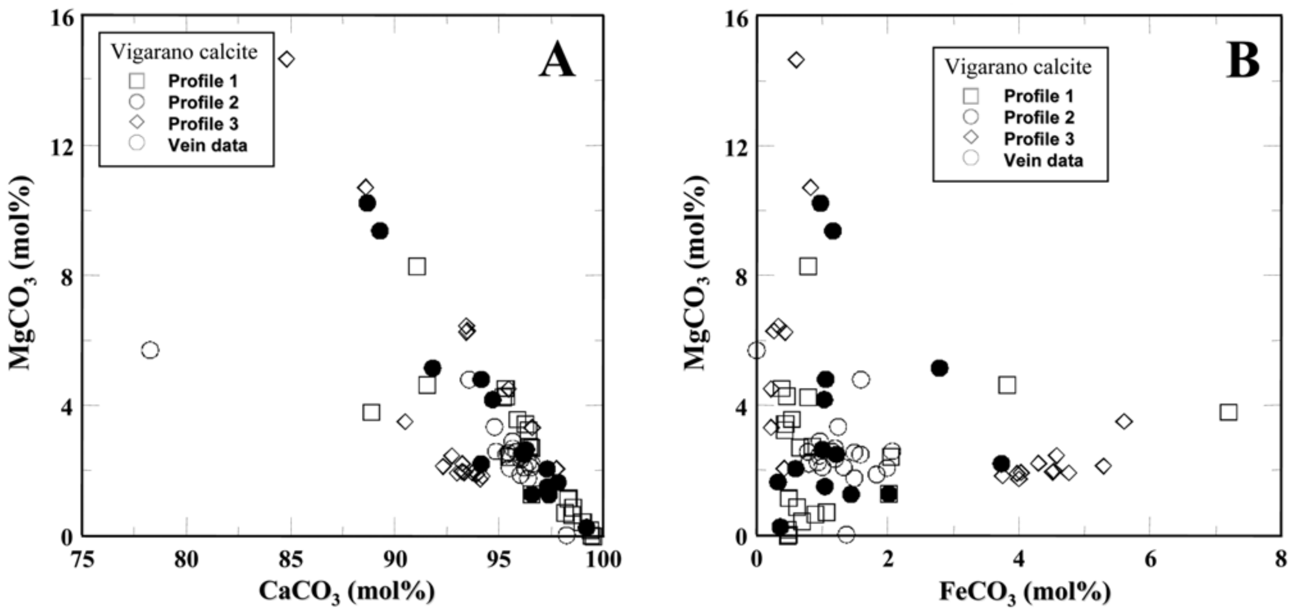

Fig. 3. a) $MgCO_3$ versus $CaCO_3$ (wt%) for three zoning profiles through the large carbonate mass shown in Fig. 2a and typical carbonate veins shown in Fig. 1. b) $MgCO_3$ versus $FeCO_3$ (wt%) for the same data set as shown in (a). These elements show no systematic elemental correlations and appear to vary independently of one another.

sample is not directly comparable with the observations on the UNM samples from the second stone. Fractures in these samples were examined carefully for evidence of calcite, but none was found. Nevertheless, calcite does occur in minor amounts within a large, disrupted type B CAI (Fig. 6), that is rimmed by an unusual, fine-grained mantle of fragmentary material. This mantle has the same mineralogy as the CAI itself (i.e., dominated by melilite), but it has a porous appearance. Small grains of calcite are relatively common within this mantle and very thin calcite veins occur locally within the coarse-grained portion of the inclusion. These veins are associated with porous regions of the inclusion that appear to be alteration products of melilite. This carbonate occurrence is similar to those described on the periphery and along the fractures of a FUN inclusion (Davis et al. 1991) and along fractures near a CAI (Mao et al. 1990) in Vigarano. However, it is not clear where specific fragments originated in either one of these studies.

Leoville

We also examined a thin section (UNM674) of the reduced CV chondrite find Leoville (UNM674) using BSE imaging and EDS analyses, for comparison with Vigarano. Leoville consists of two individual stones; the first, weighing 1.629 kg, was recovered prior to 1965 and the second 6.5 kg stone was recovered in 1966 (Kracher et al. 1985). Leoville has experienced a higher degree of terrestrial weathering than Vigarano, as it was found buried in the soil (Kracher et al. 1985), indicating that it had an extended residence time in a subsurface environment. At least one calcite occurrence has been reported in the literatures (Sylvester et al. 1993). Both stones exhibit a partially-cracked fusion crust cross cut by numerous fractures. Our SEM studies show that this meteorite contains a pervasive network of calcium carbonate veins (Fig. 7b). These veins range in thickness from <1 µm to >50 µm and extend for hundreds of microns. In general, the edges of the carbonate veins have sharply defined boundaries with the host meteorite. The carbonate vein networks are very complex, apparently consisting of more than one generation of veins. These veins often contain very thin Fe-oxide veins within them as shown in Fig. 7c. Compositionally, most of the vein material is close to pure $CaCO_3$, presumably calcite, although in some veins compositional zoning is present (Fig. 7c). Based on EDS analysis, the zoning appears to be largely the result of local variations in minor element content, but we have not investigated this phenomenon in detail.

BSE images show that some of the calcite veins contain small pockets of dolomitic composition at their periphery, as shown in the X-ray maps in Fig. 6d. However, it is also possible that they could be high-Mg calcite. In some cases the dolomite occupies the entire width of the vein. To our knowledge, occurrences of dolomite have not been recognized previously in terrestrial weathering veins in meteorites. Other veins contain a minor amount of iron oxide or oxyhydroxide as discrete mineral grains and as very thin veins (<1 µm across), as described by Kracher et al. (1985). These veins are likely to be the result of weathering of adjacent metal grains.

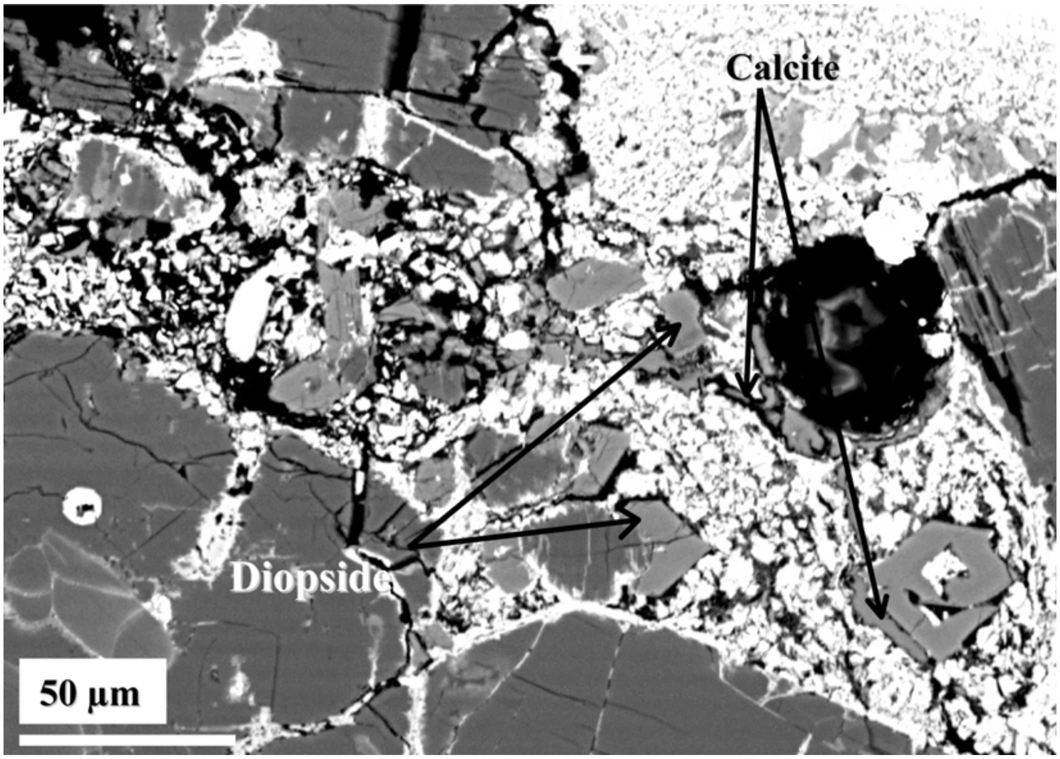

Fig. 4. A BSE image of a segment of a carbonate vein associated with several euhedral to subhedral diopside crystals. The carbonate vein follows the interface between the chondrule and the matrix and then partially crosscuts the chondrule. Finally, it occurs associated with the pyroxene crystals at the edge of the chondrules. The diopside grains do not show any evidence of calcite replacement in contrast to the calcite/augite assemblage described in Fig. 5.

DISCUSSION

The observations presented above clearly show that previously undescribed carbonate occurrences, principally carbonate veins, are widespread in at least one of the Vigarano stones. In addition, other minor occurrences of carbonate are present in the samples of Vigarano that we studied, including specimens from the pristine (first) Vigarano stone. Stable isotope studies (Grady et al. 1988) of CV chondrites have indicated that carbonate may be present and our observations, along with those of Mao et al. (1990) and Davis et al. (1991), confirm that carbonate is more widespread than was previously thought. Here we discuss possible origins and implications of the carbonate.

Carbonate Veins

Based on several lines of evidence, we conclude that the carbonate veins in Vigarano are most likely to be terrestrial in origin. The lines of evidence are as follows:

1. There is a distinct, though thin, carbonate layer present on the surface of the UNM sample from which the thin sections were prepared.
2. The carbonate veins extend from the carbonate-rich layer into the interior and cross cut the fusion crust.
3. Vesicles within the fusion crust are filled with carbonate.
4. The structure of the veins closely resembles carbonate veins in Leoville, the more heavily weathered CV chondrite find.

After the fall event in 1910, the first Vigarano stone recovered was exposed to weathering for a very limited time. Hence, the effects of weathering, while present, are extremely limited; vein-filling carbonates did not have sufficient time to form in this stone. However, in the second stone, we infer that significant carbonate development was able to occur, predominantly as veins that appear to have formed within preexisting fractures within the meteorite. This is indicated by the sharp and irregular interfaces between host meteorite and the carbonate. Some of these veins are only partially filled, indicating that carbonate precipitation probably occurred within open, fluid-filled fractures, which became partially to completely filled. The compositional zoning observed by BSE and CL imaging of the carbonates (Figs. 2a–2c) indicates carbonate deposition was a complex process that may have involved variations in fluid composition or fluctuating redox conditions (see discussion below).

The formation of veins of carbonates or other minerals as a result of terrestrial weathering is a phenomenon that has been widely recognized in meteorites collected in both Antarctica and hot deserts (e.g., Gooding 1981, 1986; Velbel 1991; Barrat et al. 1998). Our observations on Leoville also show that veining develops in more humid, temperate

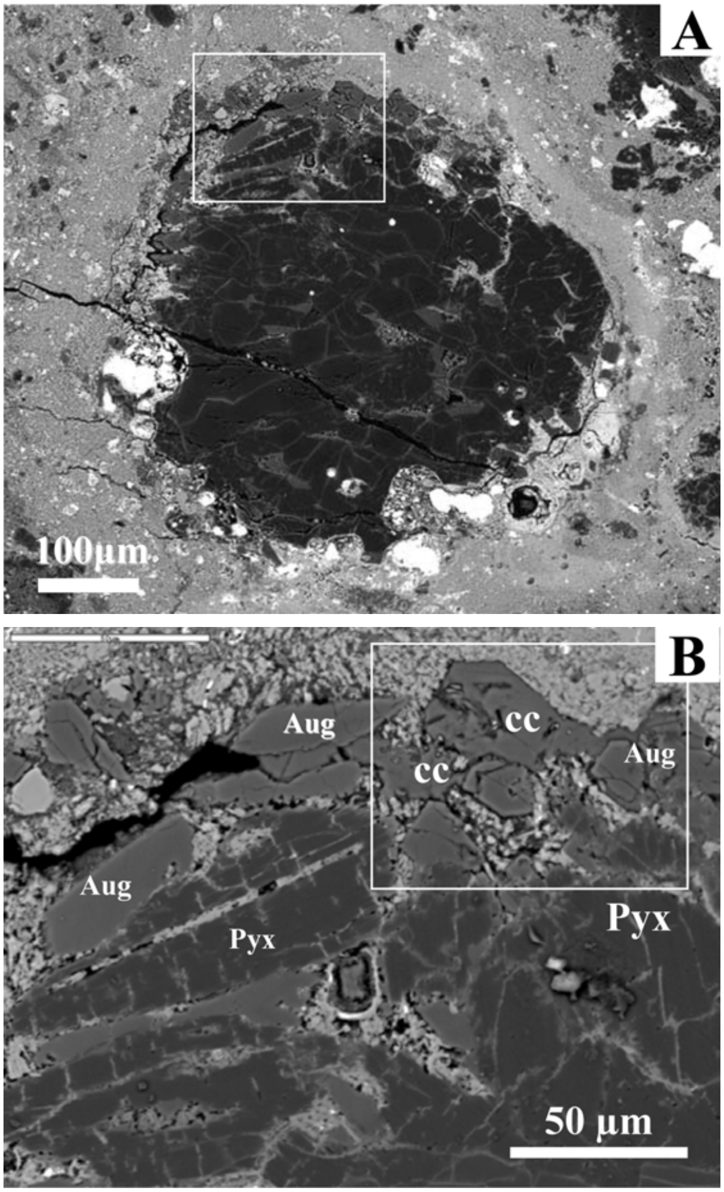

Fig. 5. a) A BSE image of a porphyritic pyroxene chondrule. On the exterior of this chondrule, augite grains exhibit pseudomorphic replacement by calcite. b) A BSE image of the exterior of a porphyritic chondrule containing several augite grains, which have been partially to completely replaced by calcium carbonate (cc). Adjacent olivine-rich matrix material and low-Ca pyroxene are unaffected.

climates, especially when weathering occurs dominantly in the subsurface. However, in all these cases, the formation of carbonate veins occurs on time scales of ten to hundreds or even thousands of years, not one month, as is the case for Vigarano. Formation of terrestrial veins on time scales of decades has been reported for the CI1 chondrite Orgueil. However, no evidence of carbonate veins has been found (Gounelle and Zolensky 2001). Studies of fragments of the Tatahouine meteorite that were recovered in 1994, 63 years after its fall in southern Tunisia in 1931, show that extensive carbonate formation has occurred in fractures and cavities that are empty in specimens recovered immediately after the fall of the meteorite. These carbonates show isotopic signatures consistent with derivation from the soil where the meteorite landed (Barrat et al. 1998), demonstrating that terrestrial carbonate formation is feasible even in an arid desert environment on a time scale of decades. In the case of Tatahouine, calcrete material was readily available because, geologically, its fall location is dominated by limestones with sandy soils (Barrat et al. 1998).

A comparison of the carbonate occurrences in Vigarano with those in the weathered CV chondrite fall Leoville provides additional evidence that the veins are terrestrial in origin. Despite the much more extended residence time of Leoville in a terrestrial soil, the calcite occurrences in both meteorites share some textural and compositional similarities,

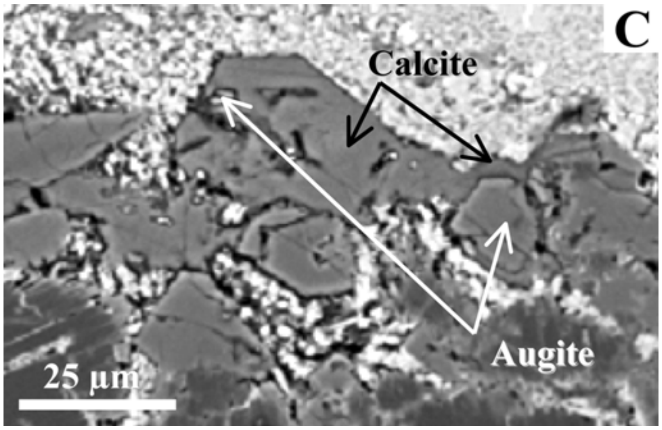

Fig. 5. *Continued.* c) A BSE image of a region containing two augite crystals partially replaced by calcite.

although there are a number of notable differences. The style of calcite veining in the two meteorites is very similar and appears to have occurred predominantly along fractures. The major differences between Leoville and Vigarano veins are that the veining in Leoville (Figs. 6b–6e) is, in general, more complex than that in Vigarano (e.g., Figs. 1a and 2) and compositional zoning is more complex and extensive than in the Vigarano veins (Fig. 6c). In particular, the presence of Mg-Ca-bearing carbonate in Leoville veins is a notable feature which is not apparent in Vigarano. Leoville also has much more extensive development of Fe-oxide associated with the carbonate veins. These differences are probably attributable to the longer alteration history of Leoville, with the Fe-oxide representing the product of extensive weathering of metal grains and Fe sulfides. However, the presence of Mg-Ca bearing carbonate in Leoville is difficult to explain. If this phase is dolomite, its presence is problematic, because of the extreme difficulty of precipitating dolomite directly from a fluid at low temperatures (e.g., Chang et al. 1996). A more likely explanation is that this carbonate is high-Mg calcite, but detailed compositional and structural data, which are beyond the scope of this study, are required to confirm this.

Table 2. Representative electron microprobe analyses of augite crystals from a Vigarano type I chondrules that have been partially replaced by calcite.

Wt% oxide					
SiO_2	53.24	54.28	53.09	52.35	54.38
TiO_2	0.64	0.48	0.75	0.75	0.56
Al_2O_3	2.65	2.13	3.23	2.81	2.29
Cr_2O_3	1.40	1.54	1.68	1.33	1.30
FeO	0.77	0.99	0.83	0.70	0.75
MnO	1.02	1.40	1.63	0.76	0.96
MgO	19.00	22.09	17.89	18.12	21.01
CaO	21.53	16.63	21.09	22.06	19.18
Na_2O	0.05	0.06	0.08	0.05	0.03
K_2O	0.01	0.02	0.01	0.02	–
Total	100.31	99.62	100.28	98.95	100.45
Formulas based on six oxygen atoms					
Si	1.916	1.942	1.914	1.912	1.936
Ti	0.017	0.013	0.020	0.021	0.015
Al	0.112	0.090	0.137	0.121	0.096
Cr	0.040	0.044	0.048	0.038	0.037
Fe	0.023	0.030	0.025	0.021	0.022
Mn	0.031	0.042	0.050	0.023	0.029
Mg	1.019	1.178	0.962	0.986	1.115
Ca	0.830	0.638	0.815	0.863	0.732
Na	0.003	0.004	0.006	0.004	0.002
K	0.001	0.001	0.001	0.001	–
Total cations	3.992	3.981	3.977	3.991	3.984

"–" indicates below detection limit.

Sources of Vein Cations

Having established with reasonable certainty that the veins in Vigarano are of terrestrial origin, one of the major questions regarding the genesis of the carbonate veins is the source of calcium and carbonate ions. Clearly, there are two possible sources: internally from Vigarano itself or externally from the terrestrial soil. Here we discuss the possible contribution of both sources to carbonate formation.

The Emilia Romagna soils, where Vigarano was found, are fine-textured, clay-dominated, fluvial sediments, which can be loosely classified as vertisols. Vertisols are seasonal, swelling-clay soils that develop from limestone and marl-rich parental materials. The Ferrara soils are rich in illite and smectite with minor amounts of chlorite and kaolinite (Felice et al. 1985), but are not significantly enriched in calcrete material. Total $CaCO_3$ contents between 3 and 19 wt% have been reported in analyses for the uppermost soil horizons in regions adjacent to Ferrara (Felice et al. 1985). However, modern soil analyses from this region may be compromised by the recent widespread addition of calcium-rich fertilizers. There is at least one report of the possibility of addition of carbonate materials to the Ferrara soils for agricultural purposes (Cenci and Cremonimi 1972). Therefore, it is not possible to produce an accurate estimate of the amount of calcium in the soil at the time that Vigarano fell, based on recent analyses. However, vertisols may also contain relatively large amounts of Ca, Fe, and Mg as components of the constituent mineral phases. Hydrolysis reactions between soil water and minerals will continually leach these elements into solution, thus providing a potential source of Ca for carbonate formation in the veins in Vigarano.

The cations necessary to form the carbonate veins may have also originated in the host meteorite matrix and may have been mobilized during terrestrial weathering. The mineral assemblages present in chondritic meteorites are far from equilibrium in the highly oxidizing and, in the case of Vigarano, humid terrestrial environment. They are, as a consequence, highly susceptible to chemical weathering. There are a number of potential sources of calcium, such as chondrule glass and Ca-rich phases in CAIs, such as melilite. In addition, the fine-grained matrix contains rare Ca-rich

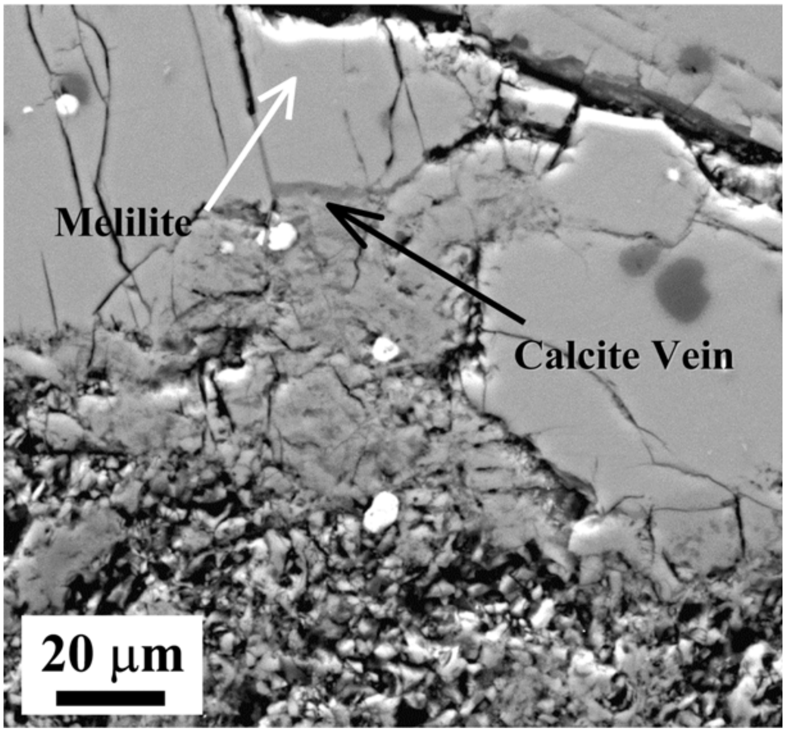

Fig. 6. A BSE image showing an occurrence of calcite in the first Vigarano stone. In this case, the carbonate occurs as a thin vein which lies long the interface between a region of porous alteration products of a melilite crystal in a type B CAI. A thin extension of the vein is also present crosscutting the melilite crystal itself (arrowed).

pyroxene grains and Fe-rich olivine grains, which contain minor amounts of CaO. We have also found minor amounts of calcite in Vigarano that may also be preterrestrial (see discussion below) and could have undergone dissolution and re-precipitation.

In principle, a modest quantity of Ca could have been released into solution from weathering of matrix grains and transported through the porous matrix to the fractures to form the carbonate veins. Experimental studies of the alteration of Allende carried out at temperatures of 100–200 °C, show that carbonate formation can occur in a matter of weeks (Duke and Brearley 1999; Jones and Brearley, unpublished data) as a result of dissolution of Ca-bearing silicate minerals, although obviously these temperatures are significantly higher than the situation for weathering in Vigarano. In comparison, Lasaga (1984) determined that the time period for the dissolution of a 1 mm-radius Ca-bearing pyroxene was approximately 6800 yr at 25 °C and pH 5—a rapid rate in geological terms, but extremely slow on the scale relevant to the formation of carbonate in Vigarano. Given the low temperatures and limited amount of time available, we conclude that it is unlikely that chemical weathering of phases within Vigarano itself would be sufficiently effective to account for more than a minor fraction of the cations required for vein formation. This observation is consistent with the very limited evidence of terrestrial weathering of matrix phases observed by TEM in the second Vigarano stone.

The most likely source for Ca therefore appears to be from soil calcium carbonate. Compositional evidence from the carbonates provides additional support that most cations for carbonate formation were derived from the soil. The presence of Sr in trace amounts (up to approximately 0.06 wt%) in the compositional profile of the zoned carbonate mass and in the carbonate veins (up to 0.19 wt%) (see Figs. 2a–d) appears to be most consistent with a terrestrial origin. Sr is present in relatively low concentrations in carbonaceous chondrites with average concentrations in CV chondrites of 15.3×10^{-6} wt% (Wasson and Kallemeyn 1988). However, Sr is present in soils in much higher concentrations, frequently between 0.0006 and 0.001 wt% (Bohn et al. 1979). Furthermore, Sr is readily mobilized by weathering processes in the soil environment (e.g., Borg and Banner 1996) and is readily incorporated into calcite (e.g., Bohn et al. 1979).

External derivation of carbonate ions also seems most likely. Surface waters all contain dissolved CO_2, present as bicarbonate ions. Internal derivation of bicarbonate ions would require either dissolution of preexisting carbonate in Vigarano or extensive oxidation of organic material. Neither of these possibilities appear very probable. Evidence for preterrestrial carbonate in Vigarano is minor (see below) and solid organic material, the dominant carbonaceous component in chondrites, is highly resistant to oxidation and unlikely to undergo any significant degradation on the short time scale required.

Mechanism of Carbonate Vein Formation

The evidence of a terrestrial origin for the carbonate veins discussed above is robust. In this section, we discuss possible mechanisms for carbonate vein formation. One issue of key importance is the question of whether it is feasible to form carbonate veins on time scales as short as one month, which would be required in the case of the second Vigarano stone. According to the terrestrial literature (i.e., McFadden et al. 1998), calcite deposition on the time scale necessary to explain the vein networks in Vigarano is extremely unlikely even in a calcite over-saturated environment. In typical terrestrial environments, carbonate vein formation occurs on the scale of years to hundreds of years, but in the case of Vigarano clearly occurred much more rapidly.

In order to address this question, we examined two possible endmember mechanisms to explain formation of the carbonate veins. The first scenario is one in which carbonate formation is largely driven and controlled by the composition of the aqueous fluid of ions from an external source (i.e., local soil and surface waters), with precipitation occurring as a result of episodic wetting and drying. In the second case, the internal microchemical environment within the meteorite largely controls carbonate precipitation, although it is coupled to some degree to external derivation of water and certain key anions and cations.

In the scenario discussed below, we assume that no free aqueous fluid phase was present in the Vigarano stone prior to its entry into the Earth's atmosphere. Once the meteoroid entered the Earth's atmosphere, atmospheric gases and moisture would be drawn into pore spaces, filling the vacuum that was present during the stone's sojourn in space. Once the Vigarano stones hit the ground, terrestrial aqueous fluids would have been drawn into the interior of the meteorite along fractures by capillary action during the month between the fall and the collection of the second stone. It is possible, and perhaps probable, that this process occurred extremely rapidly after the fall, as equilibration between atmospheric pressure and the very low internal pore pressure within the meteorite occurred. In effect, any free aqueous fluid that was present in the immediate environment would have been sucked into the meteorite during this initial period.

Carbonate Growth Controlled by Episodic Wetting and Drying

The hydrous fluids that initially entered the meteorite may have been either snow melt or soil water or a combination of both. This externally derived water contained cations leached from the soil (e.g., Ca^{2+}, Mg^{2+}), as well as dissolved atmospheric CO_2 as HCO_3^- and would drive hydrolysis reactions. Typical agricultural soils have pHs in the range ~5–7 (Miller et al. 1995) and we assume that the pH of the soil fluids that entered the meteorite was in equilibrium with the soils. The Vigarano stone resided in soil for one month after it fell, during which time it likely experienced several wetting events as a result of periodic precipitation.

To test the pedogenic origin hypothesis, we performed first-order calculations assuming the veins to be sections of tabular cracks within the meteorite with an approximate thickness of 5 μm and 500 μm by 500 μm surface area. The volume of this tabular feature is 1.25×10^{-6} cm^3, which corresponds to 3.38×10^{-8} moles of calcite at room temperature. In addition, we assume that an aqueous fluid in equilibrium with $CaCO_3$, with a P_{CO2} of $10^{-3.5}$ at 0 °C, was absorbed by the meteorite and this pH was maintained inside the meteorite. Furthermore, for the purposes of this calculation, we assume that the carbonate in the veins is derived solely from Ca dissolved in this fluid. To precipitate carbonate, we assume complete evaporation of the fluid, i.e., complete drying out of all fractures in the meteorite. Using the equilibrium values given by Drever (1982) for an aqueous fluid at 0 °C, we calculate that in order to deposit enough calcite to completely fill the calcite tabular features, approximately 5×10^{-2} ml of water would be necessary. This is approximately five orders of magnitude larger than the total volume of the tabular feature.

It seems unlikely that such a model can explain the formation of the carbonate veins in Vigarano. First, the volume of water that would be required to form the carbonate veins is extremely large and would require an unreasonably large number of wetting and drying events to produce the veins. Once saturated with water, it would be extremely difficult to completely dry the vein network out, particularly during the cool winter months when Vigarano was subject to terrestrial weathering. In addition, our model assumes that all the Ca^{2+} ions in solution were precipitated at each wetting event and that no dissolution of carbonate occurred with each separate influx of water. This is also probably an unreasonable assumption; some carbonate dissolution would be expected to occur during each new influx of water into the meteorite, a process which would effectively increase the time required for carbonate formation. Further, as noted earlier, carbonate formation in terrestrial environments, where the solutions are oversaturated with respect to carbonate, takes place on much lengthier time scales (years to hundreds of years). Finally, as discussed in detail below, we think it is unlikely that low to neutral pH values would have been maintained within the interior of the meteorite, a factor that has far reaching effects on carbonate precipitation.

Carbonate Growth Controlled by the Microchemical Environment within the Meteorite without Episodic Wetting and Drying

We now consider an alternative, and probably more plausible, model in which carbonate formation is driven by the microchemical environment within the meteorite, which results from hydrolysis reactions involving minerals that are far from equilibrium. Figure 7 shows an activity-pH diagram for Ca^{2+} ions calculated at 0 °C and HCO_3^- activity of 10^{-2}. This diagram shows that at low-to-neutral pH conditions, typical of soil, Ca^{2+} would remain in solution in the aqueous

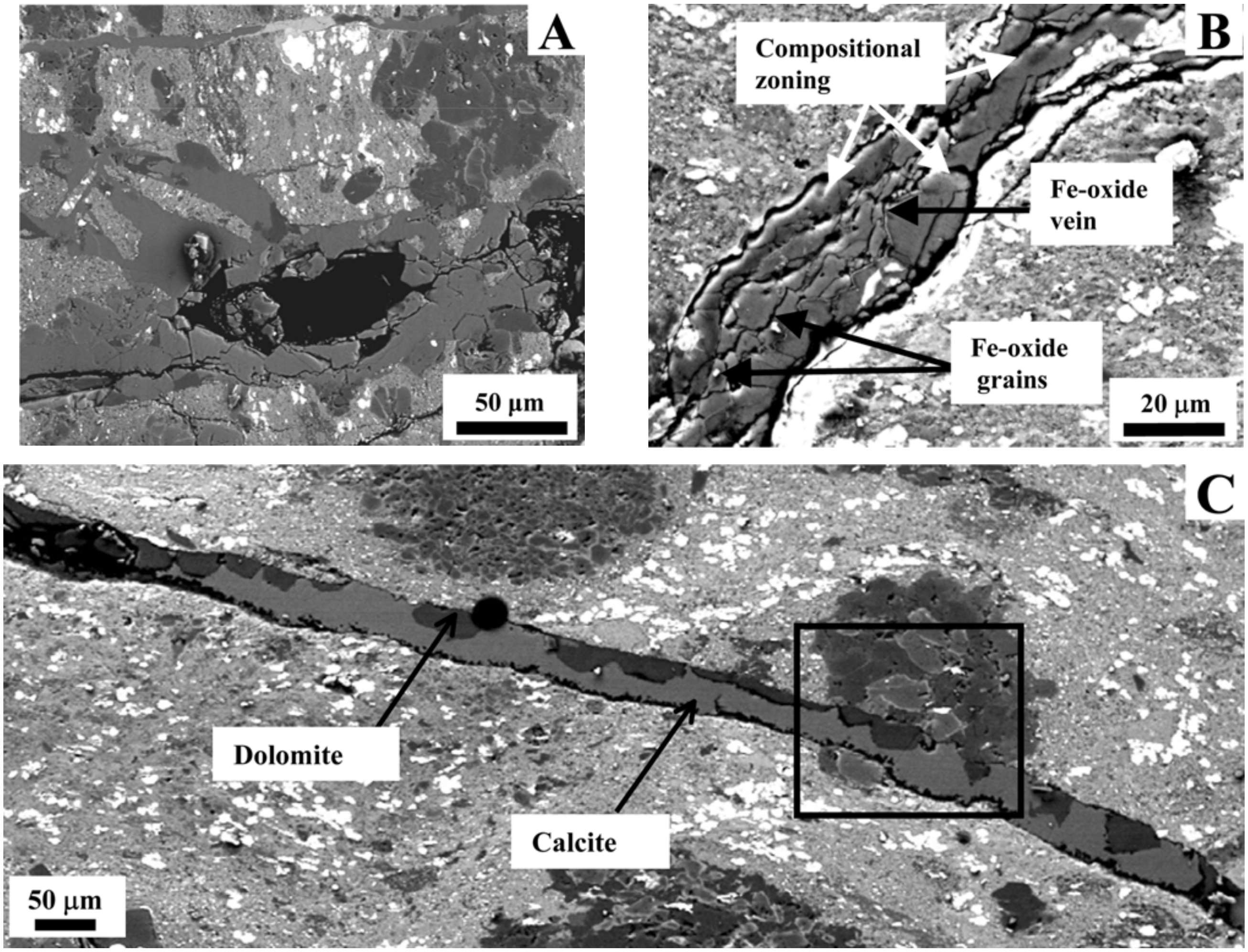

Fig. 7. BSE images of veins in the CV3 chondrite Leoville. a) A BSE image of a vein network in Leoville. Several interconnected veins run throughout the field of view crosscutting larger objects in some cases. Note the complexity of this network compared to Vigarano. b) A BSE image of a highly complex vein segment in Leoville. Note that fragments of matrix have been incorporated in the calcite filling and a thin Fe-oxide vein runs within the calcite vein. Compositional zoning is also extensive. The zoning pattern is generally associated with Mg enrichment. This degree of complexity is not observed in vein occurrences in Vigarano. c) A BSE image of a segment of a calcite vein in Leoville with small pockets of Mg-bearing carbonate along the edges. The composition of this material as shown in the X-ray maps is consistent with dolomitic carbonate in Fig. 6d.

fluid absorbed by Vigarano, unless evaporation occurs and increases the Ca concentration until supersaturation occurs as discussed in our first model. However, after entering the meteorite's microchemical environment, we suggest that the pH of the fluid was locally controlled by the weathering reactions that occur in the interior of the meteorite. Key reactions that play a significant effect on solution pH are the oxidation of Fe,Ni metal grains and the hydrolysis of silicate minerals. Both of these processes tend to increase the pH of solutions. In silicate hydrolysis reactions, H^+ ions attack and break metal-oxygen bonds and form bonds to the oxygen ions. Hence, such reactions consume large quantities of protons and the result is that the solutions become progressively more alkaline as hydrolysis proceeds.

Metal oxidation requires the consumption of large quantities of H^+ to sustain the cathode reaction at the grain surface (Porbaix and DeZoubov 1974). This is a reaction that will proceed very rapidly in the presence of aqueous solutions with significant dissolved oxygen and will also drive the solutions to higher pH values. This pH change would trigger the precipitation of $CaCO_3$, as it is the stable phase at high pH and low T (e.g., Fig. 7). The process of metal oxidation as a key driving force for promoting carbonate precipitation is consistent with the evidence of metal alteration that has been observed at the SEM scale. Additionally, early metal alteration of the second Vigarano stone in the form of metallic rust was also documented by Rosati (1910b). Under conditions of elevated pH, precipitation of carbonate would be expected to occur on a much shorter time scale than under typical soil geochemical conditions (i.e., low to neutral pH values), consistent with the development of substantial carbonate veins on a time scale of one month.

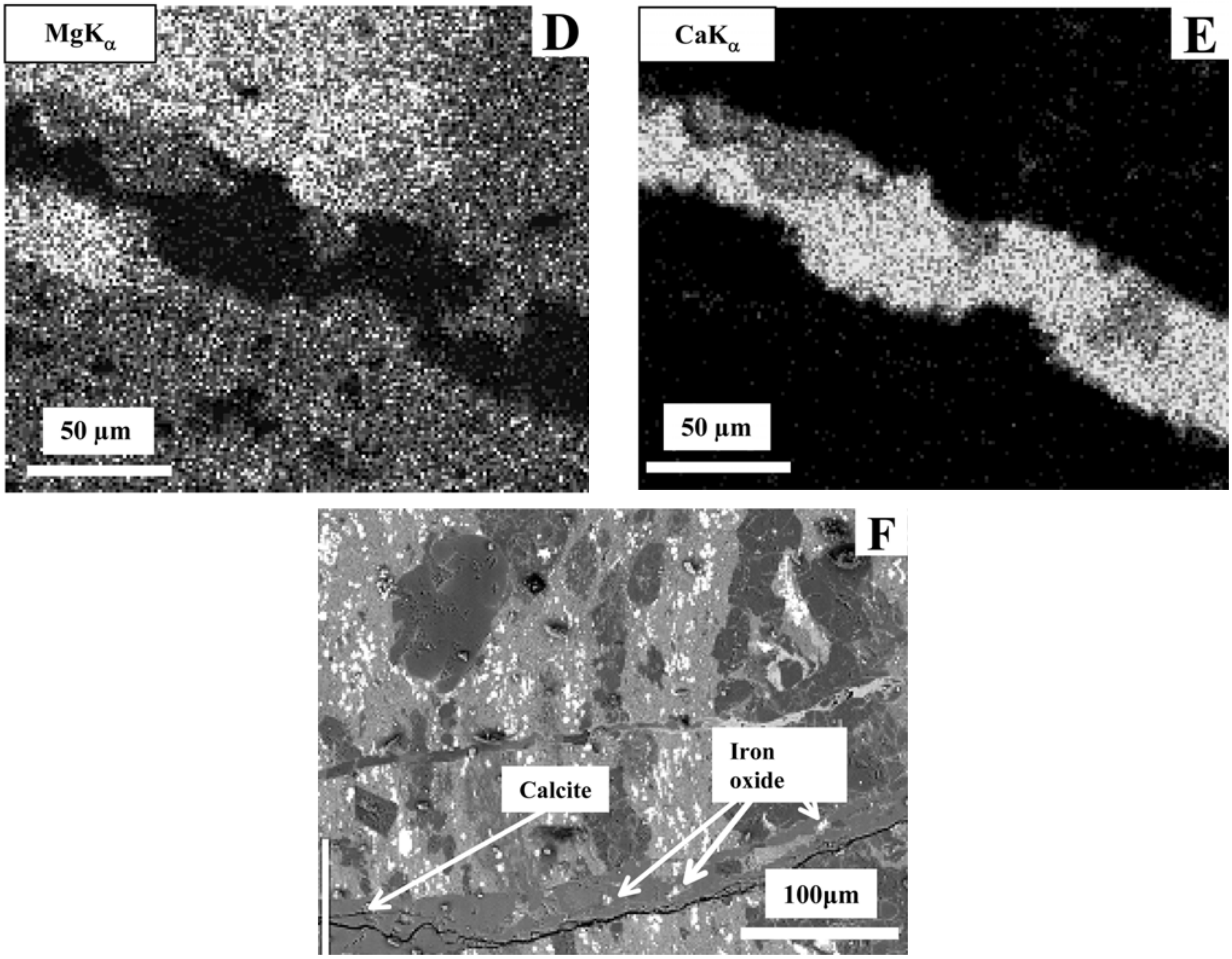

Fig. 7. *Continued.* BSE images of veins in the CV3 chondrite Leoville. d) Ca and Mg X-ray maps of a segment of a calcite vein in Leoville with small pockets of Mg-bearing carbonate along the edges. e) A BSE image of Leoville, showing two interconnected carbonate channels. Notice some of these grains have been strongly altered and the alteration product have been transported along the vein.

In this model, the amount of water in the fracture system remains essentially constant and supply of ions into the interior of the meteorite is driven by diffusion through the fluid, not by infiltration of additional amounts of mineralizing fluid (although minor additional influxes of fluid may have occurred). Precipitation of carbonate within the interior of the meteorite will set up chemical potential gradients in the fracture network that will drive diffusive mass transfer of ions from the external reservoir into the meteorite interior. Once ions in solution reach conditions in the fracture network where the pH is sufficiently high, carbonate precipitation will occur.

Origin of Compositional Zoning

Zoning in minor elements is present in the carbonate networks, suggesting that carbonate growth was a complex process. One possible explanation is that this zoning represents multiple periods of carbonate formation, rather than a single period of carbonate growth, implying that carbonate formation was episodic. One possibility is that precipitation is the result of periods of fluid-limiting conditions when evaporation of the water from the fluid network occurred. This would drive the solutions to oversaturation relative to calcite, resulting in episodic precipitation of carbonate, which would become enriched in less compatible minor elements as the solution became more oversaturated. As discussed earlier, it seems unlikely that multiple cycles of wetting and drying could have occurred in the environment under which Vigarano experienced aqueous alteration. We therefore think that this scenario is probably an unlikely explanation of the carbonate zoning, although we cannot fully rule it out.

An alternative explanation for the zoning in the carbonates is that it is a reflection of fluctuations in redox conditions during carbonate growth. The transition metal ions Mn and Fe are only incorporated into carbonates in the 2+ oxidation states (Machel and Burton 1991). Under conditions of high oxygen availability, Mn^{3+} and Fe^{3+} will be dominant and will not be

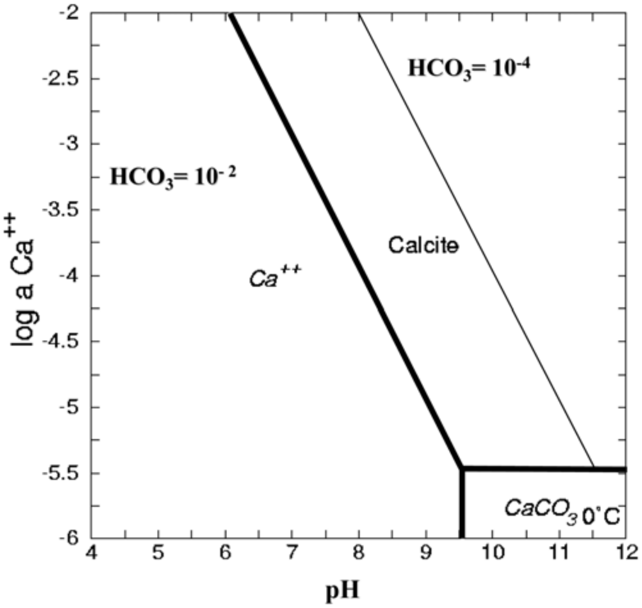

Fig. 8. Activity of Ca^{2+} versus pH at T = 0 °C. The red line corresponds to $a_{HCO3^-} = 10^{-2}$ and the black line represents a $a_{HCO3^-} = 10^{-4}$. Notice that in both cases calcite becomes the stable phase at high pHs and at low Ca^{2+} activity. Higher a_{HCO3^-} results in a broader calcite field. Hence, changes in the pH conditions caused by hydrolysis of silicate minerals and oxidation of metal grains at the edges of fractures enhance the deposition of calcite-forming veins.

incorporated into the carbonates. Oxidation reactions in the interior of the meteorite must be driven by the diffusion of dissolved oxygen through the aqueous fluid into the interior of the meteorite. It seems unlikely that the rate of supply of dissolved oxygen into the interior of the meteorite fluctuates to any significant degree, provided the fractures remain saturated with water. This means that the eH of the fluid will be largely controlled by the rate of consumption of oxygen by oxidation of Fe metal grains, compared with the rate of supply from the exterior of the meteorite. Local variations in eH might result if the rate of oxidation of metal grains in the vicinity of the carbonate veins outstripped the supply of externally-derived oxygen, resulting in a temporary lowering of the dissolved oxygen that drives oxidation reactions.

As noted earlier, CL and electron microprobe data show that the carbonate zoning is extremely complex. However, there is no clear correlation between CL intensity and high concentrations of known CL activators such as Mn. Indeed, Mn concentrations are generally below detection limits in the compositional profiles across the zoning and some high CL zones in the carbonate appear to be coincident with elevated concentrations of $MgCO_3$ and $SrCO_3$, neither of which are not known CL activators in carbonates. Fe^{2+} is the most common CL suppressor (Machel et al. 1991) of Mn^{2+}-induced CL in carbonate, but in some growth zones high CL is correlated with relatively high Fe values. An alternative possibility is that the CL zonation is caused by the presence of REEs (Machel and Burton 1991) that are also known to activate CL in carbonates, although we have clearly not investigated this possibility in detail.

Evidence for Preterrestrial Carbonate in Vigarano

Although we conclude that the calcite veins in the second Vigarano stone are the result of terrestrial weathering, we have observed two additional occurrences of carbonate for which a terrestrial origin seems to be unlikely. The first example is the occurrence of minor calcite associated with a Type B CAI that is present in the first Vigarano stone. Although carbonate development is minor, it is widespread both within the unusual rim on the CAI and associated with altered regions of coarse-grained melilite. We consider that this example of carbonate is certainly preterrestrial in origin, since it occurs in the stone that was collected very shortly after its fall. It is possible, but extremely unlikely, that these veins formed during the hours prior to collection. An alternative scenario for terrestrial formation is absorption and precipitation of carbonate during storage, as documented for sulfate veins in the CI1 chondrites (Gounelle and Zolensky 2001). However, formation of carbonate veins in meteorites under museum conditions has not been reported to date, so we consider this explanation to be improbable.

The second occurrence of carbonate, i.e., the pseudomorphic replacement of augite by calcite (Fig. 5b), is more ambiguous because it occurs in a sample of the second Vigarano stone. However, we consider that a terrestrial origin for this calcite is highly improbable, but equally a preterrestrial origin also appears to be problematic. Our observations show that the alteration of pyroxene to calcite is a process that has only affected the augite grains. The adjacent matrix shows no evidence of significant aqueous alteration that can be detected by SEM studies. In addition, replacement of augite by calcite as a result of terrestrial alteration seems unlikely because we have observed terrestrial calcite veins in contact with diopside grains on the periphery of another chondrule. In this case, the diopside shows no evidence of replacement by calcite.

To our knowledge, direct, pseudomorphic replacement of augite only by calcite has not been described in the terrestrial or meteoritic literature, although calcite does occur (as in CM chondrites) as an alteration product of phases such as melilite in CAIs (e.g., MacPherson and Davis 1994; Greenwood et al. 1994). Zolensky et al. (2002) reported pseudomorphic replacement of olivine in the type 2 carbonaceous chondrite Tagish Lake (Zolensky et al. 2002), in which calcite occurs associated with other phases, but not as the sole replacement product of the olivine. In terrestrial mafic and ultramafic igneous rocks, calcite formation commonly occurs during weathering, low-grade to greenschist facies metamorphism and, in the case of mantle xenoliths, during mantle metasomatism. However, none of these geological processes appear to cause replacement of augite by calcite. In fact, augite is usually extremely resistant to alteration; for example, in greenschist facies rocks, augite commonly persists as a relict phase, although it may sometimes be overgrown by amphibole. Dissolution of augite in a terrestrial surface environment is also a very sluggish process; significant dissolution of augite under typical alteration conditions takes place on the scale of thousands of years (Lasaga 1984). These observations are generally consistent with observations of augite in aqueously-altered carbonaceous chondrites. For example, Brearley (1995) and Hanowski and Brearley (2001) found that augite is extremely resistant to aqueous alteration in CM chondrites, being among the last phases to show evidence of replacement.

There is clear evidence of preterrestrial aqueous alteration in Vigarano, but it appears to be of very limited extent. Nevertheless, it is plausible that the replacement of augite by calcite could have occurred on the CV parent body, but the details and conditions of the alteration process remain essentially unconstrained. The replacement reaction must have required an aqueous fluid rich in CO_2 and Ca^{2+}, that had the ability to remove all other cations (e.g., Si, Al, Fe, Mg, Ti) from the altering pyroxene. The relative solubilities of these cations vary by several orders of magnitude in most aqueous solutions. For example, Al and Ti are generally considered immobile in most geochemical environments and remain at or close to the source phase where they are incorporated into secondary alteration phases. This occurs during the alteration of chondrule glass in CM2 chondrites, where Al is retained in Al-bearing serpentines or chlorite, rather than being leached into the matrix (Hanowski and Brearley 2001). The complete stripping of all cations (except Ca) is therefore highly unusual. Further, there are no terrestrial analogs to provide support for such scenario. An additional problem is that such a fluid would be expected to affect other silicate minerals associated with the augite. However, as noted above, no such evidence is apparent, either in the surrounding matrix or other phases in the host chondrule, as would be expected if alteration had taken place in the parent body.

It is possible that an essentially pure CO_2 fluid could be responsible for the formation of the carbonate and the low activity of water inhibited alteration of other, more susceptible phases (i.e., alteration of matrix olivines to form phyllosilicates). However, given that the solubility of cations will be dramatically decreased in an extremely CO_2-rich fluid (Fein and Walther 1987; Sharp and Kennedy 1965), this model is clearly incompatible with the extensive removal of cations from the altering augite.

An additional possibility is that brecciation could have juxtaposed the altered chondrule against unaltered matrix. However, such a disruption and relocation would probably destroy the petrographic relations between the partially altered augite crystals and the calcite pseudomorphs. Therefore, we think this scenario is unlikely.

An alternative scenario may be that the augite alteration occurred prior to accretion, given that texturally alteration is only apparent in the augite grains and not in matrix phases immediately adjacent to the pseudomorphs. In detail, however, this scenario is also highly problematic. Calcite is not predicted to be a stable nebular condensation product, so we rule this out as a possible formation mechanism, although we note here that a recent study suggests that carbonate may form as a result of non-equilibrium condensation in the presence of water vapor in circumstellar environments (Toppani et al. 2005). However, the textural occurrences of calcite in Vigarano are clearly not compatible with such a scenario. Alternatively, it has been suggested that, at extremely low temperatures and pressures, calcite may be formed by carbonation reactions. In this model, calcite and diopside form simultaneously by carbonation of åkermanite; however, the kinetics of this reaction at low temperature would significantly inhibit this process in a nebular environment (Meeker et al. 1983; Armstrong et al. 1982). A similar process has been proposed to explain formation of calcite-diopside assemblages in an asteroidal environment (Meeker et al. 1983; Armstrong et al. 1982). However, neither scenario can satisfactorily explain the textural characteristics of the assemblage in Vigarano. Textual relations clearly show that augite, not melilite, was the precursor phase to the calcite and that calcite and augite did not cocrystallize.

In conclusion, the evidence to support a preterrestrial origin for the calcite replacing augite in the second stone is robust, but the mechanism for the formation of the calcite in either an asteroidal or preaccretionary setting is enigmatic. We argue that the terrestrial formation can be ruled out because: a) rates of alteration of augite even under conditions of high pH are extremely slow during terrestrial weathering; b) there is no evidence of alteration of adjacent matrix, which consists of fine-grained phases that are much more susceptible to aqueous alteration; and c) the presence of carbonate veins that are clearly of terrestrial origin are juxtaposed against unaltered pyroxene crystals. Additionally, the presence of calcite alteration products in a CAI in the first Vigarano stone, that appears to be unambiguously preterrestrial, supports the idea that other occurrences of preterrestrial carbonates are present in Vigarano.

CONCLUSIONS

SEM studies of samples from the Vigarano stone that was recovered one month after the fall have revealed that carbonates are common in this specimen. Three distinct occurrences of calcium carbonates are present in the second stone: a) an extensive network of veins; b) vesicle fillings in the fusion crust; and c) a pseudomorphic replacement of augite grains associated with a porphyritic olivine chondrule. In the first stone, minor calcium carbonate also occurs replacing melilite in type B CAI. Based on robust textural criteria and comparison with carbonates in the weathered CV3 find Leoville, we conclude that the carbonate veins in the second stone formed as a consequence of terrestrial weathering. These criteria include: a) the local presence of a carbonate rind on the fusion crust; b) carbonate filling of vesicles in the crust; c) carbonate veins cross cutting the fusion crust; and d) a thinning of the veins with increasing distance from the fusion crust. We suggest that the extremely rapid precipitation of calcite in this stone was driven by the microchemical environment inside the meteorite. Hydrolysis and metal oxidation reactions that consume hydrogen ions drove the fluid pH to progressively more alkaline values, promoting precipitation of calcium carbonate. We argue that this process allowed extensive formation of carbonate without requiring the influx of large amounts of external fluid. Finally, although we cannot positively identify a single source for the calcium, it is most likely to have been derived externally (from the soil) and was transported into the interior of the meteorite by surface water.

Although the bulk of the carbonate in the second Vigarano stone is certainly of terrestrial origin, minor additional occurrences of carbonate appear to be preterrestrial in origin. In the first Vigarano stone collected the evening of the fall, calcite associated with a type B CAI appears to be unequivocally preterrestrial in origin. In addition, the presence of calcite partially replacing augite on the periphery of a chondrule in the second Vigarano stone also appears to be preterrestrial, although the origin of this replacement is unclear. It may be the result of either asteroidal or preaccretionary alteration.

These observations demonstrate that terrestrial weathering should not be disregarded in supposed meteorite falls. Vigarano consists of only two separate stones with well documented recovery times, but some meteorite falls consist of multiple stones and fragments collected over quite extended periods of time. Some caution must be exercised when studying samples of falls such as Vigarano, especially when stones recovered at different times may be available. Terrestrial weathering can potentially compromise geochemical and mineralogical studies in a very short period of time.

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