Carbonate Mineralogy in Stratospheric IDPs: Compositions, Co-Existing Smectite and Comparison to CI Carbonaceous Chondrites. D. J. Joswiak and D. E. Brownlee, Dept. of Astronomy, Box 351580, University of Washington, Seattle, WA 98195, e-mail: joswiak@astro.washington.edu, brownlee@astro.washington.edu

**Introduction.** To date no systematic study of carbonate mineralogy in stratospheric IDPs has been done. A few authors have reported single occurrences of carbonates in IDPs [1,2,3] but their extent, compositional variability and associated mineralogy are poorly known. From our ongoing study of 5 – 15 µm stratospheric IDPs, many of which have been processed for rare gas analyses, we report here on the occurrence of these carbonate minerals.

In general, carbonate minerals in IDPs are uncommon. From a total of about 135 stratospheric IDPs, we have found 6 that contain carbonates or approximately 4% of the population. Of these 6 IDPs, four also have hydrated mineralogy. Stepped He-release measurements show three of the IDPs have atmospheric entry velocities less than 14 km/s, consistent with asteroidal source regions; the fourth IDP shows an entry velocity of ~16 km/s and is also likely to have an asteroidal origin [4,5].

In most of the carbonate-bearing IDPs, smectite appears to be the dominant phyllosilicate, although cronstedtite may also be present in at least one IDP. Submicron olivine, Fo72 – Fo99, was observed in all 6 IDPs, while pyroxenes (enstatite, augite or diopside) were present in five. Sulfides (pyrrhotite and pentlandite) and silicate glass are ubiquitous; minor amounts of spinel minerals containing Mg, Al, Cr and/or Fe were found in 3 IDPs. Single occurrences of wollastonite and possibly albicic feldspar were also noted.

**Carbonate Compositions.** We have analyzed a total of 23 carbonates from 6 different IDPs; at least one carbonate within each of 5 IDPs was confirmed by SAED. All have intermediate Fe/Fe+Mg ratios and fall within the magnesite-siderite solid solution series and can be classified as either breunnerites or Mg-rich siderites (Figure 1). For simplicity the name breunnerite will be used here. The Fe/Fe+Mg ratios of these 23 carbonates vary from 0.39 – 0.71 but typically have narrower Fe/Fe+Mg ratios within single IDPs (with one exception). Texturally, the carbonate crystals exhibit rhombohedral morphology and are usually less than 200nm in size (Figure 2).

Phase equilibria studies on carbonates at low to moderate temperatures indicate a limited solubility of Ca in breunnerite [6]. This is shown in Figure 1 by the breunnerite stability phase field near the bottom of the diagram at 250 °C. At higher temperatures breunnerites can incorporate higher Ca; this is indicated in the figure by the dashed 550 °C Ca saturation solubility line. The figure also shows the dolomite/ankerite stability field and the 1, 2 and 3 phase fields for carbonate equilibria at 250 °C. The measured Ca contents from IDP breunnerites contain up to 10 mole % CaCO3, while most contain more than about 3 mole % CaCO3. It can be seen in Figure 1 that at 250 °C, most of the IDP carbonate compositions fall within the breunnerite-dolomite two phase field suggesting that dolomite or ankerite should co-exist with the breunnerites assuming equilibrium crystallization. Dolomites/ankerites, however, are not observed in any of the IDPs which may indicate that the breunnerites have equilibrated at temperatures above 250 °C.

**Co-existing Carbonate and Smectite.** In at least 4 IDPs carbonates co-exist with smectite which were confirmed by their compositions and ~1.0 – 1.4 nm basal lattice fringes. Tie lines between IDP carbonate and co-existing smectite are shown in the Si-Mg-Fe ternary diagram in Figure 3. The data points represent averaged values obtained from multiple TEM spot analyses. Carbonates which plot above the Fe-Mg join toward Si show their occurrence with smectite. Two breunnerites are also plotted in the figure that do not have tie-lines to smectite since this phase could not be confirmed by 1.0 – 1.4 nm lattice fringes.

Three of the four co-existing carbonate-smectite pairs have subparallel tie-lines indicating a positive correlation between their Fe/Fe+Mg ratios. This may suggest a co-genetic relationship between these two phases and perhaps indicates breunnerite formation from smectite in CO2-bearing aqueous fluids. Notably, in a study of Fe and Mg partitioning between carbonates and serpentines in CM and CI chondrites Johnson and Prinz (1993) show similar relationships between dolomite and serpentine [7]. One tie line from a carbonate-smectite pair in the figure that crosses the other subparallel tie lines departs from this trend. This may be explained by stepped-He release data that show this IDP was heated above 900 °C during atmospheric entry perhaps disturbing the composition of the low temperature smectite. Removal of Fe to form magnetite, which is present as a rim in the IDP, would push the composition of the smectite toward the Mg-rich end of the smectite field. It should be noted that magnetite rims are also found in the other carbonate-bearing IDPs but their atmospheric entry heating temperatures based on stepped-He release data range from 575 °C to 712 °C, temperatures which are likely to indicate less Fe redistribution. Also plotted in Figure 3 is an IDP carbonate-smectite pair taken from Germani et al. (1990) [1] where it can be seen that both the carbonate (magnesite) and smectite composition fields plot at relatively high Mg/Mg+Fe, a result consistent with the Fe/Fe+Mg trend observed in our study.

**Comparison to CI Carbonaceous Chondrites.** Mineralogy and bulk compositions [8] of chondritic IDPs are similar to CI and CM carbonaceous chondrites.
Thus it is appropriate to compare results obtained here with the CI class of meteorites. CI carbonate composition fields (Alais, Ivuna and Orgueil) are plotted in the ternary diagrams in Figures 1 and 3 [9,10]. The figures clearly show that stratospheric IDP carbonates and smectites are much more Fe-rich than their counterpart CI carbonaceous chondrites. Ca abundances in IDP carbonates are typically higher as well. Although not shown in the figures, MnCO$_3$ contents in carbonates from CI chondrites range up to 12 mole % [9] which is significantly higher than that observed in IDP breunnerites which have maximum MnCO$_3$ contents of 3 mole %. Co-existing carbonates and smectites in CI chondrites occur at lower Fe/Fe$^+$/Mg ratios than in the IDPs similar to the Fe/Fe$^+$/Mg trend seen in the IDPs.

Although IDPs and CI carbonaceous chondrites may sample similar populations of ET materials, our data seem to suggest that the processes that formed the carbonates in these two groups were somewhat different as shown by their distinct chemistries. It is likely that aqueous alteration on parent bodies was responsible for smectite alteration from anhydrous minerals. Carbonates may have precipitated from leaching of these smectites and if so, their higher Ca contents suggest that this process occurred at higher temperatures in IDPs compared to CI chondrites under equilibrium conditions.

**Conclusions.** Approximately 4% of a population of 135 studied IDPs contain intermediate Fe/Fe$^+$/Mg carbonates. Stepped-He release data indicate these IDPs originated from asteroidal source regions. Co-existing carbonate and smectite show rough positive correlations between their Fe/Fe$^+$/Mg ratios suggesting that IDP carbonates may have precipitated from leaching of their host smectites on a parent body. Lower Mn contents, higher Ca abundances and higher Fe/Fe$^+$/Mg ratios in the IDP carbonates suggest different crystallization environments than CI chondrites. Under equilibrium conditions the higher Ca contents in IDP carbonates imply higher temperature formation. However, possible temperatures of up to 550 °C indicated by the Ca contents for some of the carbonates may be too high for parent body alteration and thus may indicate carbonate disequilibrium in these IDPs.