

AQUEOUS ALTERATION IN HYDRATED INTERPLANETARY DUST PARTICLES

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ABSTRACT. Interplanetary dust particles (IDPs) characterized by chondritic composition can be divided into two principal groups, anhydrous and hydrated. This paper summarizes recent results of mineralogical and petrological studies dealing with the IDPs of hydrated type. Studies on mineralogical characteristics, infrared absorption spectra, and isotopic properties of the hydrated particles have suggested that they are primitive and may contain surviving interstellar material. The hydrated IDPs consist in major part of layer silicates and resemble CI and CM carbonaceous chondrites. Mineralogical and chemical data of both IDPs and carbonaceous chondrites have accumulated, and it is now possible to compare the mineralogies of the IDPs and the meteorites in considerable detail. Evidence was found that a significant proportion of the hydrated IDPs have been processed by aqueous alteration, and the nature of the alteration resembles that of similarly affected meteorites. The mineralogical and chemical data provide important clues to the possible origins of IDPs.

1. INTRODUCTION

Interplanetary dust particles (IDPs) collected in the stratosphere have been a subject of intense laboratory studies for the last ten years. A significant proportion of collected IDPs have a composition close to solar (or chondritic) elemental abundance. Two major groups have been recognized in the chondritic IDPs by using infrared spectroscopy [1], electron microscopy (e.g., ref. 2), and micro-beam analysis [3]. One group consists exclusively of anhydrous minerals, while the other group contains major amounts of hydrated phyllosilicates (layer silicates).

Of particular interest are the mineralogical relationships between the hydrated IDPs and carbonaceous chondrites of CI and CM types. The CI and CM chondrites are the most chemically primitive of known meteorites. These meteorites contain major amounts of layer silicates, and it is now widely accepted that they were produced by aqueous alteration that probably occurred on the meteorite parent bodies [4-6]. There is growing evidence that the hydrated IDPs also have been affected by aqueous alteration. Therefore, it is important to understand the mineralogy of hydrated IDPs and the nature of their aqueous alteration, and thus to

clarify the details of their relationship to the carbonaceous chondrites.

2. INFRARED SPECTRAL AND ISOTOPIC PROPERTIES

Infrared spectroscopy has shown that most chondritic IDPs can be divided, based on major silicate types, into three groups, olivine-rich, pyroxene-rich, and layer-silicate-rich [1]. Among them, the layer-silicate-rich (hydrated) particles exhibit infrared spectra closely similar to those of CM chondrites. Spectra of some hydrated particles are also similar to a telescopic spectrum of a protostar W33A [1]. Sandford and Walker [1] tried to fit spectra of IDPs to that of comet Kohoutek, and found that the superposition of roughly equal amounts of spectra of layer-silicate-rich and pyroxene-rich IDPs give rise to an excellent match, suggesting that some comets may contain layer silicates and pyroxene.

McKeegan et al. [7] showed, using ion microprobe, that five out of twelve hydrated particles that they studied have large deuterium enrichments relative to terrestrial D/H values. One particle exhibited particularly large deuterium enrichments, up to +2191‰ relative to standard mean ocean water. Even larger deuterium excesses have been observed in some interstellar molecular clouds, and the deuterium enrichments in IDPs appear to be best explained by the surviving molecules in interstellar molecular clouds [7,8]. These results of both infrared spectroscopy and ion microprobe analysis suggest that hydrated IDPs are primitive and some may contain material that predates the formation of the solar system.

3. MINERALOGY AND COMPOSITION OF HYDRATED IDPs

Hydrated particles have relatively smooth surfaces and compact appearance, while anhydrous particles have a more porous texture. Therefore, hydrated particles are often called "chondritic smooth (or CS)", and anhydrous particles are called "chondritic porous (CP)" [9]. (As an exceptional case, there is a report that minor amounts of layer silicates were found from a CP IDP [10].) Schramm et al. [3] reported that CS and CP particles comprise 37% and 45% of 200 IDPs they studied, respectively. Although both types of particles exhibit almost identical bulk compositions, they are distinct from one another in internal mineralogy and texture. To examine specific, detailed physical and mineralogical properties of IDPs, transmission electron microscopy (TEM) is the most powerful method. So far twenty three particles that belong to the hydrated class have been studied by TEM in various details [2,10-16], and it has been found that the hydrated particles can be further divided into two subgroups, smectite-rich and serpentine-rich. Most particles contain one or the other type of these layer silicates. Constituent minerals of hydrated IDPs are listed in Table 1.

3.1 Smectite-rich IDPs

This group constitutes ~70 % (sixteen in total) of the hydrated IDPs studied by TEM [2,10-15]. Smectite occurs in extremely small crystals (<500 Å in diameter) that are commonly poorly crystallized. It shows a wide range of compositions, but predominant is the Mg-Fe-rich smectite, whose composition is represented by $[\text{Mg}_{1.9}\text{Fe}_{1.0}\text{Al}_{0.1}](\text{Si}_{3.8}\text{Al}_{0.2})\text{O}_{10}(\text{OH})_2$. Another prominent phase is glass, which occurs in Fe-rich and Si-Mg-Al-

TABLE 1. Constituent minerals of hydrated IDPs

Layer silicates (hydrated)	Smectite*	$(\text{MgFe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
	Serpentine*	$(\text{MgFe})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$
	Cronstedtite*	$(\text{FeMg})_6(\text{Fe}^{3+}\text{Si})_4\text{O}_{10}(\text{OH})_8$
Anhydrous silicates	Pyroxene	$(\text{MgFe})\text{SiO}_3$
	Olivine	$(\text{MgFe})_2\text{SiO}_4$
	Fassaite	$\text{Ca}(\text{Al},\text{Mg})(\text{SiAl})_2\text{O}_6$
	Diopside	$\text{CaMgSi}_2\text{O}_6$
Glass	(Si-rich)	SiO_2
	(Fe-rich)	$\text{Fe}_1\text{-Si}_m\text{-Mg}_n\text{-O}_p$
Sulfides	Pyrrhotite	Fe_{1-x}S
	Pentlandite	$(\text{FeNi})_9\text{S}_8$
Carbonates	Breunnerite*/ Siderite*	$(\text{Mg},\text{Fe},\text{Ca})\text{CO}_3$
	Calcite*	CaCO_3
Others	Magnetite	Fe_3O_4
	Chromite	FeCr_2O_4
	Metal	(FeNi)
	Tochilinite*	$\text{Fe}_{1.3}\text{Ni}_{0.1}\text{SO}_{1.4}(\text{OH})?$
	Carbon (Amorphous/ Graphitized)	C
	Organic polymers	$\text{C}_1\text{-H}_m\text{-O}_n$

* Minerals exclusively found in the hydrated class of IDPs

TABLE 2. Comparison of mineralogies

	IDPs		Carbonaceous chondrite		
	Smectite	Serpentine	matrices		
	-rich	-rich	CI	CM	CO/CV
Smectite	●	•	●		
Serpentine	•	●	●	●	
Cronstedtite		•		●	
Pyroxene	•	•			•
Olivine	•	•			●
Glass	•	•			
Pyrrhotite/Troilite	•	•	•	•	•
Pentlandite	•	•	•	•	•
Breunnerite/Siderite	•		•		
Dolomite			•		
Calcite		•		•	
Magnetite	•	•	•	•	•
Chromite	•	•	•	•	•
Metal	•	•	•	•	•
Tochilinite		•		●	
Ferrihydrite			●		
Sulfates			•		
Carbon/Organic polymers	•	•	•	•	•

The black filled circles indicate the presence of minerals. The large circles indicate predominant minerals.

rich compositions [2,14]. The Mg-rich and Fe-rich smectites and the glass are commonly intimately intergrown on a scale $<1000 \text{ \AA}$.

Ca-Mn-bearing Mg-Fe-rich carbonates, primarily breunnerite and siderite, are abundant constituents and characteristic of this class of IDPs, [13,14]. They occur as relatively large (500 to 3000 \AA in diameter) rhombohedral grains and also as smaller (100 to 1000 \AA) rounded grains. Carbonaceous material including amorphous and graphitized carbon is present [14] and is probably a major carrier of deuterium [7]. There are unusual aggregates of small rounded grains (<100 to 500 \AA) of a variety of minerals embedded in a carbonaceous matrix [2].

Most smectite-rich IDPs contain minor amounts of anhydrous silicates such as Mg-rich pyroxene and olivine. Some of the pyroxene crystals have platelet or whisker morphologies like those found in anhydrous particles [2,12]. Minor amounts of Ca-Al-rich clinopyroxenes (fassaite and diopside) are also present [12,14]. Other minerals contained in this class of particles include Fe-Ni sulfides (pyrrhotite and pentlandite), magnetite, chromite, and Fe-Ni metal.

3.2 Serpentine-rich IDPs

Only seven particles of this group ($\sim 30\%$ of the hydrated population) have been reported to date [2,14-16], and detailed data on this class are limited relative to the smectite-rich class. (An eighth particle was studied by an X-ray powder diffraction method [17], but TEM data are not available.) Serpentine in the IDPs shows a wide range of Mg/Fe ratios. Cronstedtite (very Fe-rich serpentine) was identified from one particle [16]. The serpentines in this class of particles commonly show larger crystal sizes and higher crystallinity than the smectites in the smectite-rich class. Fe-rich and Si-rich glasses occur in some of the particles, but olivine and pyroxene appear to be less common than in the smectite-rich particles. Other minerals include pyrrhotite, pentlandite, magnetite, kamacite (Fe-Ni alloy), and fassaite. Bradley [16] reported tochilinite from one particle, which occurs as intimate intergrowths with cronstedtite. In contrast to the smectite-rich particles, carbonates appear to be rare; only a grain of Ca carbonate, possibly calcite, was identified [14]. Serpentine-rich IDPs, in general, appear to be more homogeneous in internal elemental distributions than smectite-rich IDPs [14].

3.3 Comparison to meteorites

Table 2 compares major minerals in IDPs, both smectite-rich and serpentine-rich, and carbonaceous chondrite matrices. For the comparison, it should be noted that there is a large difference in scale between IDPs and meteorite matrices; most IDPs are $<20 \mu\text{m}$ in size, while the matrices of meteorites are larger than 1 mm and commonly exhibit mineralogical variations on a scale of <1 to $10 \mu\text{m}$. Therefore, it is not always possible to compare directly an individual IDP to a meteorite matrix. We need a relatively large group of IDPs to make an appropriate comparison.

Layer silicates in CI chondrites are mostly Mg-rich smectite (saponite) and serpentine [18], and those in CM chondrites are serpentines with various Mg-to-Fe ratios as well as cronstedtite [5,19]. Layer silicates in CI chondrites are commonly very poorly crystallized, while those in CM

chondrites are much larger in size and their crystal structures are more ordered. The comparison of the layer silicates and other major minerals appears to indicate that smectite-rich IDPs have a general similarity to CIs and serpentine-rich IDPs to CMs.

4. AQUEOUS ALTERATION: COMPARISON TO METEORITES

CI and CM chondrites show abundant evidence of secondary alteration that probably occurred by the activity of aqueous solutions on their parent body regolith, and that the layer silicates in these meteorites were produced by alteration of previously condensed olivine and pyroxene. It is beyond our scope to discuss here details of alteration experienced by the carbonaceous chondrites. The readers are recommended to refer to some of the following articles for that information: refs. 4-6,18.

Several lines of evidence for aqueous alteration were reported from hydrated IDPs. Tomeoka and Buseck [12] found evidence that smectite was produced by alteration of pyroxene (see Fig.2 in ref.12). Bradley [2] found that glass and layer silicates are intimately intergrown and interpreted that the layer silicates were formed by alteration of the glass. It is known from the studies of meteorites that pyroxene and glass are particularly susceptible to aqueous alteration and are preferentially altered to layer silicates.

A recent discovery of tochilinite and cronstedtite in a serpentine-rich IDP [16] provided strong mineralogical evidence for aqueous alteration. Tochilinite is one of the most mineralogically distinctive minerals that only occurs in CM chondrites [5,20]. Tomeoka and Buseck [5] showed that tochilinite was produced by alteration of metal and sulfides and formed complex intergrowths with cronstedtite during successive alteration.

The effect of aqueous alteration is also reflected in elemental abundances in the IDPs. Schramm et al. [3] performed bulk analysis of 200 IDPs, by using an energy dispersive X-ray (EDX) method, and found that hydrated IDPs show systematic depletion of Ca relative to solar abundance, while anhydrous IDPs do not show such depletion. Ca is water-soluble and tends to be leached at early stages of aqueous alteration in carbonaceous chondrite matrices [21], and deposited mostly as carbonates and sulfates.

One of the most important mineralogical differences between hydrated IDPs and meteorite matrix is that the former contain considerable amounts of submicron-to-micron size grains of glass and anhydrous silicates such as pyroxene and olivine, while the latter lacks those phases. The presence of glass and anhydrous silicates may indicate that alteration in the IDPs occurred over a very limited range. The microbeam analysis of hydrated particles at a size scale of $<1000 \text{ \AA}$ [14] indicates that the distributions of Si, Mg, and Fe are much broader than those in the carbonaceous chondrite matrices, suggesting that the IDPs are more inhomogeneous in elemental composition than the meteorite matrices. These observations and analyses support the view that IDPs were less processed by aqueous alteration than the meteorites.

Ca-sulfate, Mg-sulfate, and Na-bearing sulfate are other typical minerals that were deposited during aqueous alteration in CI chondrites [21,22]; thus, Na and S (like Ca) tend to be depleted in these meteorite matrices [21]. Ferrihydrite, poorly crystallized Fe^{3+} hydroxide, is another major phase in the CI matrices, and was interpreted to have been formed

together with the sulfates [18]. However, none of these phases and no depletions of Na and S are observed in the hydrated IDPs. The discrepancies, however, appear to be explained by the recent studies of a new Antarctic CI chondrite Yamato-82162. It has been revealed that Y82162 lacks sulfates, and its matrix and layer silicates are more enriched in Na than those in non-Antarctic CI chondrites [23]. (Sulfur is depleted in its matrix, but that is regarded as due to thermal metamorphism.) Tomeoka et al. [23] attributed these features to a much lesser degree of aqueous alteration than that experienced by non-Antarctic CI chondrites. Therefore, the lack of sulfates and ferrihydrite, and the non-depletions of Na and S in the hydrated IDPs may be other indications that the IDPs were less affected by aqueous alteration than CI chondrites.

5. THE SOURCES OF IDPs

Although there are a number of possible sources for the interplanetary dust, the major ones are considered to be comets and asteroids [e.g., 24]. However, until recently, there has been no way to limit the possibilities for the sources of IDPs. The results of mineralogical and chemical studies on both IDPs and meteorites provided much insight into the question.

As discussed in the previous sections, mineralogy of hydrated IDPs is similar to CI and CM chondrites, and hydrated IDPs have been processed by aqueous alteration analogous to these meteorites. The recent finding of tochilinite and cronstedtite in a serpentine-rich IDP [16] provided especially strong evidence for a link between the IDP and the CM chondrites. It is widely accepted that the most probable sources for meteorites are asteroids [25]. Recent analyses of telescopic reflectance spectra of the main-belt asteroids [26] suggested that aqueous alteration affected surfaces of some primitive-type asteroids.

Various authors have related the highly porous texture of anhydrous IDPs to the prior presence of volatile ices, and thus suggested that the anhydrous IDPs are cometary [e.g., 17,27]. On the other hand, the low porosity of the hydrated IDPs may have resulted from compaction process that occurred in relatively large parent bodies, i.e., asteroids. Fe/(Fe+Mg) distributions in pyroxene-rich anhydrous particles at submicron scale resemble Comet Halley dust, while those distributions in hydrated particles are similar to the Orgueil CI meteorite (see Fig. 9 in ref. 2).

The mineralogical and chemical information suggest that the hydrated IDPs are from asteroids and the pyroxene-rich anhydrous IDPs are from comets. Observational and experimental studies on atmospheric heating of IDPs [28] appear to indicate that main-belt asteroids, and comets having low inclinations and perihelia outside 1.2 AU, are the best candidates for the sources of these two types of dust. Sandford and Bradley [28] suggested that many of the olivine-rich IDPs may have been strongly heated during atmospheric entry, and thus they came from comets having more eccentric orbits.

Although it has not been established that extensive alteration can occur on comets, McSween and Weissman [29] recently proposed a hypothesis that significant aqueous alteration may occur in comet nuclei. Rietmeijer [30] has pointed out the possibility of cryogenic ($<0^{\circ}\text{C}$) alteration in comet nuclei. If the alteration indeed occurs in comets, the link between hydrated IDPs and meteorites would be somewhat blurred. The possibility

of alteration in comets needs to be further evaluated and clarified in the future.

6. SUMMARY AND CONCLUSION

1. Hydrated IDPs can be divided into two subgroups, one dominated by smectite and the other by serpentine. The smectite-rich IDPs are mineralogically similar to CI chondrites, and the serpentine-rich IDPs are similar to CM chondrites, although they are not perfect matches.
2. There is evidence that the layer silicates in the IDPs were formed by aqueous alteration of glass and pyroxene. However, the presence of anhydrous silicates and glass and the compositional heterogeneity on a scale $<1000 \text{ \AA}$ in the IDPs suggest that the alteration occurred over a very limited range. The degree of alteration in the IDPs was much lesser than those in meteorites.
3. It appears to be a current consensus of the majority of IDP researchers that most hydrated IDPs were derived from asteroids and most anhydrous IDPs were derived from comets.

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