Refractory Interplanetary Dust Particles

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Criteria are described by which refractory interplanetary dust particles (IDPs) can be differentiated from the products of spacecraft debris. These criteria have been used to discover and characterize IDPs that are composed predominantly of refractory phases. Two of these particles contain hibonite, perovskite, spinel, refractory glass, and a melilite; only hibonite was identified within a third. The grain size for all particles ranges from 0.05 to 1 micrometer, so that they are much finer grained than the refractory calcium- and aluminum-rich inclusions in meteorites. The glass-containing refractory IDPs may be primitive nebular condensates that never completely crystallized and thus have been preserved extant.

REFRACTORY MINERAL–RICH INTERPLANETARY dust particles (IDPs) would be expected to have compositional and structural similarities to the calcium- and aluminum-rich inclusions (CAIs) that are found in most carbonaceous and some ordinary chondrites (*1, 2*). These CAIs contain refractory metals, oxides, and silicates that experimental and theoretical work indicates should be the first phases to have condensed from the cooling solar nebula (*3*) and that are considered to be among the most primitive extraterrestrial material available for study. These refractory materials would also be present in the phases most likely to have survived melting and evaporation during the hypothetical T-Tauri stage of the sun. An important avenue of recent research has been a search for isotopic effects that indicate the presence of presolar materials in CAIs (*4*). However, the isotopic effects that have been identified have probably been diluted or obscured by subsequent alteration processes that affected the CAIs, which include melting and partial or complete evaporation in the solar nebula as well as thermal and shock metamorphism, hydrous alteration, and diagenetic processes on the meteorite parent body (*2, 5*). However, materials incorporated into cometary bodies should have undergone little or no parent body alteration because of the presumed low-energy environment of these bodies. The interpretation of the physicochemical characteristics of the presolar molecular cloud and the early history of the solar system would be much simpler from such pristine materials.

For the past decade the National Aeronautics and Space Administration (NASA) has collected and studied particles found within the earth's stratosphere (*6*). A varying proportion (through time) of all of these particles are composed mostly of refractory elements. Some of these particles are undoubtedly IDPs (*7*) and are possibly from comets. Thus such particles could include presolar grains, remnant condensation products from the early solar system, and residue from the incomplete evaporation of presolar dust or early solar nebula condensation grains (*3, 8*), all preserved from further reaction with the solar nebula or planetary alteration processes.

Little work has been performed on the refractory particles collected from the stratosphere because of their similarities to the products of solid propellant rockets and ablating spacecraft debris. However, recent examination of the microstructures and chemistry of ablating aerospace materials has indicated that this material can be differentiated from true extraterrestrial refractory particles (*7, 9*). For example, Zolensky (*7*) observes that the refractory phases hibonite [$Ca(Al,Ti)_{12}O_{19}$], perovskite ($CaTiO_3$), and the melilites [gehlenite (geh), $Ca_2Al(SiAl)O_7$, to akermanite (aker), $Ca_2MgSi_2O_7$] do not appear to form from the ablation of aerospace materials. These phases are believed to be among the earliest to condense within the cooling solar nebula (*3*). Thus a systematic search for refractory mineral–rich IDPs within the stratospheric particle collection was made with these cited criteria for distinguishing such particles from spacecraft material.

The stratospheric dust particles studied were obtained from the NASA collection. These particles were examined with both a JEOL 35CF scanning electron microscope (SEM) and a JEOL 100CX scanning transmission electron microscope (STEM). The former was equipped with a windowless detector for the energy-dispersive x-ray (EDX) analysis of elements with an atomic number below that of sodium (*10*). All phase identifications were made on the basis of these compositional analyses together with electron diffraction (ED). Particles were selected for detailed characterization based on some combination of enrichment in aluminum, calcium, or titanium and a nonspherical shape to minimize confusion with the products of rocket exhaust and spacecraft debris.

Semiquantitative EDX analysis revealed that particle W7029 H15 contains major amounts of aluminum, silicon, oxygen, and calcium and minor amounts of magnesium and titanium. A minor amount of sulfur is also present, which probably arises from contamination from stratospheric aerosols (*11*). This particle is an aggregate that consists of euhedral to anhedral grains that are 0.05 to 1 μm in average diameter (Fig. 1A). Particle W7029 H15 is 11 by 16 μm overall. Most of the constituent grains are clustered together into micrometer-sized rounded aggregates (see Fig. 1B), which give portions of the particle a botryoidal appearance. Within W7029 H15 are grains of perovskite (essentially stoichiometric $CaTiO_3$), gehlenite (approximately $geh_{90}aker_{10}$), and hibonite (approximately $CaAl_{11}Ti_{0.5}Mg_{0.5}O_{19}$). Subsequent EDX analysis of a small portion of this particle indicated the additional presence of a phase whose composition is consistent with spinel (*12*). In addition, wisps of silicate glass (as revealed by ED) are present (see Fig. 1B) that partially to completely encase some crystalline grains and bridge some grain clusters. The composition of this glass could not be determined beyond the limits imposed by the overall refractory particle composition because of the close proximity of finer grained crystalline phases. Because this particle was not disaggregated prior to phase characterization by ED, only grains along the edges of the particle could be examined. Thus the distribution of each of these phases within the particle could not be adequately determined. Additional mineral phases may be present in this particle but on the basis of overall particle composition I conclude that the major phases have been identified.

Particle W7017 1A55 contains major amounts of aluminum and oxygen and minor amounts of silicon, titanium, calcium, and magnesium. This particle is 15 by 10 μm and consists of rounded and tabular grains that are closely packed and of submicrometer sizes and that are separated by larger smooth regions (see Fig. 1C). All phases appear to have the same size distribution. The rounded grains consist of perovskite and a melilite; the tabular crystals were hibonite. The EDX analysis of these phases

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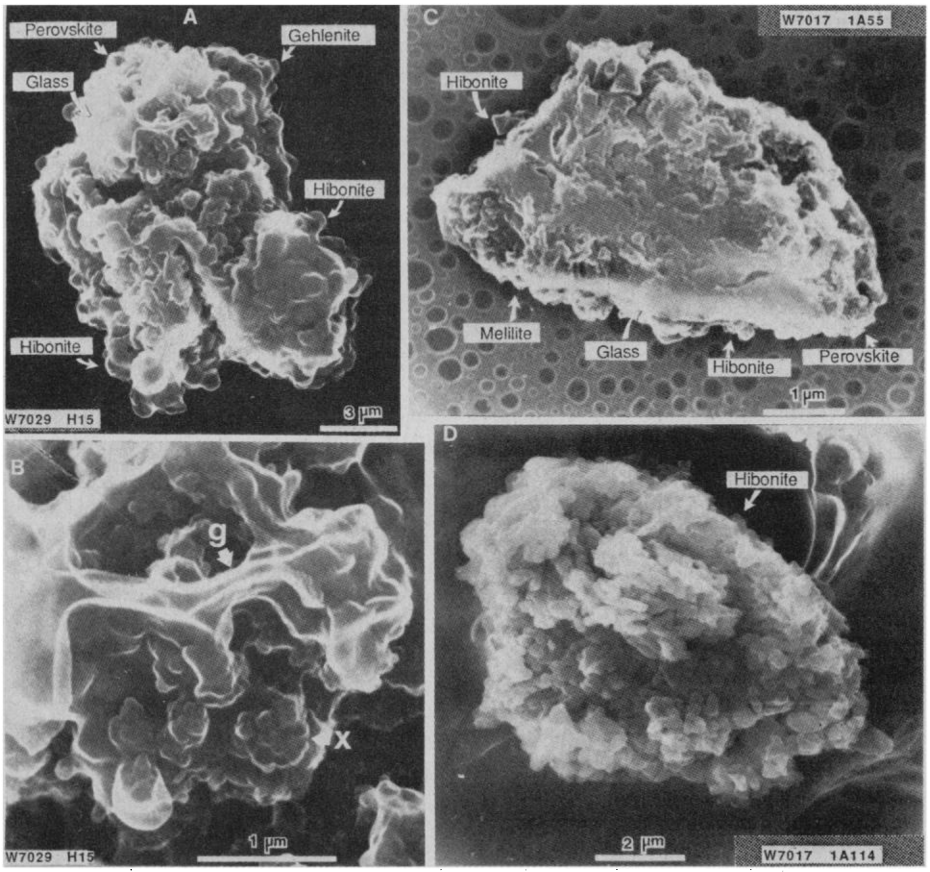

Fig. 1. (**A**) Mineralogy of particle W7029 H15. This particle is composed of submicrometer-sized monomineralic grains of hibonite, gehlenite, and perovskite that are clustered into micrometer-sized, rounded aggregates. Glass can cover and surround the grains. (**B**) Close-up view of the upper portion of particle W7029 H15, which illustrates the clustering of individual crystalline grains (labeled X) into rounded aggregates. Glass is labeled g. (**C**) Mineralogy of particle W7017 1A55. As in particle W7029 H15, glass is intimately associated with the submicrometer-sized crystalline grains of hibonite, melilite, and perovskite. (**D**) Particle W7017 1A114, which is a porous aggregate of well-sorted, submicrometer-sized grains that are rounded to vermiform in shape. Hibonite is the only mineral that was identified within this particle.

was inadequate to calculate accurate compositions but were roughly consistent with these mineralogical identifications. The position of the melilite within the akermanite-gehlenite series could not be adequately determined. As with particle W7029 H15, a subsequent EDX study of this particle also indicated that spinel may be present (*12*). The smooth regions of this particle contain higher relative proportions of silicon compared with the bulk particle. Because they lack crystallinity (as determined by ED), these regions are predominantly glass of refractory composition, as in particle W7029 H15.

The semiquantitative whole-particle EDX analysis of particle W7017 1A114 shows that calcium, silicon, oxygen, and magnesium are major constituents and that iron, titanium, and aluminum are minor ones. This particle is an aggregate; it measures approximately 5 µm in its largest dimension and consists almost entirely of spherical to vermiform grains that measure from 0.1 to 0.3 µm across and up to 1 µm in length (Fig. 1D). This particle has an unusually uniform grain size. The only mineral that could be confidently identified within this particle was hibonite with the approximate composition $CaAl_8Ti_2Mg_2O_{19}$. Additional phases including silicates are undoubtedly present in this particle, as indicated by the overall composition.

Based upon the mineralogy and morphologies of these particular particles, which together are completely unlike known terrestrial materials of natural or artificial origin (*6, 7, 9*), I suggest that all are IDPs. Confirmation of this suggestion is provided in an accompanying report (*13*), in which the oxygen isotopic composition of these particles is described. Thus these are the first IDPs to be identified that consist predominantly (or solely) of refractory minerals (*14*).

The small size of these particles (none larger than 16 µm in maximum dimension) essentially precludes the possibility that they were processed by frictional heating during passage through the atmosphere (*15*). In addition, excesses of ^{16}O are reported for these particles (*13*), which is contrary to the oxygen fractionation reported for atmospheric ablation (*16*). Thus the refractory glass noted within particles W7029 H15 and W7017 1A55 must have a preterrestrial origin. There are three possible explanations for this glassy material: (i) this vitreous material may reflect a heating or shock event on a particle parent body; (ii) these particles may have undergone partial melting in space, perhaps during the T-Tauri stage of our sun; or (iii) these two particles may originally have been entirely or partly noncrystalline and have only partly crystallized. The results of recent experiments that model condensation under appropriate nebular conditions have suggested that amorphous material may have condensed initially and then crystallized later (*17*). Particles W7017 1A55 and W7029 H15 may be two natural examples of such material in an arrested stage of crystallization. This state may easily have occurred if these particles were held until recently within a cold cometary body in which little energy was available for crystal nucleation and growth.

The constituent grain sizes for the three particles described in this report rarely attain 1 µm and are predominantly between 0.05 and 0.2 µm. These grain sizes are thus at least an order of magnitude smaller than the finest grained meteoritic CAIs previously reported (*1, 18*). Thus the refractory IDPs described in this report are inherently different from analogous materials (CAIs) found within meteorites, and represent a new class of extraterrestrial material. Although such particles have compositions and mineralogies similar to very primitive refractory inclusions found within chondritic meteorites, they also exhibit significant differences from meteoritic CAIs, including much finer grain size and (in two out of three reported cases) the presence of refractory glass (*19*), which may mean that they are more primitive than CAIs. These particles are also excellent candidates for ion probe analyses of such elements as titanium, magnesium, and oxygen [compare with (*13*)]. The identification of probable presolar interstellar grains within refractory-rich IDPs (verified by isotopic analyses) would add a new dimension to the study of extraterrestrial materials.

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20. I thank D. S. McKay for access to the electron microscopy laboratories of the Solar System Exploration Division, NASA/Johnson Space Center, D. S. McKay, K. McKeegan, and three anonymous referees for helpful reviews of this report, K. Thomas-Ver Ploeg, D. A. Wark and U. B. Marvin for valuable discussions, and the NASA Planetary Materials and Geochemistry Program for funding this study.

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Oxygen Isotopes in Refractory Stratospheric Dust Particles: Proof of Extraterrestrial Origin

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The oxygen and magnesium isotopic compositions of five individual particles that were collected from the stratosphere and that bear refractory minerals were measured by secondary ion mass spectrometry. Four of the particles exhibit excesses of oxygen-16 similar to those observed in anhydrous mineral phases of carbonaceous chondrites and thus are extraterrestrial. The oxygen and magnesium isotopic abundances of one corundum-rich particle are consistent with a terrestrial origin. Magnesium in the four extraterrestrial particles is isotopically normal. It is unlikely that these particles are derived from carbonaceous chondrites and thus such particles probably represent a new type of collected extraterrestrial material.

THERE IS MUCH EVIDENCE THAT most, and probably all, of the particles collected from the stratosphere that have elemental abundances similar to those of carbonaceous chondrites are samples of interplanetary dust particles (IDPs). The mineralogical, optical, and isotopic properties of these "chondritic" IDPs show that they are a diverse assemblage of primitive materials from the solar nebula (*1*). Some IDPs have apparently undergone less chemical and thermal alteration on their parent bodies than have carbonaceous meteorites, and it is probable that many IDPs, especially the highly porous ones (*2*), are derived from comets. One notable difference between IDPs and most carbonaceous chondrites is the relatively low abundance of high-temperature mineral phases in IDPs. Although many chondritic IDPs contain enstatite laths and ribbons that have been interpreted as evidence for high-temperature vapor-to-solid condensation processes (*3*), in only two particles have the more refractory mineral phases that occur in the calcium- and aluminum-rich inclusions (CAIs) of carbonaceous meteorites been found (*4, 5*). One possible reason for this dearth of very refractory material in chondritic IDPs is that they formed at lower temperatures than those necessary for calcium-aluminum oxides to be stable in a gas of solar composition (*6*). Another possible explanation is that particles with high abundances of refractory oxide minerals are by definition not chondritic and so may have simply been overlooked, since most studies have concentrated on chondritic particles.

The primary difficulty in identifying nonchondritic IDPs in the National Aeronautics and Space Administration (NASA) stratospheric collection is distinguishing them from the abundant terrestrial contaminant particles. Circumstantial evidence for an extraterrestrial origin of single-mineral mafic silicate grains and of iron-sulfur-nickel particles is provided by their frequent association with chondritic material (*7*). The difficulties in identifying refractory extraterrestrial particles are exacerbated by pollution in the stratosphere, which includes refractory materials from rocket exhaust and spacecraft debris (*8*). In particular, the large abundance of aluminum-oxide spherules in the stratosphere leads to a possibility that these particles could get mixed with chondritic material on the collection surface. The only rigorous means for proving that small particles collected on Earth are of extraterrestrial origin is to measure either effects that can only be attributed to prolonged space exposure (for example, the presence of solar-flare nuclear particle tracks) or isotopic abundances that cannot be derived from the terrestrial composition by naturally occurring physical or chemical processes (for example, radioactive decay or isotopic mass fractionation). Previous hydrogen and mag-

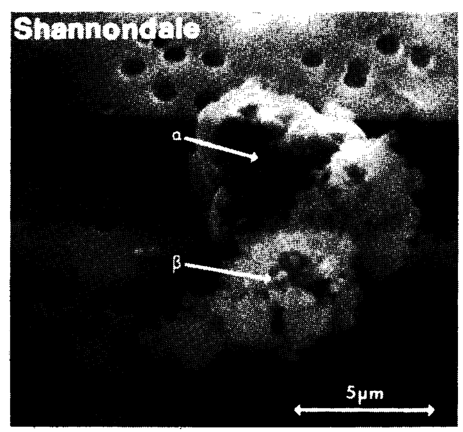

Fig. 1. Secondary electron micrograph of the IDP Shannondale. The energy-dispersive x-ray spectrum of spot α shows aluminum only, whereas that of spot β is chondritic.

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