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INTERSTELLAR GRAINS WITHIN INTERSTELLAR GRAINS;
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In this paper we report the discovery of crystals of titanium carbide in an interstellar graphite spherule. The titanium carbide is another species in the growing list of interstellar grains which have been discovered in chemically processed samples of primitive meteorites. The new species is particularly interesting in that it has come to us in a protective wrapping (the graphite spherule) which has eliminated the possibility of chemical alteration during its residence in the interstellar medium and in the meteorite in which it was discovered. It thus looks today just as it did when it formed in the atmosphere of some carbon-rich star, at a time before the sun and the planets came into existence.

For more than a half century astronomers have been aware of the presence of interstellar dust from its obscuring effects on the light from stars. From various kinds of studies they have also been able to divine some notion of its composition and particle sizes. Large clouds of interstellar dust and gas can gravitationally collapse to form new stars. Nuclear reactions within these new stars alter the composition of the original gas and dust constituents, and stellar winds spew this altered material back into the interstellar medium. Thus, the chemical composition of the galaxy evolves with time.

Cosmochemists have long known that the sun and the planets owe their particular compositions to a mixture of interstellar gas and dust, but it was thought until fairly recently that all vestiges of the original constituents had been erased by complete homogenization of the dust component very early in the formation of our solar system. The evidence for this idea was based on the observation that the isotope composition of the more abundant elements was the same regardless of whether one was making measurements on a terrestrial rock, a moon rock or a meteorite. Any differences that were observed were usually explicable as the result of well-understood nuclear and chemical processes that occur within the solar system. However, some poorly understood variations in isotope composition occurred in the noble gases, which are generally present in very low abundances in solid materials. It was in an effort to isolate the mineral carriers of these noble gases that Edward Anders and his colleagues at the University of Chicago began nearly two decades ago to chemically treat primitive meteorites in order to dissolve away unwanted minerals and concentrate the carriers of unusual neon and xenon. These chemical processing procedures eventually led to the discovery of meteorite grains which could unambiguously be pronounced as stardust -- grains which condensed in the atmospheres of diverse types of stars, were expelled from these atmospheres and existed for a time as interstellar grains, and which finally were incorporated into the interstellar cloud from which our solar system formed, but nonetheless had survived all of these tumultuous events.

To date, small interstellar grains of diamond, silicon carbide and graphite have been found. It is fair to ask how we can be confident that these grains really are stellar condensates, and not simply minerals that formed in our own solar system. Because of advances in microanalytical techniques, it is possible to measure the isotope composition of some abundant elements in individual grains, many of which are so small as to be invisible to the naked eye. We find that the compositions of some are dramatically different from the average solar system composition. For example, in typical solar system material, variations of a few percent in the proportions of the two carbon isotopes ^{12}C and ^{13}C would normally be considered large; but in individual interstellar carbon grains the proportions can be as much as fifty times the solar system average value. This difference is comprehensible if we consider that carbon in the solar system represents an average of carbon from many different stars, while an individual interstellar graphite grain represents only the carbon from one particular star, which need not have carbon isotope abundances similar to this average.

In our current work we have combined isotope studies of individual interstellar graphite grains from the Murchison meteorite with studies of the interiors of these grains with the transmission electron microscope (TEM). These grains are very small (only a few thousandths of a millimeter in size), yet after isotope measurements it is nonetheless possible to pick up a particle with delicate apparatus, imbed it in a special hard resin, and slice it, using a microtome with a diamond blade, into dozens of wafers, each only several hundred atoms thick. This is necessary because, even though the particles are very small, they are too thick to be studied in the TEM. Once such slices have been obtained, it is possible to view features of the grain even down to the size of individual layers of atoms.

The graphite particles are roughly spherical in shape, and have two basic kinds of internal structure. In one type, the graphite is arranged in circular layers, much like the inside of an onion. In the other type of interstellar graphite, the structure is that of a ball of small scales. Both kinds of structure are peculiar, and not observed in terrestrial graphite. An unexpected but very exciting discovery was the presence of small crystals, a hundred or so atomic diameters in size, within one of the scaly graphite particles. In addition to getting pictures of the crystal lattice structure of the included crystals, we could also study their composition and crystal structure in the TEM, and from these studies we learned that the crystals are titanium carbide, a mineral not previously found in meteorites.

Chemical equilibrium calculations made in 1978 by Lattimer, Schramm and Grossman at the University of Chicago had in fact predicted that these two minerals, graphite and titanium carbide, would be the first to condense in the atmosphere of a carbon-rich star. According to their calculations, graphite should condense first, followed by titanium carbide, at temperatures of 1200-1700 degrees Celsius. The fact that we observed titanium carbide crystals *inside* of the graphite must mean that the growth of graphite was somewhat delayed from what calculations based on chemical equilibrium suggest--an effect which had also been predicted by some astronomers. From studying the internal structure of the interstellar graphite spherules and the included titanium carbide we can make some educated guesses about the formation of the spherules. First, they probably formed at high temperatures and were the first grains to condense in their particular stellar atmospheres; second, they may have formed relatively rapidly (possibly in times measured in days, for example), since the graphite layers are often not very well developed, as they would be expected to be if condensation proceeded slowly; third, the grains may have been expelled from their stars to regions of substantially lower gas pressure (interstellar space?), since we don't find the other minerals which would have condensed after graphite and titanium carbide.

No one has yet observed titanium carbide by conventional astronomical measurements of stars or the interstellar medium. This is perhaps not surprising, since this mineral comprises only a few parts per million of one of the graphite spherules we studied. But it points out that the laboratory study of interstellar grains extracted from primitive meteorites may yield a far richer and more complete picture of how such grains form than can be gotten from astronomical study alone. The laboratory observations also pose interesting challenges to theoreticians who model the chemistry of stars and the formation of solid grains in their atmospheres.