Silicon Isotopic Composition in Large Meteoritic SiC Particles and ^{22}Na Origin of ^{22}Ne

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Large silicon carbide (SiC) particles extracted from acid-insoluble residues of carbonaceous chondrites are isotopically anomalous in both silicon and carbon and contain isotopically extreme noble gases. These particles are thought to have originated in mass outflows from red giant stars and to have existed in the interstellar medium at the time the solar system formed from an interstellar cloud. Calculations show that the silicon isotope correlations in those large SiC particles can be generated only in the most massive carbon stars. Consequently, the almost pure neon-22 (^{22}Ne) in those particles must be interpreted as the condensation of radioactive sodium-22 (^{22}Na) in the particles as they flowed away from the stars. The ^{22}Na is produced through proton capture by ^{21}Ne at the base of the surface convection zone. Neon-22 does not exist abundantly in helium shells hot enough to burn magnesium, which is necessary to establish the measured silicon isotopic composition.

Since the first discoveries of isotopically anomalous xenon gas in acid-resistant meteoritic residues, it has seemed likely that some insoluble dust therein had condensed during mass loss from red-giant stars. One specific component (*1*) is heavily enriched in those three (A = 128, 130, 132) of xenon's nine stable isotopes that should be enriched by neutron irradiation of stellar matter (*2*). It is called s-process Xe (s-process is a nucleosynthesis path in which the lifetime for neutron capture is greater than the lifetime for beta decay). Had it not been promptly trapped in particles as they left the stars, the s-process Xe would have mixed with and been diluted by interstellar Xe. Subsequent isolation, purification, and characterization of that residue identified it as SiC particles (*3*), which suggests an origin in carbon-rich stars so that SiC could condense without being oxidized. Carbon stars are advanced double-burning-shell, asymptotic-giant-branch (AGB) stars (*4*) in which the C/O abundance ratio has been so augmented by internal nucleosynthesis of C that molecular lines of C_2 and carbides appear in the spectrum whereas oxides do not. The s-process heavy elements are also much enriched in these stars.

These indicators of the origin of meteoritic SiC particles and a summary of all available noble gas data are discussed in coordinated works (*5, 6*) that argue that the winds from AGB stars were the specific sites of SiC condensation. They emphasize the possible acquisition of the trapped ^{22}Ne-rich anomalous gas, called Ne-E(H) (*7*), by implantation with a wind from the ^{22}Ne-rich, He-burning shells of low-mass AGB stars. This process requires the He shells to be exposed, which happens only at the very end of the stars' lifetimes when the envelopes have been totally lost. The envelopes of low-mass AGB stars, wherein the SiC is presumed to condense, retain too much initial ^{20}Ne (*7*) for them to be a source of Ne-E(H), even after repeated dredge-ups (*4*) of ^{22}Ne from the He shell to the surface. In our alternative picture motivated by a problem with the isotopic composition of the Si itself, the Ne-E must instead be attributed to the condensation of radioactive ^{22}Na in the SiC particles. This old general idea (8) had previously been suspected to explain the origin of Ne-E.

When studies with the sputtering ion microprobe (*9–11*) showed that the Si from which the particles had grown was isotopically heavy, it seemed plausible that neutron capture by Si was responsible. Its isotopic composition might then be attributed to the neutron flux responsible for the observed enrichment of AGB atmospheres in s-process elements. Moreover, the large SiC particles were shown (*9–11*) to be isotopically heavy in C as well. When compared to solar isotopic composition, the ^{29}Si deviation, defined as

$$^{29}\delta = 1000[(^{29}\text{Si}/^{28}\text{Si})/(^{29}\text{Si}/^{28}\text{Si})_{\odot} - 1] \quad (1)$$

is correlated with the analogous ^{30}Si deviation but along a line with slope near 1.4. The good quality of this correlation line for large SiC particles strongly suggests that each is an admixture of two isotopic components, one near solar composition and one with isotopically heavy Si at the upper end of that correlation line. The correlation slope 1.4 subsequently came to be seen as an obstacle to interpreting the SiC as AGB stardust, however, because neutron capture produces a correlation slope $^{29}\delta = 0.46 ^{30}\delta$ (*6, 12, 13*). The large cross section for the ^{33}S(n, α)^{30}Si reaction prevents a slope larger than 0.5 for neutron capture reactions (*12, 13*). These constraints on Si do not necessarily apply to the majority of the SiC particles, which are much smaller and can only be measured as aggregates. These aggregates do not show clear evidence of a correlation having a slope of 1.4.

A way around this obstacle (*13*) makes use of charged-particle reactions. We demonstrated that if the AGB He shell flashes were as hot as 450×10^6 K, 15% hotter than suggested by existing models of AGB stars (*4, 14*), then both the ^{22}Ne and the resulting heavy Mg isotopes release neutrons through the (α, n) reactions as normally envisioned. The ^{26}Mg(α, n)^{29}Si reaction so enriches ^{29}Si that its excess can be larger than that of ^{30}Si. More specifically, parameterized AGB shell evolution models (*13*) developed a shell composition that saturated (*15*) near $^{29}\delta = 1.4 ^{30}\delta$. For the first time it appeared likely that mixing between that shell composition and the remaining envelope could generate the observed array of particles near the Si-isotope line of slope 1.4. Figure 1 shows, in its inset window, our three-isotope correlation calculated in the envelope of a 5.5-$M_{\odot}$ AGB star model. Parallel to the dashed Si-isotope line of slope 1.4, near which individual particles lie (*9–11*), is the solid line envelope track of the Si isotopic composition in that 5.5-$M_{\odot}$ AGB star. The asterisk near the bottom end of that track locates the pulse when the envelope first became a C star (that is, first became C-rich rather than oxidized). Carbon excess is a requirement for SiC thermal condensation.

The solid track in Fig. 1 shows that the envelope eventually becomes much more isotopically heavy than the observed particles, which have δ values <100 parts per thousand (*9–11*). However, the histogram in Fig. 1 shows the amount of mass lost in the wind as a function of the ^{30}Si excess. One sees there that most of the mass leaves on the lower part of the three-isotope evolutionary track, whereas the much more anomalous material on the upper portion of the track is carried by only a small amount of mass. The most anomalous envelope occurs only late in the evolution. At this point, the small mass of the remaining envelope becomes subject to large isotopic change from shell admixtures, which are dredged up after the pulses (*4*). This result is encouraging because it shows that most of the SiC particles in the winds will carry modest δ values. We will describe more fully the dependence of this result on the many uncertainties associated with the mass-loss rate and with the parameterized prescriptions for dredge-up in a more specialized publication (*16*). We did employ standard expressions from other workers on AGB stars and did not attempt to find special relations that would give this result. The result came naturally except for the presumption of 15% higher shell tempera-

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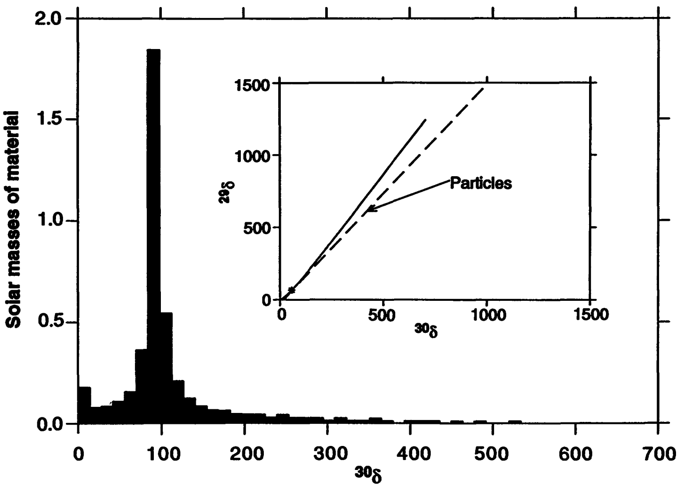

Fig. 1. The isotopic composition of the 5.5-$M_\odot$ AGB star envelope evolution, where $M_\odot$ is the mass of the sun. The inset shows the line of slope 1.4 defined by the large SiC particles (dashed) and the evolution of the atmospheric composition (solid). The asterisk locates the point on the upward evolution when the star becomes rich in C. The delta notation describes the isotopic excess of that Si isotope in parts per thousand (Eq. 1) relative to terrestrial isotopic composition. The histogram shows the amount of envelope mass lost as stellar wind as a function of its ^{30}Si excess. Most of the SiC particles should have modest excesses near $^{30}\delta$ = 100 rather than the tenfold larger values that characterize shell Si.

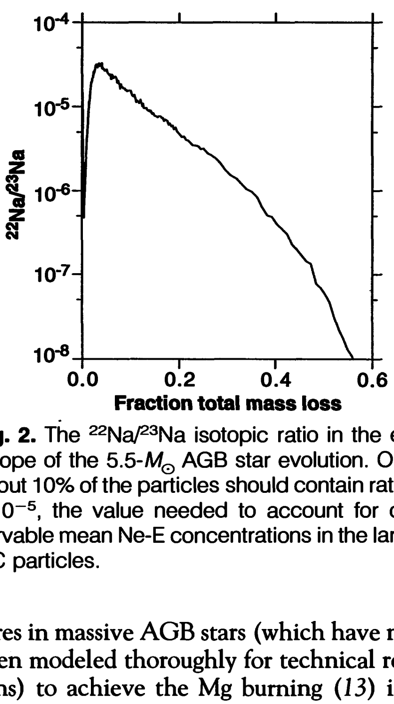

Fig. 2. The ^{22}Na/^{23}Na isotopic ratio in the envelope of the 5.5-$M_\odot$ AGB star evolution. Only about 10% of the particles should contain ratios $>10^{-5}$, the value needed to account for observable mean Ne-E concentrations in the large SiC particles.

tures in massive AGB stars (which have not been modeled thoroughly for technical reasons) to achieve the Mg burning (*13*) implied by the Si isotopic composition.

We assume that SiC condensed in the stellar wind as it was flowing away from the envelope. Indeed, one may question whether other options exist. The grains cannot condense deeper in the star because they would evaporate (above perhaps 2500 K). On the other hand, when the wind is well away from the star it becomes too dilute to nucleate and too cool to form the mineralized thermal SiC structure. One alternative might be some uncommon (terrestrially) chemistry during which collisions create SiC in circumstellar settings. Frenklach, Carmer, and Feigelson (*17*) present a stimulating chemical view of a scenario in which the SiC nucleates at higher temperature but is later grown larger by reaction with polycyclic aromatic hydrocarbons.

The success of this model for Si isotopes places the ^{22}Ne richness of the gas trapped in the SiC particles in a new light. To find the correct isotopic slope for large SiC particles we can use only massive AGBs that are capable of Mg burning (*13*). But if the shell is hot enough for Mg burning, its initial ^{22}Ne is totally consumed in each pulse of the shell. That is, there exists no ^{22}Ne for the wind to implant. This problem is avoided in our model by a ^{22}Na parent for Ne-E.

Hot-bottom burning occurs at the base of the surface convection zone in the massive AGB stars—certainly so in the 5.5-$M_\odot$ model with which we illustrated these ideas (Fig. 1). With an envelope code, we found that ^{22}Na was produced by ^{21}Ne(p, γ)^{22}Na at the hot base of that convection zone, which reaches to the surface of the star. This process requires that base temperature exceed 60×10^6 K, which is achieved in massive AGB models. Furthermore, the convective turnover times are quite rapid for these stars (~1 year), so that the ^{22}Na is mixed through the whole envelope faster than it can decay (3.76-year mean lifetime). After this mixing, it flows away in the C-rich wind, partially condensing into the SiC particles. We next present a quantitative model of this process.

Brown and Clayton (*13*) describe the construction of the AGB models. For the present calculation we added a network of proton reactions to the envelope nucleosynthesis. For the 5.5-$M_\odot$ model, the essential aspect of this synthesis is the ^{21}Ne(p, γ)^{22}Na reaction, whose rate (*18*) allows rapid (in comparison to stellar evolution times near 10^5 years) conversion of ^{21}Ne into ^{22}Na. Our time-dependent convective transport allows for the 3.76-year (mean lifetime) radioactive decay of ^{22}Na. The hot-bottom burning during the interpulse period destroys all ^{21}Ne in the surface convection zone. Thus, ^{22}Na would decay altogether except for the episodic replenishment of ^{21}Ne by the ^{20}Ne(n, γ)^{21}Ne reaction in the He shell neutron burst and the subsequent dredge-up of shell matter into the envelope. This chain maintains a ^{22}Na/^{23}Na ratio in the envelope. That ratio is displayed as a function of the mass lost in the surface wind in Fig. 2.

It is of considerable interest that the peak ^{22}Na/^{23}Na ratio of 3×10^{-5} is adequate to account for the mean ^{22}Ne concentrations if the SiC particles are assumed to have an Na/Si abundance ratio of 5×10^{-3}. In the absence of measurement, we estimate this ratio as 0.1 times the solar abundance ratio (which also happens to be the depletion of Al relative to Si (*19*) in the SiC particles). That Na/Si ratio must be measured because it may be much less in SiC particles than the value we adopted, in which case the ^{22}Na parent may become implausible. The mean ^{22}Ne concentration in large SiC particles is 3×10^{-4} ml g^{-1} at standard temperature and pressure (*6*), which is 8×10^{15} ^{22}Ne atoms per gram. At an atmospheric ^{22}Na/^{23}Na ratio of 3×10^{-5}, the SiC particles would have contained 2×10^{15} ^{22}Na atoms per gram if grown quickly in the atmosphere and if ^{23}Na = 7×10^{19} g^{-1} as assumed. This order of magnitude agreement between measured concentration and this first calculation suggests that ^{22}Na condensation may be the origin of Ne-E. Calculation of the ^{22}Na concentration in the AGB atmosphere has many uncertainties, so that order-of-magnitude agreement is all that can be expected in this first calculation.

Only a small fraction (~10%) of the mass lost carried ^{22}Na/^{23}Na as great as 10^{-5} (Fig. 2). The physical explanation in our models for the decline in ^{22}Na during the later phases of mass loss (Fig. 2) is that, when about a quarter of the atmosphere has been lost, the base of the surface convection zone falls below $T = 60 \times 10^6$ K because of the reduction in pressure necessary to support the residual envelope. The ^{21}Ne(p, γ)^{22}Na reaction then shuts off. Thus, our results suggest that only about one particle in ten carries Ne-E at detectable levels. Interestingly, this finding has been obtained experimentally (*20*), lending further credence to this interpretation. However, interstellar and protosolar processing of the SiC particles must be addressed before firm conclusions can be drawn. On the other hand, if only 10% of the SiC particles contain Ne-E, those particles must have a higher concentration to account for the mean concentration in bulk collections of SiC particles. Thus, our calculated ^{22}Na/^{23}Na atmospheric ratio may not be quite adequate for those rich carriers. Our model also does not yet explain naturally why the fraction of particles rich in ^{22}Ne is also rich in ^{4}He. That correlation does seem natural in the model (*5, 6*) based on a wind from the He shell in a low-mass AGB star, whose shell is not hot enough to burn the ^{22}Ne that exists there (*4*). The latter model, on the other hand, has not accounted for the Si compositions of the particles. Thus, problems in interpretation abound for these competing pictures.

Because the ^{22}Na-bearing particles are formed at a special epoch in the star's evolution (the onset of the "superwind phase"), further correlations or anticorrelations between Ne-E content and other isotopes become plausible. In addition, the ^{22}Na interpretation required by our model may be correct even if some other explanation for the Si-isotope correlation can be found. We especially note that almost one-third of the large graphite particles in the residues carry an even purer form of Ne-E (*7*) without the accompanying ^{4}He (*20*). These particles may also find natural interpretations in the ^{22}Na production scheme because the C star atmospheres have tenfold more C than Si and should therefore also condense graphite. The graphite simply lacks the Si diagnostic (unless Si can be detected as a trace element in those particles).

Our approach is not to seek the most plausible explanation of the noble gas contents of the SiC particles. Rather, we explore the implications for Ne and other noble gases of a specific theoretical model that can account for the Si isotopes. After all, the particles are built of Si. To constrain this model, new work is needed. The Na concentration in the large particles must be measured so that their implied ^{22}Na/^{23}Na ratio can be accurately inferred. Other isotopic clues must also be interpreted. Foremost among these is the puzzling variation of the ^{13}C/^{12}C ratio, which is strongly impacted by the same hot bottom burning that creates the ^{22}Na. The crucial clue of Ne-E has been reinterpreted in terms of the old suggestion (*8*) of ^{22}Na parentage in stellar outflows, which describes it as an extinct radioactivity. This success ties the massive AGB star picture (*13*) to more data. Another puzzle is why only massive AGB stars have made the large SiC particles when low-mass AGB stars are more numerous. It is not clear whether a single nearby massive AGB star has produced all of these presolar particles and injected them into the placental solar cloud, as Cameron (*21*) advocates for other reasons. Another possibility is that only massive AGB stars are able to nucleate and grow the large SiC particles, as we (*13*) advocate. In the former case the data describe details of the formation of the sun and of that particular AGB star (*21*). In the latter case, they describe a general interstellar aspect of "cosmic chemical memory" (*22*) and of the entire spectrum of AGB star evolution.

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7. The largest 3- to 5-μm SiC particles have ^{20}Ne/^{22}Ne ratios as small as 0.1 (*5*), in stark contrast to atmospheric or solar ratios near 13. Low-mass AGB He shells are also rich in ^{22}Ne (*4, 5*), which leads to the suggestion (*5, 6*) that implantation of a terminal AGB wind from the He shell could be the source of Ne-E. The Ne-E in the SiC particles is called Ne-E(H) in meteoritics literature to distinguish it from the Ne-E(L) in graphite particles. The letters H and L refer to high- and low-density separates of the carbonaceous residues. The Ne-E(L) in graphite is even more purely ^{22}Ne, with ^{20}Ne/^{22}Ne as low as 0.01.
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23. We thank R. H. Nichols, Jr., and E. K. Zinner for discussions of their data before publication. We thank I. Iben, Jr., for the use of his envelope code and G. Bazan for several aspects of its implementation. Supported by the National Aeronautics and Space Administration under the Planetary Materials and Geochemistry Program and the Origins of Solar Systems Program.

19 June 1992; accepted 27 August 1992

Chemical Contrast in X-ray Microscopy and Spatially Resolved XANES Spectroscopy of Organic Specimens

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The scanning transmission x-ray microscope at the National Synchrotron Light Source has been used to record x-ray absorption near-edge structure (XANES) spectra from 0.01-square-micrometer regions of organic specimens. The spectral features observed reflect the molecular structure of the dominant absorbing atoms and provide the contrast mechanism for high-resolution imaging with chemical sensitivity. This technique was used with x-ray energies near the carbon *K* absorption edge to identify and map separate phases in various polymer blends and to map the DNA distribution in chromosomes with a spatial resolution of 55 nanometers.

Although electron microscopy is a standard technique for high-resolution imaging of organic specimens and electron energy loss spectroscopy (EELS) is frequently used to obtain chemical information at reduced spatial resolution, radiation damage poses serious limitations for methods that use electron beams (*1*). Recent work in x-ray absorption spectroscopy by Kirtley *et al.* (*2*) indicates that resonance structures near the *K* shell absorption edge of nitrogen provide a means to differentiate chemical species such as DNA and protein. These authors suggest that this resonance structure should provide a good contrast mechanism for bond-specific x-ray imaging. Their observation confirms earlier suggestions by Solem and Baldwin (*3*) and by Solem and Chapline (*4*) that near-edge resonances of nitrogen could be exploited in biological x-ray microscopy.

In this report, we present evidence that an analogous contrast mechanism exists in the x-ray absorption near-edge structure of

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