

Figure 1. The Big Bang and expansion of the universe versus time. Photography sourced from NASA.

# First glass: Formation of silicate in the early universe

By S. K. Sundaram

Silicate glass—the basis of the world’s most commercially important glasses—first formed more than 7 billion years ago.

Melting of silicate glasses dates to about 6000 BCE, while evidence of glass tools dates to 10000 BCE.<sup>1</sup> However, geological glasses that formed by impact and other processes are much older, for example, Libyan Desert glasses are about 28.5 million years old.<sup>2</sup>

Chondrules are some of the oldest known examples of geological glasses. These small, spherical, glass-rich inclusions are found in chondrites, i.e., stones from meteorites.<sup>3</sup> The glass matrix contains several minerals, namely olivines and pyroxenes, along with metals and sulfides made of magnesium, iron, calcium, and nickel.<sup>4</sup> Silica content of these glassy matrices varies over 40–85 wt.%. Chondrules are  $4,567.32 \pm 0.42$  to  $4,564.71 \pm 0.30$  million years old.<sup>5</sup> Chondrites also have other inclusions rich in calcium and aluminum condensed  $4,567.30 \pm 0.16$  million years ago. These time scales, which are supported by uranium isotopic measurements, closely match with the estimated age of our solar system.

While cauldrons in the cosmos continue to reveal complex chemistries,<sup>6</sup> the exact origin of glasses remains an exciting puzzle. To determine when and where the very first glass was birthed in the universe, we need to go back in time to the Big Bang, look closely, and follow the timeline of expansion of the universe and nucleosynthesis processes.

Doing so will allow us to determine when chemical elements, particularly oxygen and silicon, formed and interacted to form silica tetrahedra, the building block of silicate glasses and rock-forming minerals that remain in abundance in the earth's crust even today. That will perhaps help us in defining the very moment the first glass was born.

## The Big Bang and slow birth of the universe

The Big Bang occurred about 14 billion years ago. As of 2018, astronomers estimated the age of the universe at  $13.787 \pm 0.020$  billion years. Figure 1 shows an overview of the Big Bang, the universe, its expansion, and timeline. In the span of about 13.8 billion years, one can observe evolution of hierarchical structures on all scales encompassing nuclei, elements, galaxies, and planets in the universe.

Though the first atom formed about 300,000 years after the Big Bang, it took a few hundred million years before oxygen and silicon atoms formed and a few more billion years before other heavy elements came into existence in the solar system. After about 9 billion years, the sun, the planets, asteroids, comets, and other objects formed out of debris left behind by earlier generations of stars. The first sign of life was not until about 10 billion years after the Big Bang.

Stellar births result from the collapse of small condensation areas scattered throughout large molecular clouds in the galactic disks. As the core becomes hotter, the star can start "burning," thus producing energy through nuclear fusion via stellar nucleosynthesis.<sup>8</sup> Initial mass of the star dictates whether it continues to burn or dies. If the star weighs less than about 8 solar masses ( $M_{\odot}$ ), it will burn helium and become unstable, ending up as white dwarfs, which contain carbon and oxygen produced by helium burning. The solar mass  $M_{\odot}$  is a standard unit of mass, equal to about  $2 \times 10^{30}$  kg, to show the masses of stars and other objects.

If a star weighs more than about  $8 M_{\odot}$ , the burning will continue with carbon, neon, oxygen, and silicon as fuels, leading to formation of heavier nuclei. As the outer shell is a cooler and not dense

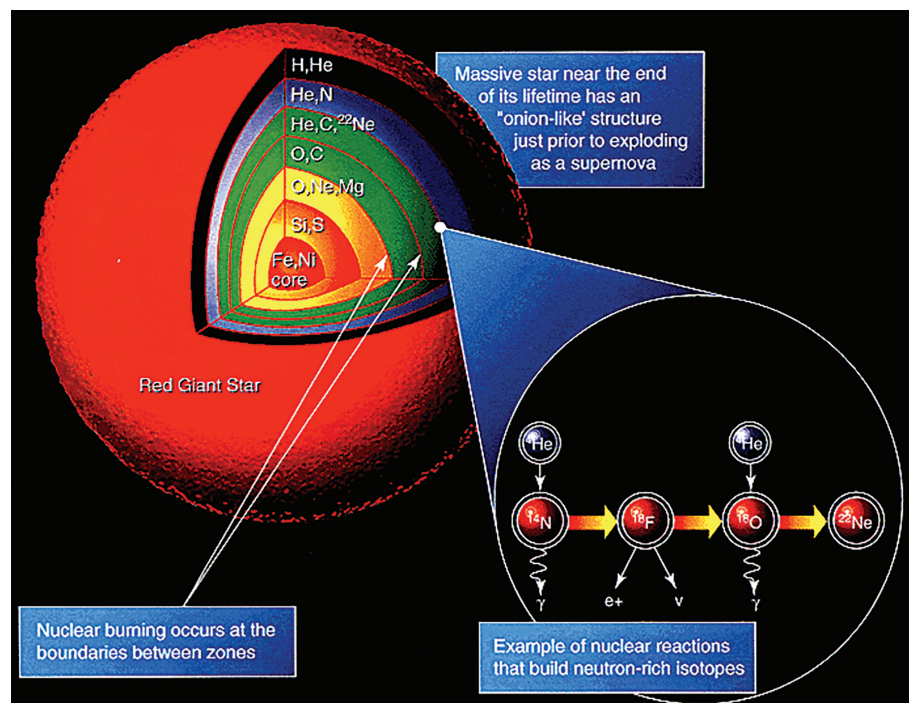


Figure 2. Massive star with onion-like structure.

region, the burning happens with a specific shell chemical composition. With hydrogen burning, for example, hydrogen burns into helium forming the outer shell. The process continues sequentially at interfaces of carbon,

oxygen, neon, and silicon burning shells. This process leads to formation of an onion-like, presupernova structure illustrated in Figure 2. The most important reaction during the oxygen burning process, i.e.,  $^{16}\text{O} + ^{16}\text{O} \rightarrow ^{28}\text{Si} + ^4\text{He}$ , occurs at about  $2 \times 10^9$  K. When the silicon burning begins, the final stage at about  $5 \times 10^9$  K produces a series of reactions starting with the photodisintegration of  $^{28}\text{Si}$ :  $^{28}\text{Si} + \gamma \rightarrow ^{24}\text{Mg} + ^4\text{He}$ . Then, the  $^4\text{He}$  continues to produce heavier nuclei via successive capture reactions. Heavy elements settle into layers.

Elemental oxygen and silicon come into contact for the first time during their burning cycles. At the stage of silicon burning, equilibrium ratios of all nuclear products up to  $^{56}\text{Fe}$  is reached and energy production ceases, an event

called the "iron catastrophe." Beyond that, neutron capture processes will be required to produce elements heavier than iron. The stars of mass greater than  $8 M_{\odot}$  become supernovas. Explosive burning continues, leading to formation of other elements. Table 1 shows a summary of stellar nucleosynthesis for a large star of  $15 M_{\odot}$ .<sup>9</sup>

## Nucleosynthesis and abundance of elements

The earliest history of the universe involved primordial nucleosynthesis of the nuclei of the light elements. After the Big Bang's short inflationary period, there was a hot soup of particles at a temperature of about  $10^{15}$  K. Within a millisecond, the universe cooled to a few trillion degrees ( $10^{12}$  K). The hot

Table 1. Summary of stellar nucleosynthesis and evolutionary time scales for a  $15 M_{\odot}$  star. Adapted from Reference 9. Credit: Longair, Cambridge University Press

Burning stage	Products	Time scale	Temperature ( $10^9$ K)	Density ( $\text{gm cm}^{-3}$ )
Hydrogen	He, N, Na	11 million years	0.035	5.8
Helium	C, O	2 million years	0.18	1390
Carbon	Ne, Na, Mg, Al	2,000 years	0.81	$2.8 \times 10^5$
Neon	O, Mg, Al	0.7 year	1.6	$1.2 \times 10^7$
Oxygen	Si, S, Ar, Ca	2.6 years	1.9	$8.8 \times 10^6$
Silicon	Fe, Ni, Cr, Ti	18 days	3.3	$4.8 \times 10^7$
Iron core collapse	Neutron star	1 second	>7.1	$>7.3 \times 10^9$



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The evolving composition of the universe

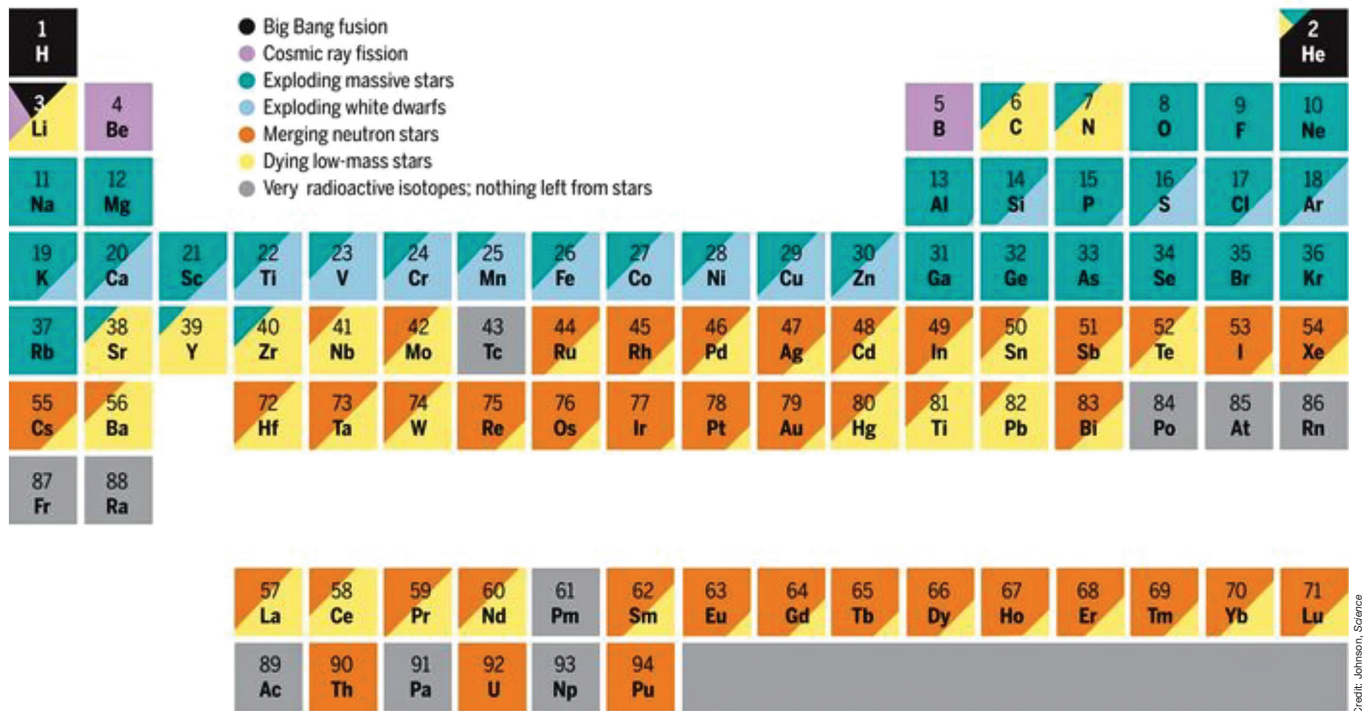


Figure 3. Nucleosynthesis and elements in our solar system. Each element is color-coded by the relative contribution of nucleosynthesis sources, scaled to the time of solar system formation.<sup>10</sup> Reprinted with permission.

plasma was composed of many particles including neutrons, protons, electrons, and photons. As the universe cooled to a billion kelvins ( $10^9$  K), deuterium ( $^2\text{H}$ ) formed followed by  $^4\text{He}$  via fusion. Additional reactions between protons, neutrons,  $^3\text{He}$ , and  $^4\text{He}$  led to production of  $^7\text{Li}$ . On further cooling, the rate of nucleosynthesis slowed down significantly. Within the first three minutes,<sup>7</sup> the primordial process ended with two elements, 75% hydrogen and 25% helium, and the universe was left with trace amounts of  $^2\text{H}$ ,  $^3\text{He}$ ,  $^4\text{He}$ , and  $^7\text{Li}$  for a few hundred million years. All other naturally occurring elements were created through stellar evolution and explosions, i.e., stellar nucleosynthesis.

A recent review paper captures a high-level view of when and how nucleosynthesis produced naturally occurring elements, as shown in Figure 3.<sup>10</sup> Out of all primordial elements, predominantly 75% hydrogen and 25% helium and trace elements, only 2% were consumed since the Big Bang to produce all naturally occurring elements in the periodic table.

Figure 4 shows the abundance of these elements in Earth's crust. Note the number of atoms is normalized to silicon and all rock-forming elements that are abundant in the crust. As the Earth's core is hotter, various elements formed and settled, leaving distinguishable lithophilic (rock forming) elements in the crust and siderophilic (metal-rich) elements in the bulk. Dense elements such as iron and nickel settled down closer to the core. Light materials such as silica partitioned in the crust. This settling had a significant impact on current geographic distribution and availability of these elements.

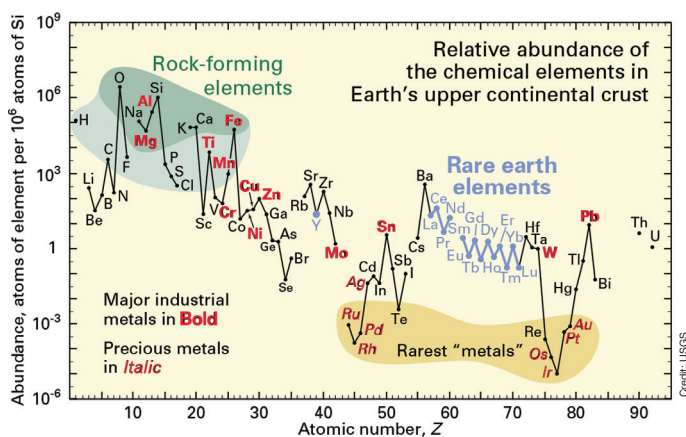
## Presolar materials

Pre-solar system (presolar) grains range in size from nano- to micrometers. They contain many high-temperature minerals and amorphous phases. Some silica and silicate minerals (e.g., olivine, pyroxene) have been identified. These grains formed in many different environments, including explosive deaths of supernovae several billions of years before the solar system formed, thus challenging the current estimate for age of the oldest chondrule glasses at about 4.6 billion years.

Since the discovery of presolar silicate grains in the 2000s, hundreds more have been identified and reported in the literature.<sup>12</sup> Two supernova silica grains in some chondrites reported in 2013 were interpreted to result from condensation of silica dust in supernova ejecta, which cooled rapidly under nonequilibrium conditions.<sup>13</sup> The authors attribute formation of these grains to reactions over time during star formation. These observations are supported by oxygen isotopic measurements, Auger spectroscopy, transmission electron microscopy, and surface characterization using nanoscale secondary ion mass spectrometry (NanoSIMS) data.

Several large presolar silicon carbide grains from a meteorite were reported in 2020.<sup>14</sup> These grains were exposed to cosmic rays several million to a few billion years before the existence of the solar system. The authors hypothesized these grains condensed less than 4.9 billion years ago due to an event of enhanced star formation, which happened about 7 billion years ago, forming many more stars than normal at that time.

In 2021, several presolar silicate and oxide grains in chondrites found in northwest Africa that condensed in different



**Figure 4. Abundance of elements in Earth's crust.<sup>11</sup>**

stellar environments were reported.<sup>15</sup> The relative difference in element distribution from silicates and silica along the fine-grained chondrule rims are due to preferential destruction of silicates due to terrestrial weathering. Isotopic measurements, NanoSIMS, scanning electron microscopy, and mapping of magnesium iron and silicon confirmed these observations. SEM and maps are shown in Figure 5. The dashed turquoise line shown in the figure marks the outer boundary of the rims in the sample. Scale bars shown on the images mark 500  $\mu\text{m}$ .

## Conclusion

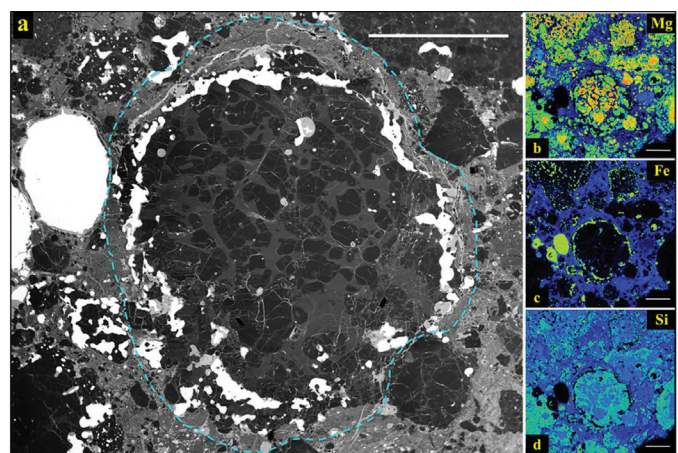
Determining when and where the very first glass was birthed is complex as one needs to connect various nucleosynthesis processes happening in elementary particles, nuclei, stars, and galaxies over billions of years to reach an estimate. Considering that the earliest contact between oxygen and silicon was a few hundred million years to a billion years after the Big Bang and that presolar grains made of amorphous silica, silicates, and other phases condensed out under various stellar formation conditions, the oldest glasses were evidently billions of years older than the start of our solar system. While the universe continues to reveal and surprise, the birth of the first silicate glass was likely at least 7 billion years ago.

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**Figure 5. SEM backscattered image and elemental maps of a chondrule sample.<sup>15</sup> Reprinted with permission.**

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