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Headline Article

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Minerals Track Chemical Reactions in Interstellar Space and in the Protoplanetary Disk

Giant Molecular Cloud W51
Composite: X-ray: NASA/CXC/PSU/ L.Townsley et al.2014; and Infrared: NASA/JPL-Caltech

--- Mineral intergrowths in cosmic dust and primitive meteorites reveal processes that operated in interstellar space and in the protoplanetary disk surrounding the Sun before the planets formed.

Written by G. Jeffrey Taylor
Hawai'i Institute of Geophysics and Planetology

Our Solar System formed when dust and gas collapsed from a huge interstellar molecular cloud. The dust was composed of amorphous (non-crystalline) silicates, carbon, and assorted ices. A significant, but unquantified fraction of the dust was melted, vaporized, and crystallized during formation of our Solar System, but rare grains were preserved in the frigid far reaches of the Solar System and deposited into comets. Hope Ishii (University of Hawaii) and colleagues in Hawaii, Lawrence Berkeley National Laboratory, the University of Washington (Seattle), NASA Ames Research Center, and Washington University in St. Louis studied nanometer-sized dust grains in interplanetary dust particles thought to derive from comets. They found that small grains inside glassy objects called GEMS (Glass Embedded with Metal and Sulfide) are surrounded by organic carbon. The type of bonds between carbon and oxygen and carbon and nitrogen in the organic carbon indicates formation in a cold environment without any significant heating after formation. Ishii and colleagues conclude that the grains formed in interstellar space and survived their incorporation into comets, giving us samples of the materials from which our Solar System (including us) formed.

Moving slightly forward in time, Mutsumi Komatsu (Waseda University, Japan) and colleagues from Waseda, the University of Hawaii, Harvard University, Ibaraki University (Japan), and the National Institute of Polar Research (Japan), studied phases in an amoeboid olivine aggregate (AOA) in an unmetamorphosed carbonaceous chondrite. The AOA they studied has a set of constituents that indicate formation over a wide range of temperature. Oxygen isotopic compositions of minerals in the AOA indicate formation in the same environment as calcium-aluminum-rich inclusions (CAIs), which would have condensed from the protoplanetary disk at about 1800 Kelvin. Surprisingly, the AOA also contains quartz (a mineral form of SiO_2, silica), which would form at 1150 Kelvin. The authors infer the low-temperature silica formed from the same gas as the CAIs, but after rapid cooling and substantial condensation of the refractory minerals. Komatsu and coworkers argue that this sample might explain the presence of silica in distant protostellar disks, as determined by telescopic observations in infrared wavelengths.

References:

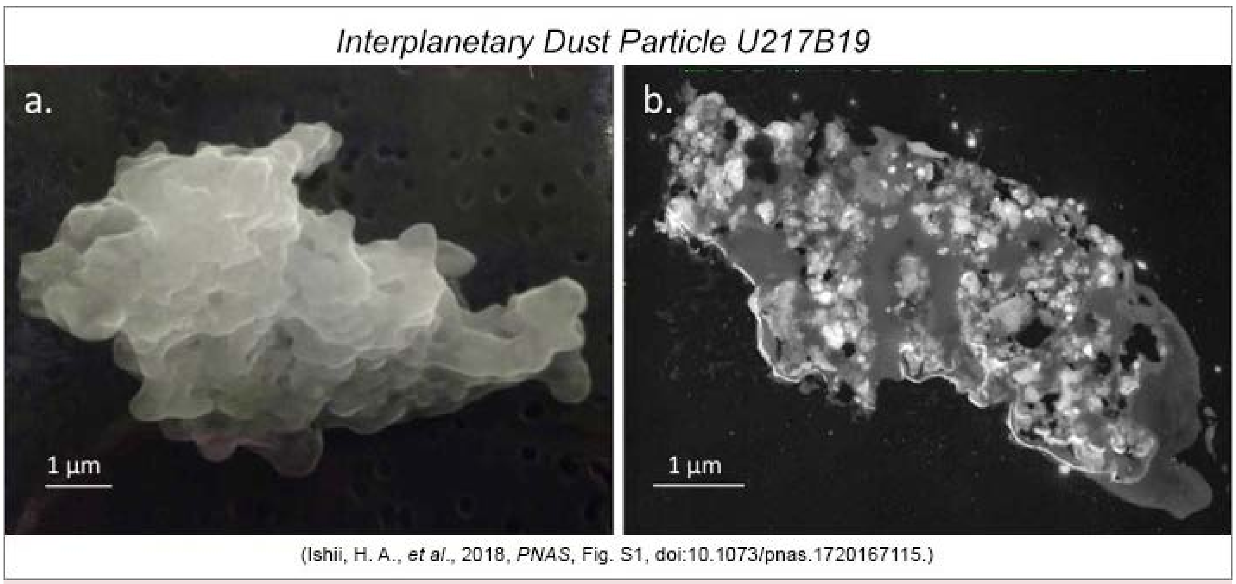
- Ishii, H., Bradley, J. P., Bechtel, H. A., Brownlee, D. E., Bustillo, K. C., Ciston, J., Cuzzi, J. N., Floss, C., and Joswiak, D. J. (2018) Multiple Generations of Grain Aggregation in Different Environments Preceded Solar System Body Formation, *Proceedings of the National Academy of Sciences*, doi: www.pnas.org/cgi/doi/10.1073/pnas.1720167115 [**article**]
- Komatsu, M., Fagan, T. J., Krot, A.N., Nagashima, K., Petaev, M. I., Kimura, M., and Yamaguchi, A. (2018) First Evidence for Silica Condensation Within the Solar Protoplanetary Disk, *Proceedings of the National Academy of Sciences*, doi: www.pnas.org/cgi/doi/10.1073/pnas.1722265115 [**article**]

- **PSRDpresents:** Minerals Track Chemical Reactions in Interstellar Space and in the Protoplanetary Disk --**Short Slide Summary** (with accompanying notes).

Interplanetary Dust Particles and GEMS

Hope Ishii and her colleagues obtained two samples of Interplanetary Dust Particles (**IDPs**) collected by NASA in the upper atmosphere. A highly-successful NASA program collects the particles in the stratosphere using a high-flying ER-2 reconnaissance plane, basically the same as the old U-2 spy plane (but completely different from the rock band U2). During each collecting flight, the plane carries flat plate collectors that are free of contaminants and smeared with silicone oil. The collectors remain flat against a wing until the plane reaches its cruising altitude of about 20 kilometers (about 65,000 feet). Once at cruising altitude, the collectors are deployed and gently-drifting particles hit them, like bugs on a windshield. Most of the particles are extraterrestrial (bits of comets and asteroids), but some are volcanic dust particles, exhaust from solid rocket motors, and other types of earthly aerosols.

The team studied two IDP samples. One, designated U217B19, was an entire IDP that measured a whopping 10 micrometers in its longest dimension. The other was a fragment, designated LT39, of a "giant" cluster particle (U220GCA), measuring a couple of hundred micrometers across. (There is a reason for the D in IDP: everything is tiny.) An overview of U217B19 is shown below.

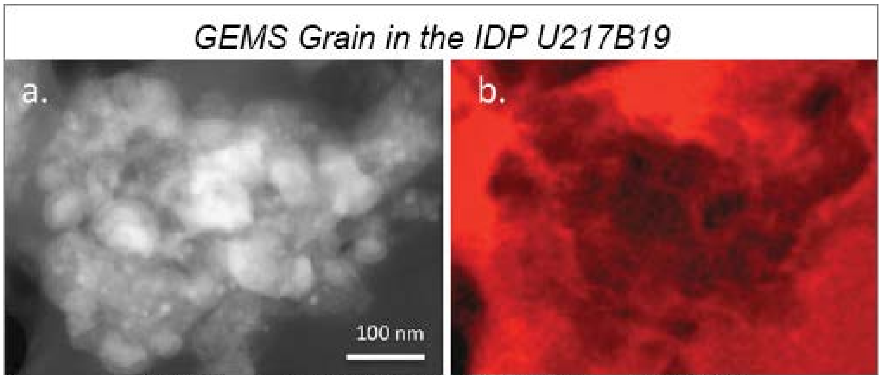


Interplanetary dust particle U217B19, as shown [left] in a secondary electron image and [right] in a transmission electron microscope image of an ultrathin (75 nanometers) section cut through the center of the particle. The bright inclusions are GEMS (glass embedded with metal and sulfides) and the uniform surrounding material is organic carbon.

The investigators focused on GEMS, fascinating objects in IDPs. The term was coined by co-author John Bradley in 1994. Usually less than one micrometer in diameter, GEMS grains are made of nanometer-sized sub-grains of kamacite (FeNi metal) and Fe-Ni sulfide embedded in a Mg-Fe-Al **amorphous** silicate matrix. Like many things in cosmochemistry, investigators have proposed more than one model for how and where GEMS formed. In this case the crux of the debate is whether the grains formed in interstellar space before our Solar System took shape, or whether they formed in the **solar nebula**.

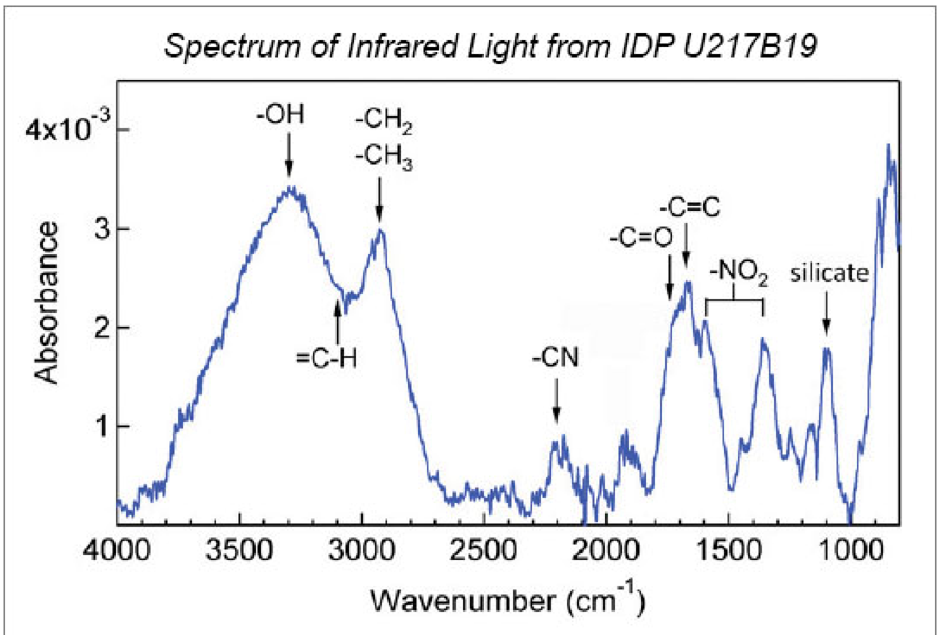
The presolar-origin hypothesis says GEMS grains began as free-floating, crystalline mineral grains that were exposed to **supernova** shock waves and ionizing radiation in the interstellar medium (**ISM**). In this scenario, the grains were chemically and **isotopically** homogenized by prolonged sputtering and redeposition during irradiation processing before being swept into the cloud of dust and gas from which our Solar System formed. The solar nebula-origin hypothesis says GEMS grains are Solar System products that formed as late-stage non-equilibrium condensates. Lindsay Keller and Scott Messenger (NASA Johnson Space Center) have championed this idea, arguing that GEMS grains display enormous chemical variability, which is inconsistent with the idea of chemical homogenization. They say the observed heterogeneities point to non-equilibrium conditions during grain formation and may reflect the changing composition of the gas from which they condensed. While Keller and Messenger agree that a small percentage of GEMS grains could be surviving presolar grains they contend the overwhelming solar isotopic compositions indicate a solar nebula origin. They also suggest GEMS grains have complementary compositions to the crystalline silicate components in IDPs and perhaps they all formed from the same reservoir in the inner Solar System before being transported out to the comet forming region. Ishii and collaborators counter that isotopic homogenization does not require chemical homogenization and that chemical variations may result from alteration, including atmospheric entry heating and terrestrial contamination. Ishii and collaborators also point out that complementarity has not been demonstrated in IDPs and that GEMS compositions are approximately solar when contamination effects of collection are addressed.

Hope Ishii and her collaborators analyzed the two IDPs in depth, using an array of instruments to show that the samples are composed of roughly equal amounts of GEMS and organic carbon. The organic nature of the carbon was shown by infrared spectral analysis and supported by Electron Energy-Loss Spectroscopy (EELS). Infrared spectroscopy revealed the characteristic spectral finger prints of specific carbon-carbon, carbon-oxygen, carbon-hydrogen, and carbon-nitrogen bonding, indicative of organic compound functional groups. Crucially important is the presence of some bonds that are unstable at temperatures above about 450 **Kelvin**. This implies that the temperature was never hot, arguing against an origin in the **protoplanetary disk** around our Sun. The organic carbon likely was deposited on and within GEMS grains as carbon-rich ices in cold interstellar space.



(Ishii, H. A., *et al.*, 2018, *PNAS*, Fig.1, doi:10.1073/pnas.1720167115.)

These electron microscope images show [left] the overall texture of a single GEMS grain in the IDP U217B19, revealing that it contains subgrains. The image on the [right] shows the distribution of carbon. The materials surrounding the GEMS are clearly rich in carbon (which infrared spectroscopy, see below, shows to be organic carbon), and carbon also occurs as rims around the subgrains within the GEMS particle. This relationship suggests that the amorphous silicate grains were coated with organic carbon before being incorporated into the final GEMS object.

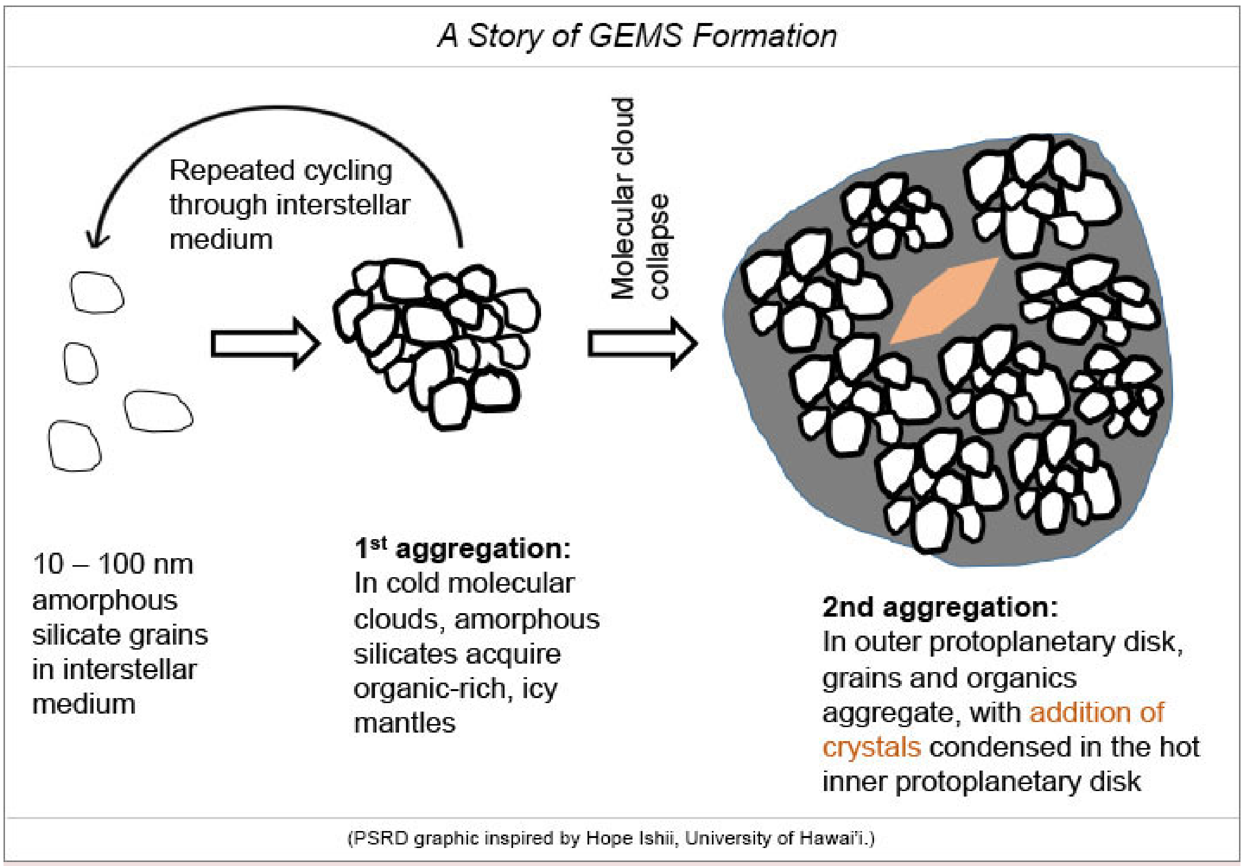


(Ishii, H. A., *et al.*, 2018, *PNAS*, Fig.2, doi:10.1073/pnas.1720167115.)

The spectrum of infrared light emitted from a thin section of IDP U217B19. Wavenumber is the number of waves per centimeter. Radiation was provided by a synchrotron at the Advanced Light Source (Berkeley, California). The data were converted from a bunch of sine waves to a spectrum by using a mathematical technique called Fourier Transform. Specific peaks can be used to identify different types of carbon bonds. The mix of such bonds shown here are definitive evidence of the presence of organic compounds.

Aggregating Grains

Ishii and coauthors propose that the cosmic dust particles they studied formed in two sequential episodes of aggregation, as depicted in the illustration below. The protracted history begins with small (10 – 100nanometers) amorphous silicate grains floating in space within a cold **molecular cloud** (left), long before our Solar System began to form. The silicates were created when exploding stars spewed dust, some crystalline, into interstellar space where they were modified and converted to amorphous materials. The grains become coated by organic compounds and ices, then aggregate together (1st aggregation), making GEMS. Interstellar space is not static, so the aggregates are cycled through the interstellar medium where the gases are ionized and the aggregates affected by shock processing and radiation by cosmic rays, eventually returning to a cold molecular cloud. This process continues until the molecular cloud begins to collapse, initiating formation of our Solar System. As the protosolar disk heated up near the proto-Sun, the GEM aggregates were destroyed. However, in the cold, far reaches of the protosolar disk far from the Sun, the interstellar relics were preserved, allowing grains and organics to aggregate, including additional organic materials. Because of transport from the hot inner Solar System, some high-temperature, crystalline silicates also aggregated into the growing GEMS-containing aggregates.



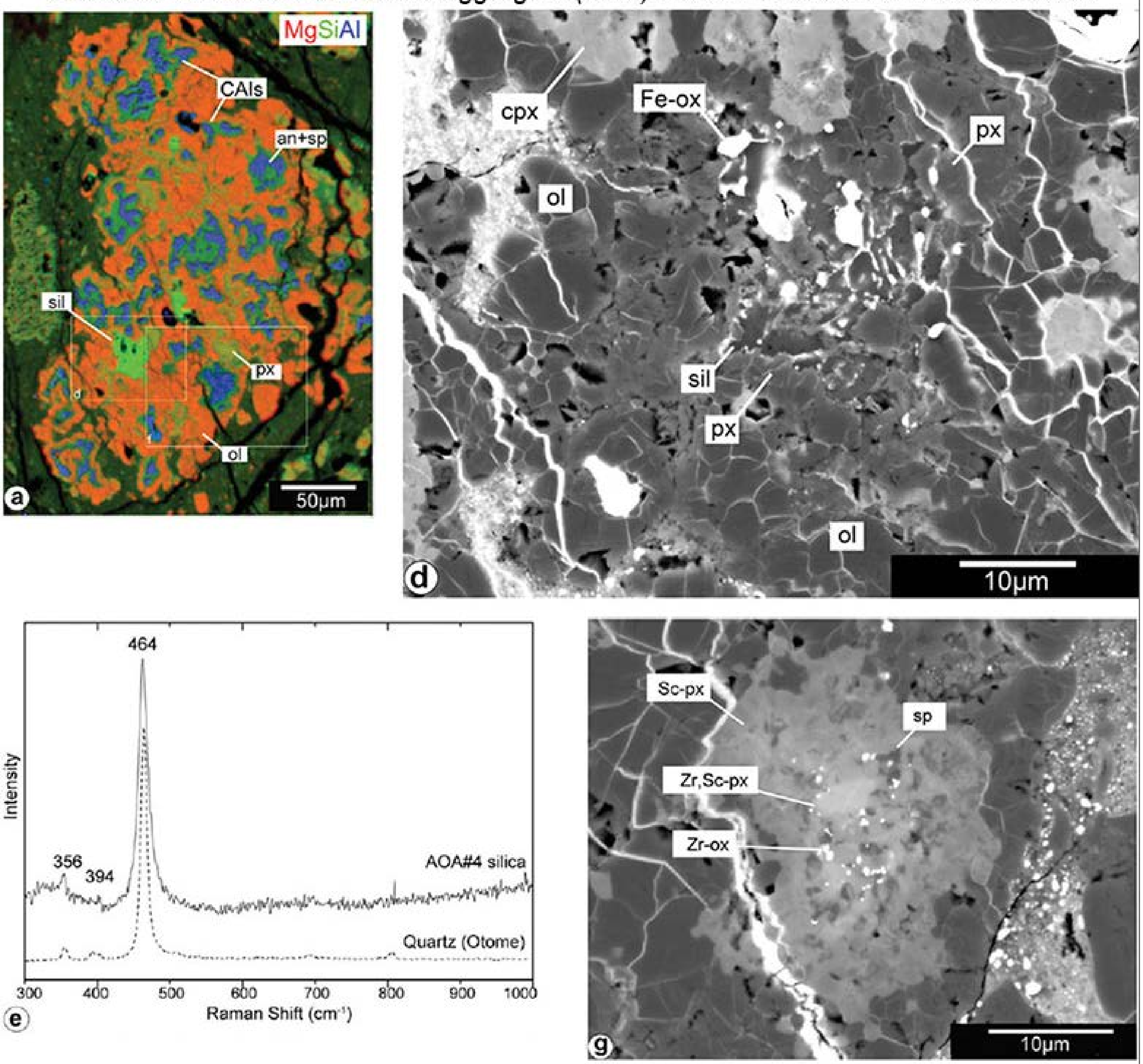
Cartoon depicting formation of GEMS and more complex objects. See text for details.

Fractional Condensation in the Solar Nebula

Mutsumi Komatsu and colleagues used a variety of techniques to study an unusual ameboid olivine aggregate (AOA) in the CR chondrite Yamato 793261. This meteorite has the great virtue of not having been subjected to strong thermal metamorphism, which the authors show through an analysis of organic compounds. Thus, the meteorite's constituents contain a record of their histories before being thrown together by the forces of accretion. Komatsu and coworkers focus on a particularly interesting AOA in the rock, designated number 4 (cosmochemists keep track of samples and subsamples and even sub-subsamples).

As shown by imaging and element maps (see below), AOA 4 in Y-793261 has some interesting ingredients. Olivine, of course, is present, as is magnesium-rich pyroxene. As also expected, calcium-aluminum-rich inclusions (CAIs) are also in the aggregate. A bit surprising is that some of the calcium-aluminum rich fragments are exceptionally rich in refractory elements, which Komatsu and colleagues refer to as ultra-refractory. These contain calcium-rich pyroxene grains that contain exceptional amounts of zirconium (ZrO_2 of 1.6 to 7.0 wt%) and scandium (Sc_2O_3 of 2.7 to 8.2 wt%), plus pure zirconium oxide as separate grains. Zirconium and scandium are far less abundant than calcium, aluminum, and magnesium, but highly refractory, hence the excitement over these high values of zirconium and scandium. Even more surprising is the presence of grains of pure silicon dioxide (SiO_2, often called silica). Using Raman spectrometry, Kamatsu and coworkers show that the silica mineral is quartz, an abundant mineral in most sands on beaches decorating the coastlines of continents.

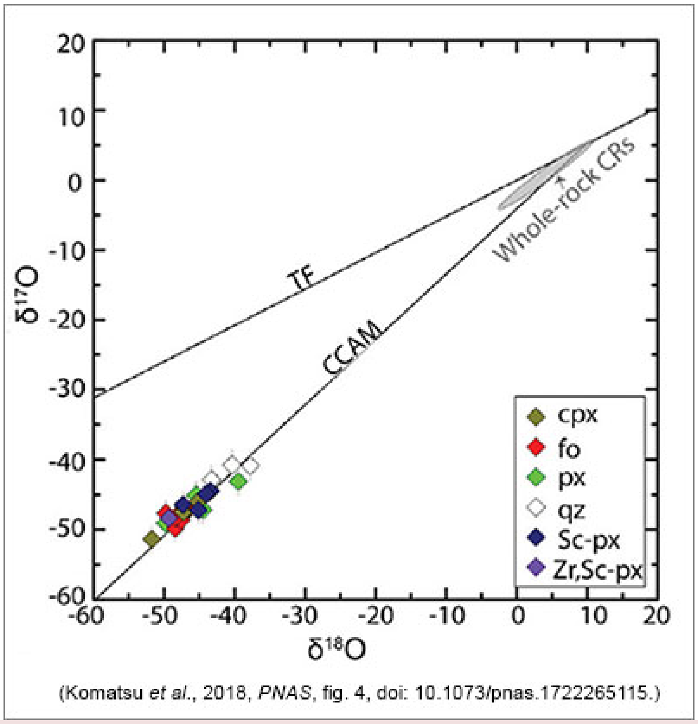
Details of the Amoeboid Olivine Aggregate (AOA) Studied in Meteorite Yamato 793261



(Komatsu *et al.*, 2018, *PNAS*, fig. 2, doi: 10.1073/pnas.1722265115.)

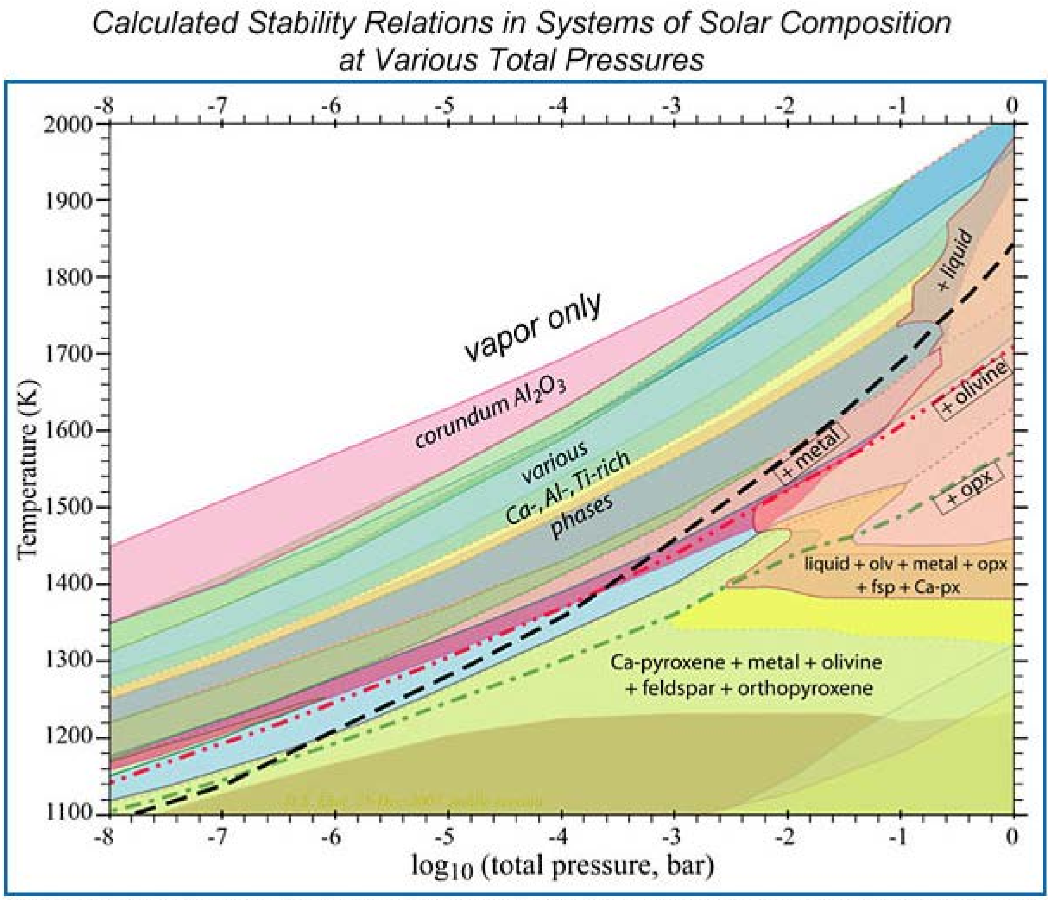
a) Elemental map of AOA 4 in Y-793261. Elements are color coded as shown in the upper right of the image. Basically, there are three major types of material present: major silicates, such as olivine and pyroxene (reddish to orange), CAIs (rich in refractory element aluminum, hence blue in the image), and the green region enriched in silica, including quartz. d) Backscattered electron image of the area containing the silica grains, which tend to be intergrown with pyroxene grains. Also note the white veins cutting across the image. These are weathering veins produced on Earth, but do not interfere with analysis of the other minerals. e) Raman spectra of a terrestrial quartz compared to a silica grain in AOA 4. This is definitive proof that the grain analyzed is quartz, rather than another form of SiO2. g) Close up of an ultra-refractory region in AOA 4. Labels refer to scandium-rich pyroxene (Sc-px), pyroxene rich in both zirconium and scandium (Zr,Sc-px), zirconium oxide (Zr-ox), and the aluminum-rich mineral spinel (sp).

The refractory nature of AOA 4 is firmed up by its oxygen isotopic composition. Measurement by secondary ion mass spectrometry of the oxygen isotopes in all minerals, including quartz, in AOA 4 show that they must have originated in a region relatively rich in oxygen-16, like typical refractory-rich materials in chondrites.



Oxygen isotopic compositions (expressed in delta notation, see "Oxygen Isotope Plot") cluster in the region occupied by CAIs and other refractory materials, near the carbonaceous chondrite anhydrous mineral (CCAM) line. Even non-refractory quartz plots with the other minerals, suggesting a link to the same nebular gas in which the refractory elements condensed.

The presence of quartz is surprising because when a gas of solar composition condenses, the minerals that form first are the ones found in CAIs, followed by olivine and pyroxene, which are both found in chondrules. Quartz or another silica mineral does not form. This is a consequence of our Solar System having a composition with more Mg than Si, hence never having excess Si to form SiO_2. So where did it come from?



Ebel,D.S.(2006) Condensation of Rocky Material in Astrophysical Environments. In *Meteorites and the Early Solar System II* (D. Lauretta *et al.*, eds.) U. Arizona, Tucson. p. 253-277, + 4 plates (after plate 1).

Calculated sequence of minerals that condense as solids from a gas of solar composition at various pressures (the right side of the diagram is for the highest pressure, equal to that at the surface of Earth). Note that corundum (aluminum oxide) and assorted minerals rich in calcium (Ca), aluminum (Al), and titanium (Ti) are the first to form. These make up the main ingredients of the most refractory CAIs. Chondrules form from lower temperature condensates (region labeled Ca-pyroxene + metal + olivine + feldspar + orthopyroxene) or at higher pressure (right side of diagram), which might have been attained in dust-rich regions of the protoplanetary disk (see **PSRD** article Tiny Molten Droplets,Dusty Clouds, and Planet Formation. Believe it or not, this complicated diagram is a simplified version! Click for more information.

Komatsu and team argue that the oxygen isotopic compositions link all the minerals to the same gaseous environment. Condensation calculations like those shown above do not form quartz. There is a work around, though. Komatsu and coworkers did thermal calculations using a program called GRAINS, written by coauthor Michail Petaev. The program allows for non-equilibrium calculations. They also used different amounts of H,sub>2 (and helium), which changes the oxidation conditions. Using a range of pressures and calculating grain growth rates, the team found that silica will condense if H,sub>2 is depleted by a factor of 10 and the cooling rate is around 50 Kelvin/hour (assuming a pressure of 0.0001 atmospheres). Quartz becomes stable below 1169 K. Thus, the AOA and its included CAIs, chondrules, and quartz formed in a gas that was more enriched in dust compared to the average protosolar disk concentration and cooled from about 1800 Kelvin to about 1170 Kelvin at 50 K/hour, implying rapid reprocessing in the protosolar disk from which the planets formed—but *before* the planets formed.

Silica grains have been detected by infrared observations in the dust surrounding some stars (specifically oxygen-rich asymptotic giant branch stars). Komatsu and associates suggest that the silica in these dusty regions may have formed by condensation of silica at the same time as condensation of refractory materials.

Minerals Record Reworking Events Before Planets Formed

These nanometer- to micrometer-scale studies of primitive extraterrestrial materials illustrate the startling amount of information tied up in tiny pieces of rock. Minerals, amorphous materials, and organic compounds and how they are intergrown provide solid evidence for processes that took place in interstellar space and in the early years of our Solar

System. Studies of these products provide a strong link to astronomical observations, allowing us to study nature from nanometers to light years.

Additional Resources

Links open in a new window.

- **PSRDpresents:** Minerals Track Chemical Reactions in Interstellar Space and in the Protoplanetary Disk -- **Short Slide Summary** (with accompanying notes).

- Bradley, J. P. (1994) Chemically Anomalous, Preaccretionally Irradiated Grains in Interplanetary Dust from Comets, *Science,* v. 265, p. 925-929, doi:10.1126/science.265.5174.925 [**NASA ADS entry**].
- Bradley, J. P. (2011) Investigation of Atomic and Electronic Structure of Primitive and Synthesized Amorphous Silicated Using High-Resolution Electron Energy-Loss Spectroscopy (HREELS), *Workshop on Formation of the First Solids in the Solar System*, Nov. 7-9, 2011, Kaua‘i, Hawai‘i [**Abstract**].
- Ishii, H., Bradley, J. P., Bechtel, H. A., Brownlee, D. E., Bustillo, K. C., Ciston, J., Cuzzi, J. N., Floss, C., and Joswiak, D. J. (2018) Multiple Generations of Grain Aggregation in Different Environments Preceded Solar System Body Formation, *Proceedings of the National Academy of Sciences*, doi: www.pnas.org/cgi/doi/10.1073/pnas.1720167115 [**article**]
- Keller, L. P. and Messenger, S. (2011) On the Origins of GEMS Grains, *Geochimica et Cosmochimica Acta,* v. 75, p. 5336-5365, doi:10.1016/j.gca.2011.06.040 [**NASA ADS entry**].
- Komatsu, M., Fagan, T. J., Krot, A.N., Nagashima, K., Petaev, M. I., Kimura, M., and Yamaguchi, A. (2018) First Evidence for Silica Condensation Within the Solar Protoplanetary Disk, *Proceedings of the National Academy of Sciences*, doi: www.pnas.org/cgi/doi/10.1073/pnas.1722265115 [**article**]

- **Presolar Grain Database**, with isotopic data for over 10,000 presolar grains, hosted by Washington University in St. Louis.