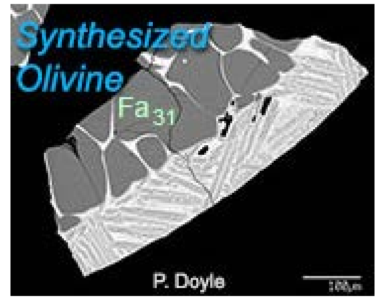
PLANETARY SCIENCE RESEARCH
PSRD Discoveries



Headline Article

June 29, 2015 New Bonus Material Added in December 2015

Chondritic Asteroids–When Did Aqueous Alteration Happen?

--- New dates determined for aqueous alteration on chondritic parent bodies, based on a new mineral standard, have big implications on the timing and location of accretion.

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Using a synthesized fayalite (Fe_2SiO_4) standard for improved ^{53}Mn-^{53}Cr radiometric age dating, Patricia Doyle (previously at the University of Hawai‘i and now at the University of Cape Town, South Africa) and coauthors from Hawai‘i, the National Astronomical Observatory of Japan, University of Chicago, and Lawrence Livermore National Laboratory in California, analyzed aqueously formed fayalite in the ordinary chondrite Elephant Moraine 90161 (L3.05) and in the carbonaceous chondrites Asuka 881317 (CV3) and MacAlpine Hills 88107 (CO3-like) from Antarctica. The data obtained indicate that liquid water existed–and aqueous alteration started–on the chondritic parent bodies about three million years earlier than previously determined. This discovery has implications for understanding when and where the asteroids accreted. The ^{53}Mn-^{53}Cr chronology of chondrite aqueous alteration, combined with thermodynamic calculations and physical modeling, signifies that hydrated asteroids, at least those sampled by meteorites, accreted in the inner Solar System (2–4 AU) near the main asteroid belt 2–4 million years after the beginning of the Solar System, rather than migrating inward after forming in the Solar System's colder, outer regions beyond Jupiter's present orbit (5–15 AU).

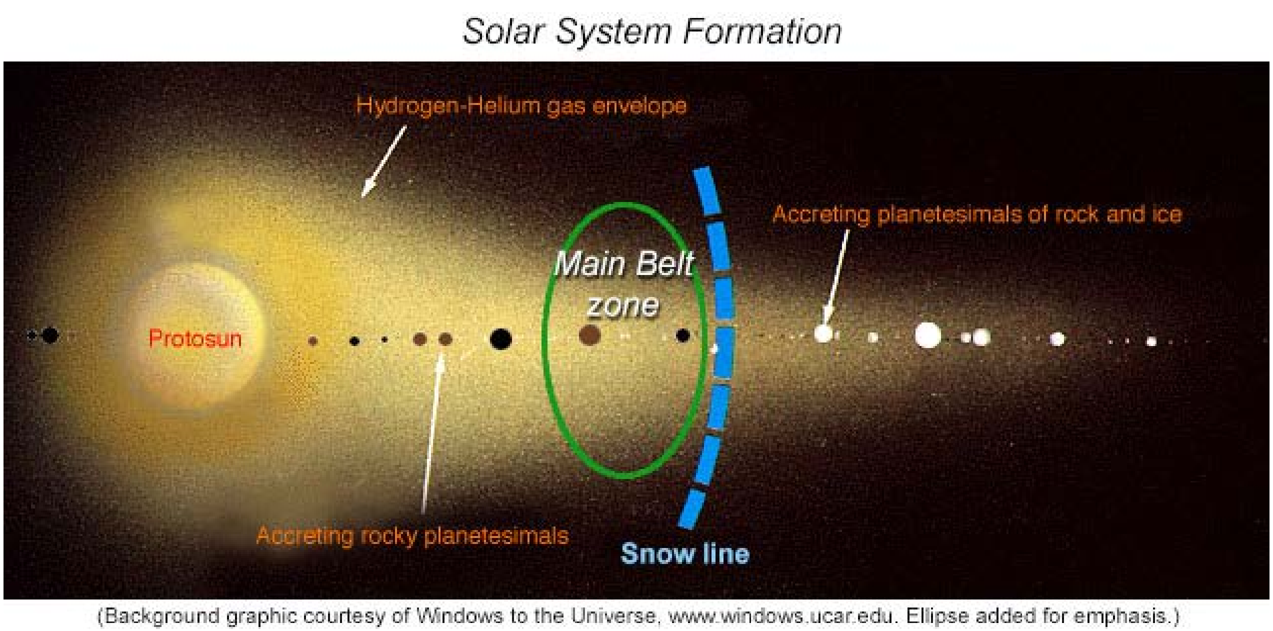
Reference:

- Doyle, P. M., Jogo, K., Nagashima, K., Krot, A. N., Wakita, S., Ciesla, F. J., and Hutcheon, I. D. (2015) Early Aqueous Activity on the Chondrite Parent Asteroids Recorded by Fayalite, *Nature Communications,* v. 6, no. 7444, doi: 10.1038/ncomms8444. [**abstract**]
- **PSRDpresents:** Chondritic Asteroids–When did Aqueous Alteration Happen?--**Short Slide Summary** (with accompanying notes).

Water Alteration in Asteroids: When and Where

Many chondritic meteorites are mixtures of anhydrous minerals formed at high temperature and minerals formed at low temperature by reactions between the anhydrous minerals and water. These damp reactions, collectively called aqueous alteration, produced a diverse set of minerals. These minerals contain important information about the amount of water compared to rock involved in the alteration process (experts call this the water/rock ratio), when the alteration occurred, and where the asteroids were located when they formed.

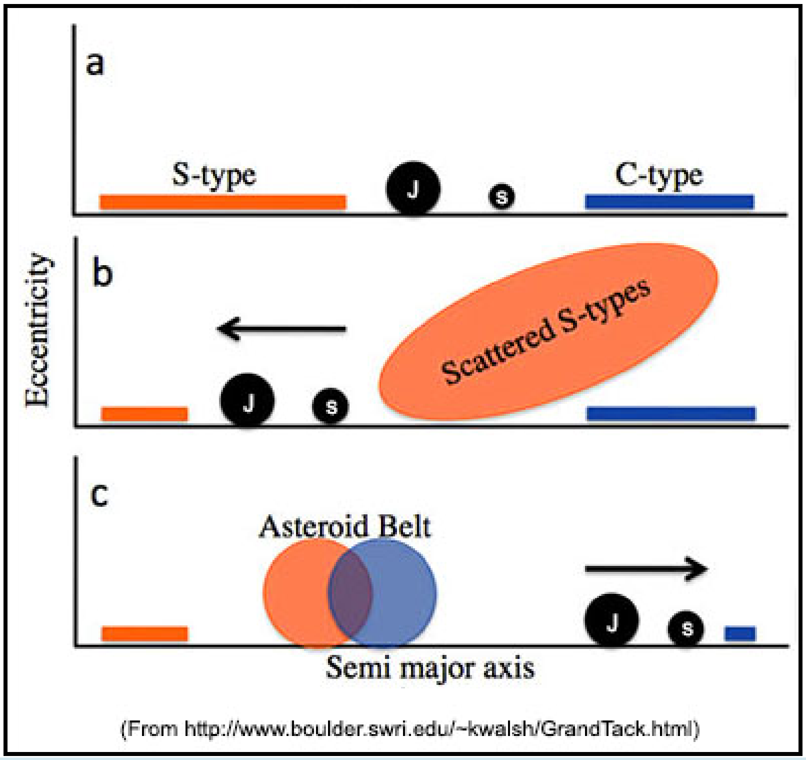
Where were asteroids located when they formed? Isn't the answer obvious: the asteroid belt. Not necessarily. That's where they are now, but a lot might have happened during formation of the Solar System from its initial state as a massive cloud of interstellar dust and gas to its current configuration. As the spinning cloud formed a flattened disk, making the Sun in the center, the temperature was hotter near the proto-Sun and cooler further out, reaching temperatures so frigid that in addition to water ice, ices also formed out of compounds we generally consider gases, such as carbon dioxide and methane. Somewhere between the inner Solar System (where the Earth ended up residing) and the outer Solar System (where the giant planets now reside), there was a "snow line," a region where H_2O vapor skips the liquid phase and condenses directly into solid ice. This ice accreted along with high-temperature minerals (such as olivine and pyroxene) to make asteroids and the planetesimals that accreted to form the inner planets. As asteroids were heated by the decay of short-lived radioactive isotopes such as aluminum-26, the ice melted and began to react with the original minerals, making the mineralogical products of aqueous alteration.



During early Solar System formation, chondritic meteorite parent bodies may have formed in the inner Solar System near the main asteroid belt or they may have formed farther out past the snow line.

The snow line was not a sharp boundary. Properties of the dusty gas cloud varied with time due to changes in the brightness of the Sun, density of dust in the cloud, and other factors. Some models of the proto-solar disk indicate that the snow line was located about 5 astronomical units (**AU**) from the Sun, not far from Jupiter's current orbit. However, asteroids reside between about 2 and 4 AU, so either ice formed in that region or asteroids were delivered to that region from further out. One mechanism for delivering ice-bearing asteroids into the asteroid belt is called the Grand Tack model, an idea developed by Kevin Walsh and colleagues at the Southwest Research Institute, Boulder, Colorado. Based on current models for planetesimal and planet interaction in the early Solar System, the Grand Tack model depicts Jupiter being affected by the presence of millions of planetesimals and slowly moving inwards from 3.5 AU to about 1.5 AU, scattering planetesimals of all sizes inwards and outwards. Eventually the inwards migration stopped, probably due to the growth of Saturn, and Jupiter drifted out to its current location at 5 AU. The Grand Tack model therefore predicts that bodies formed beyond Jupiter, so beyond the snow line, were introduced into the asteroid belt.

A Sketch Describing the Grand Tack Scenario



The basic idea of the Grand Tack is captured by Kevin Walsh in this simple sketch. Eccentricity is a measure of how elliptical an object's orbit is; semi major axis is half the distance of the larger axis of an ellipse. Panel (a) shows the initial state, where Jupiter (black circle labeled J) and a not-complete Saturn (black circle labeled s) lie between an inner, somewhat warm region of the Solar System that gave rise to differentiated asteroids of assorted kinds, designated by S-type, and an outer region of C-type asteroids containing water and minerals formed by aqueous alteration. Panel (b) shows that as Jupiter and proto-Saturn slide in towards the Sun/protosun, S-type asteroids are scattered to the outer Solar System. Panel (c) shows the position of Jupiter and the now larger Saturn after they changed course. The big circles in the center depict the asteroid belt after the process is over, with asteroids from the inner Solar System and wet asteroids from the outer Solar System orbiting mostly in separate regions of the asteroid belt. Courtesy of Kevin Walsh.

How can we distinguish between ice accretion at 2–4 AU or farther out (with subsequent scattering inwards, as described by the Grand Tack model)? To answer this question, our team used isotopic measurements and thermal modeling to determine when aqueous alteration took place in three chondrite groups. We focused on ^{53}Mn-^{53}Cr dating of fayalite (iron-rich **olivine**), which formed by aqueous alteration. But before doing that, we needed to make an appropriate set of standards. All scientific measurements need standards, and sometimes you just have to make your own.

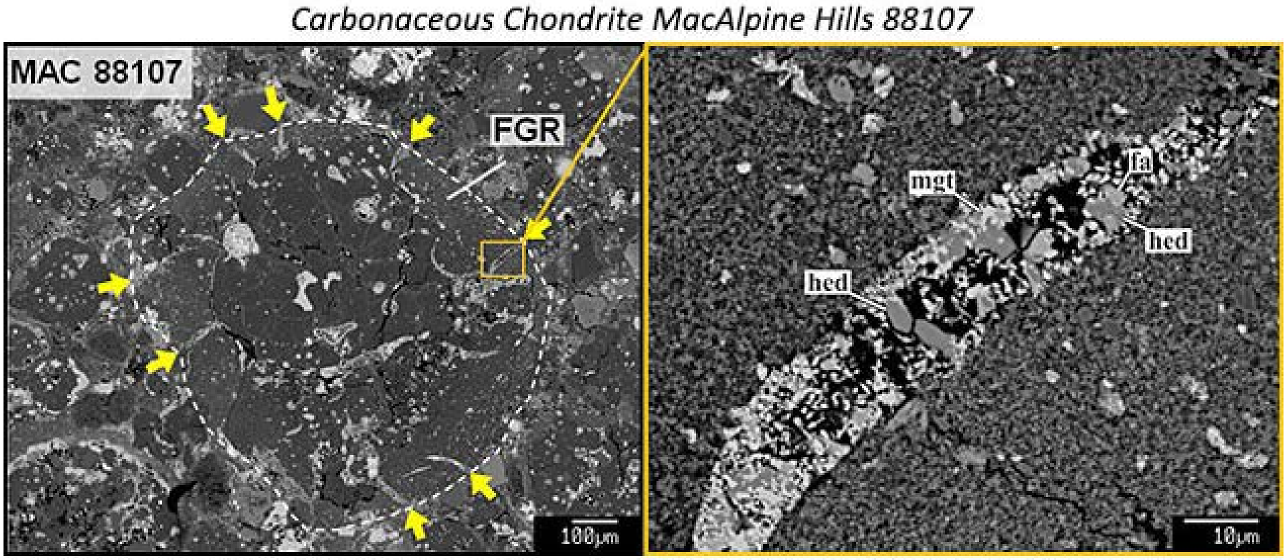
What's So Exciting About Olivine–Particularly Fayalite?

Olivine is a silicate mineral that contains magnesium (Mg) and iron (Fe). Magnesium and iron cations with a 2^+ charge can substitute for one another in the olivine structure, forming what is known as a complete solid solution between the magnesium-rich end-member (forsterite: Mg_2SiO_4) and the iron-rich end-member (fayalite: Fe_2SiO_4). Olivines with <10% atomic Fe/(Fe+Mg), i.e. Mg_2SiO_4 to $Mg_{1.8}Fe_{0.2}SiO_4$ (known in short-hand as having a fayalite (fa) number of $Fa_{<10}$) are a common constituent in mantle rocks. As the mantle comprises ~85% of the Earth, forsteritic olivine is one of the most abundant minerals on Earth!

Iron-rich (ferrous) olivine ($Fa_{>50}$) may be found on Earth in igneous rocks that are Fe,Mg-rich and silicon (Si)-poor (ultramafic) or, less commonly, associated with the mineral amphibole in more Si-rich (acidic) or alkaline igneous rocks. Moreover, in meteorites that have not melted, known as undifferentiated chondrites, nearly pure fayalite ($Fa_{>90}$) has occasionally been reported.

Meteorites are grouped according to texture and their major, trace, and isotopic compositions. Some show evidence for being heavily altered in the presence of water, whereas others have been heated up to the point where minerals start recrystallizing. Meteorites from parent bodies that have undergone very little aqueous alteration and/or heating are considered pristine and are classified as type 3. Fayalite is found within type 3 chondritic meteorites (both ordinary and carbonaceous) from the low-iron (L) and low-iron, low-metal (LL) ordinary chondrites to Vigarano-like (CV) and Ornans-like (CO) carbonaceous chondrites.

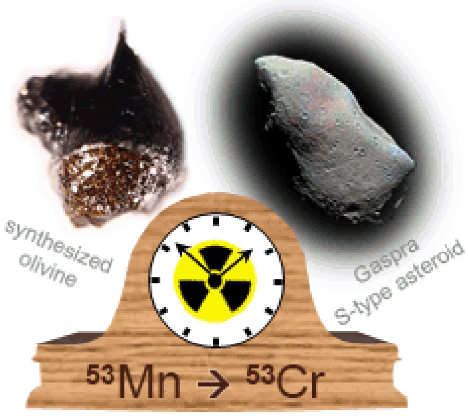
An increasing body of evidence shows that meteoritic fayalite formed in situ on the ordinary, CV, and CO chondrite parent bodies. For example, the textural relationships and composition of minerals such as fayalite, the Fe^{2+},Fe^{3+}-bearing oxide magnetite and the Fe,Ca pyroxene hedenbergite indicate that these minerals are secondary, having formed on the parent body (see images below). Furthermore, thermodynamic analysis by the groups of Alexander (Sasha) Krot (University of Hawai‘i) and Mikhail Zolotov (Arizona State University) show that nearly pure fayalite ($Fa_{>90}$) is stable at temperatures of ~100–200 ^{o}C and water/rock mass ratios of ~0.1–0.2, which is low when compared to the average Solar System water/rock mass ratio of ~1.2. The low temperatures are also consistent with fayalite formation within a parent body, rather than by high-temperature nebular processes; and these conditions are therefore inferred to be present on chondritic parent bodies when fayalite formed. As such, the formation age of fayalite constrains when there was liquid water on the parent bodies and, through computer modeling, enables us to infer when and where the meteorite parent bodies accreted.



(Patricia M. Doyle, University of Hawai'i.)

Backscatter electron images of meteorite MacAlpine Hills 88107 showing the secondary minerals fayalite (fa) Fe_2SiO_4; hedenbergite (hed) $CaFeSi_2O_6$; magnetite (mgt) $FeFe_2O_4$ in veins (see arrows) that crosscut the fine-grained rim (FGR) of a chondrule (outlined by dashed line). The boxed area in the left image is enlarged in the right image.

Standards, Standards Everywhere, But Not One Suitable for Measurement–Until We Made It



Most scientific studies aim to quantify the physical aspects of a material or a process, and standards are crucial for such measurements. We can have confidence that a meter-long ruler in Europe is the same as that in Africa and America because the length of each can be checked against the standard International Prototype Meter, which is safely held in France by the *Bureau International des Poids et Mesures* (the International Bureau of Weights and Measures).

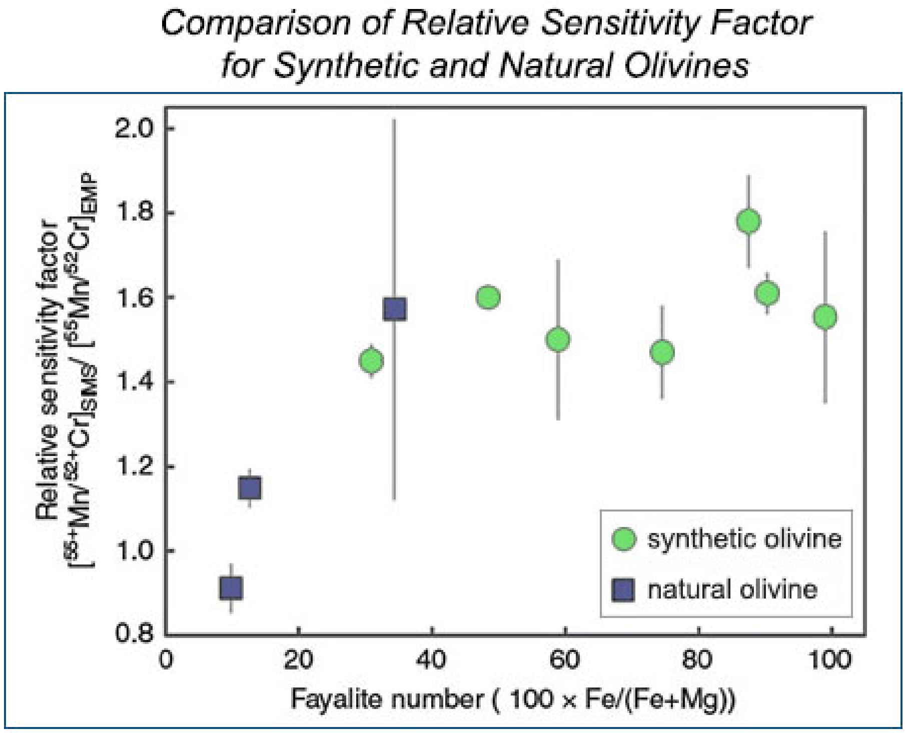
The same principle holds true for time calibrations and determining ages using short-lived **radionuclides** such as manganese-53 (^{53}Mn), which decays to chromium-53 (^{53}Cr) with a **half-life** ($t_{1/2}$) of ~3.7 million years (Myrs). Relative ages determined using the ^{53}Mn-^{53}Cr **isotope** system are useful for constraining planet forming processes within the first ~20 million years of the Solar System.

Previous work by a team based at the University of Tokyo, Japan, led by Naoji Sugiura and Wataru Fujiya, shows that standards need to have the same composition as the unknown for measurement of ^{53}Mn-^{53}Cr isotopes using secondary ion mass spectrometry (**SIMS**). Their team made synthetic calcite ($CaCO_3$) in order to date carbonates (calcite and dolomite; $CaMg(CO_3)_2$) that formed in the presence of water on an asteroid, rather than use the magnesium-rich olivine forsterite ($Fe_{0.2}Mg_{1.8}SiO_4$; Fa_{10}). The ages they calculated were younger than previously reported, but still not equal to the young ^{53}Mn-^{53}Cr ages reported for fayalite, which also formed in the presence of water in a chondrite parent body.

Our Hawai‘i-based group measured Mn-Cr isotopes in fayalite from meteorites in order to determine when liquid water was present on the meteorite parent bodies. Previous studies had used forsterite as a standard because natural, chromium-bearing fayalite is rare. To have a standard of the same composition as the meteoritic fayalite, our team made a synthetic analogue in a controlled laboratory setting. The details of how we made the synthetic standard are covered in the **Bonus Material: Making Synthetic Standards**.

We collected and measured Mn-Cr isotopes in fayalite from our samples of the meteorites Elephant Moraine 90161 [**Data Link** from the Meteoritical Bulletin], Asuka 881317 [**Data Link**], and MacAlpine Hills 88107 [**Data Link**] using SIMS. The values needed to be converted into meaningful concentrations. This is where standards play a crucial role. Firstly, instrumental bias corrections are made using standards measured with the same instrumental setup as the unknown, to guard against artefacts caused by the instrument and/or technique (for example, mass-dependent fractionation during the measurement). Secondly, the values obtained by the measurement (for example, the $^{55}Mn^{+}/^{52}Cr^{+}$ isotope ratio) can be converted into a ratio or concentration by using a true $^{55}Mn/^{52}Cr$ ratio that is measured using an independent technique. This calculation is particularly important for isotope ratios of different elements as the ionization efficiency of $^{55}Mn^{+}$ may differ significantly from $^{52}Cr^{+}$. This appears to be the case for minerals with different compositions.

$^{55}Mn/^{52}Cr$ ratios are crucial for determining an initial $^{53}Mn/^{55}Mn$ ratio and ^{53}Mn-^{53}Cr ages for meteoritic fayalite. The measured $^{55}Mn^{+}/^{52}Cr^{+}$ ratios are corrected using a relative sensitivity factor (RSF), which is a ratio of the measured/true $^{55}Mn/^{52}Cr$ ratios from a standard. To check if the relative sensitivity factor is dependent on olivine composition, Mn-Cr isotopes were collected from a suite of natural and synthetic olivines ranging from forsterite (Fa_{10}) to fayalite (Fa_{99}). The relative sensitivity factor, plotted as a function of fayalite number (see the plot below), shows that the iron content in olivine changes the relative sensitivities of the ^{55}Mn and ^{52}Cr ions, and consequently the relative sensitivity factor. This turned out to be a big correction as the difference of RSFs between Fa_{10} and Fa_{99} is as large as ~60%.



(Based on Doyle *et al.*, 2015, *Nature Communications*, v. 6:7444, doi:10.1038/ncomms8444.)

The relative sensitivity factor depends on olivine composition. When $Fa_{>30}$ the relative sensitivity factor is nearly constant at ~1.6.

Determining New Ages

We measured Mn and Cr isotopes in chondrites collected in Antarctica: Elephant Moraine 90161 (type L3.05), Asuka 881317 (type CV3), and MacAlpine Hills 88107 (type CO3-like). Short-lived radionuclides, such as ^{53}Mn, decay at such a rapid rate that the parent nuclide is no longer detectable. However, an age can be calculated relative to another sample for which an initial (^{53}Mn/^{55}Mn) ratio has been defined because the half-life is known. If the second sample has been accurately dated using a long-lived radionuclide system (for example U-corrected Pb-Pb dating), then it acts as an age-anchor that can be used to obtain an absolute age for the first object.

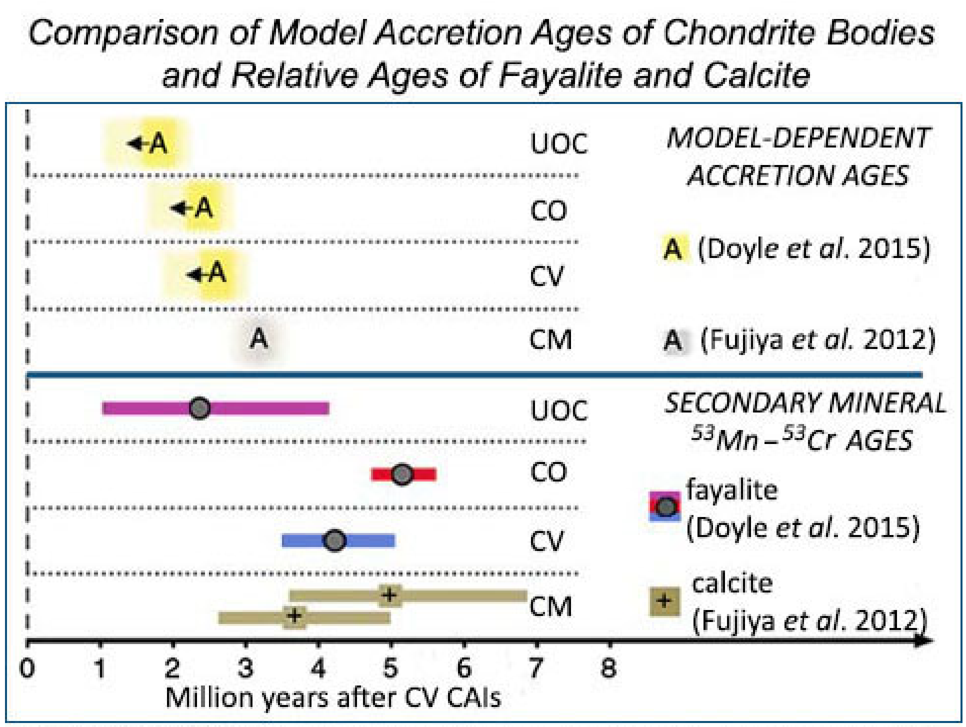
Calcium-aluminium-rich inclusions (**CAIs**) are dated to be the oldest Solar System materials, so many ages are quoted with reference to CAIs from the CV carbonaceous chondrites. Unfortunately, the initial ^{53}Mn/^{55}Mn ratio in CV CAIs has not been determined due to a lack of primary CAI minerals that have high Mn/Cr ratios. Instead, the ages can be calculated relative to basaltic meteorites (**angrites**) which have both accurate initial (^{53}Mn/^{55}Mn) ratios and U-corrected Pb-Pb ages. Our Hawai'i group chose the angrite D'Orbigny [**Data Link** from the Meteoritical Bulletin] as the age-anchor, as D'Orbigny formed ~4 Myr after CV CAIs, and would therefore have ^{53}Mn present in concentrations that can be precisely measured. In addition, its fine-grained texture means the rock cooled quickly, so most of the mineral-clocks would have been set at the same time–crucial for a good time-anchor.

When and Where the Parent Bodies of Fayalite-Bearing Meteorites Accreted

The model ages of fayalite in the CO carbonaceous chondrites measured using a matrix-matched synthetic fayalite standard (Fa_{99}) are listed below. The ages are approximately 3 million years older than that determined on the previously used San Carlos olivine standard (Fa_{10}). Our model ages are in agreement with the age of secondary calcite that formed in the presence of water in CM (Mighei-like) carbonaceous chondrites (see graph below).

Meteorite and corresponding fayalite formation age in millions of years after 4567.3 ± 0.16 Ma (also see graph below)	
Elephant Moraine 90161 (UOC)	$2.4^{+1.8}_{-1.3}$
MacAlpine Hills 88107 (CO)	$5.1^{+0.5}_{-0.4}$
Asuka 881317 (CV)	$4.2^{+0.8}_{-0.7}$

As thermodynamic modeling indicates that minerals such as fayalite and calcite formed in the presence of water, the ^{53}Mn-^{53}Cr ages of fayalite and calcite indicate that liquid water was present in asteroids early in the Solar System's history—millions of years earlier than previously reported. Alteration in the presence of water appears to be spatially restricted, so water ices were probably incorporated, along with high-temperature phases, into the accreting parent bodies. As the short-lived radionuclide ^{26}Al ($t_{1/2}$ ~0.7 Myr) was still extant, heating by radioactive decay of ^{26}Al is a very plausible mechanism for melting in situ water ice.



(Based on Doyle *et al.*, 2015, *Nature Communications*, v. 6:7444, doi:10.1038/ncomms8444.)

Chronology of secondary fayalite and calcite in carbonaceous chondrites and the model-dependent accretion ages of their parent bodies. Time zero on this plot is 4567.3±0.16 Ma, the age of the Solar System based on the U-corrected Pb-Pb absolute age of CV CAIs.

The age of fayalite formation, together with parameters such as the peak metamorphic temperature recorded by the meteorites, can be used to infer when and where the parent bodies of fayalite-bearing meteorites accreted. Using detailed thermal modeling, Shigeru Wakita (National Astronomical Observatory of Japan) determined that the parent bodies of the ordinary, CO and CV chondrites accreted 1.8–2.5 Myr after the start of the Solar System. At that time, the snowline is thought to be positioned at 2–3 **AU**. This led us to suggest that the parent bodies of the ordinary, CV, and CO chondrites accreted close to the current position of the main asteroid belt (located between 2 and 4 AU from the Sun), rather than being injected from beyond Jupiter (>5 AU). Indeed, the water-rock mass ratios (~0.1–0.2) in which fayalite is thermodynamically stable, and which are inferred to be representative of the fayalite forming region in the ordinary, CO, and CV parent bodies, are much lower than that expected for bodies which formed well beyond the snowline, based on the average Solar System water/rock mass ratio of ~1.2. The results indicate that the fascinating Grand Tack idea isn't required for the chondrites we studied. The time and location of parent body accretion, combined with the age and composition of secondary fayalite, also have big implications for the source of Earth's water, but that is a story for another day in our ongoing quest to understand our Solar System origins.

Additional Resources

Links open in a new window.

- **PSRDpresents:** Chondritic Asteroids–When did Aqueous Alteration Happen?--**Short Slide Summary** (with accompanying notes).
- Doyle, P. M., Jogo, K., Nagashima, K., Krot, A. N., Wakita, S., Ciesla, F. J., and Hutcheon, I. D. (2015) Early Aqueous Activity on the Chondrite Parent Asteroids Recorded by Fayalite, *Nature Communications,* v. 6, no. 7444, doi: 10.1038/ncomms8444. [**abstract**]
- Doyle P. M., Jogo, K., Nagashima, K., Huss, G. R., and Krot, A. N. (2016) Mn-Cr Relative Sensitivity Factor in Ferromagnesian Olivines Defined for SIMS Measurements with a Cameca ims-1280 Ion Microprobe: Implications for Dating Secondary Fayalite, *Geochimica et Cosmochimica Acta,* v. 174, p. 102-121, doi: 10.1016/j.gca.2015.10.010. [**abstract**]
  See Bonus Material: Making Synthetic Standards, based on this publication.
- Doyle, P. M., Nagashima, K., Jogo, K., and Krot, A. N. (2013) Relative Sensitivity Factor Defined for ^{53}Mn-^{53}Cr Chronometry of Secondary Fayalite, *44th Lunar and Planetary Science Conference,*, abstract #1792. [**abstract**]
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- Walsh, K. J., Morbidelli, A., Raymond, S. N., O'Brien, D. P., and Mandell, A. M. (2011) A Low Mass for Mars from Jupiter's Early Gas-driven Migration, *Nature,* v. 475, p. 206-209, doi:10.1038/nature10201. [**abstract**]
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