NON-STOICHIOMETRIC AL-RICH SPINEL IN AN ULTRA-REFRACTORY INCLUSION FROM CO CHONDRITE. H. Yurimoto1 A.E. Rubin2, S. Itoh1 and J.T. Wasson1, 1 Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan, yuri@geoititech.ac.jp, 2 Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA.

Introduction: Refractory inclusions or Ca-Al-rich inclusions (CAIs) consisting of refractory minerals are found in chondritic meteorites and are widely believed to be the first solid objects formed in the solar nebula [1]. The most significant distinguishing characteristics of refractory inclusions are their 16O-rich isotopic signatures [2] and their isotopic record of short-lived nuclides such as 26Al having half-lives <10 Ma [3]. Here we describe a unique refractory inclusion having non-stoichiometric Al-rich spinel in the exceptionally pristine CO3.0 chondrite Yamato 81020. There is a tradition to name unique refractory inclusions. This refractory inclusion has an ovoid-shaped core and is, in our opinion, a gem; we therefore gave it the Japanese name Tama, a word which includes both of these meanings. The inclusion is similar to compound chondrules in that it experienced two melting events.

Petrography: The 200x180 µm Tama inclusion is located in section 56-4 of the Yamato 81020 CO3.0 chondrite; it has core-mantle structure and minimal porosity (Fig. 1). The ovoid core (170x80 µm) is composed of hibonite (~50 vol%), spinel (~42 vol%), melilite (~6 vol%), an alumina-rich phase (~2 vol%), and perovskite (~1 vol%). The hibonite has a composition Ca(Al,Mg)12-xTixO19; 0<x<1, 0.94<Al/(Al+Mg)<0.99. The intergrown spinel crystals are highly non-stoichiometric, as shown in the following formula: MgO·(1+δ)Al2O3, 0.4<δ<6.3. Such a large Al-excess in spinel solid solution has not previously been reported in refractory inclusions, but it is known from laboratory experiments. The high-Al2O3 spinel solid solution coexists with an unidentified alumina-rich phase that can be written: Al2O3·xMgO, 0.06<x<0.11.

According to a recent phase diagram of the MgO-Al2O3 system [4], the alumina-rich phase is a mixture of corundum and spinel. However, because conclusive experimental data are lacking in this temperature region, the alternative possibility is that the alumina-rich phase is δ-Al2O3 [5] or metastable γ-Al2O3 [4]. Only a few other inclusions having high Al2O3 contents have such high formation temperatures [1]. Melilite with an almost pure gehlenite composition (Åk1-2) occupies the interstitial space between hibonite and spinel; such pure gehlenite is very rare. These minerals enclose small perovskite crystals up to 4 µm across.

The mantle of Tama is mainly composed of clear melilitic crystals (Fig. 1). The largest grain is 60X100 µm and may be a fragment. The mantle melilite contains some perovskite crystals although the abundance is smaller than in the core. A thin layer of melilite at the outer edge of the mantle and at the core-mantle boundary have been partly converted to submicron alteration products, probably composed of nepheline and FeO-rich pyroxenes.

The mantle melilite is zoned from Åk2 to 25. Condensation from a gas could not have produced this zoning with the more refractory geihlenitic melilite confined mainly to the exterior. The zoning seems more likely to reflect the growth of the melilite crystals from a liquid.

Bulk and core composition was calculated from the modes and the mean composition of the minerals. In a liquid having the bulk composition of the combined core and mantle, grossite (CaAl12O19) would be the first liquidus mineral; hibonite and the alumina-rich phase are not liquidus phases in a liquid having this bulk composition. In contrast, crystallization from a liquid having the core composition starts with spinel, then switches to coprecipitation of spinel and hibonite. According to the phase diagram of the Al2O3-MgO system [6], the crystallization temperature of the first spinel is about 2100 K; thus Tama experienced temperatures at least this high.

Isotopic properties: O isotopic compositions of Tama scatter along the carbonaceous chondrite anhydrous minerals (CCAM) line.

The O isotopic compositions of core hibonite and spinel are homogeneous, enriched in 16O (Δδ17O=26‰). In contrast, the O-isotopic compositions of melilite are distributed over the range from 16O-rich (Δδ17O=26‰) to 16O-poor (Δδ17O=4‰). The 16O-rich end member of melilite seems to be slightly less negative than the values of hibonite and spinel. Melilite having a 16O-poor composition exists only in the mantle region. The degree of 16O-enrichment of core melilite seems to be highest in the center and become smaller towards the core-mantle boundary.

Variations of O isotopic composition of mantle melilite do not correlate with the position in Tama such as distance from the outer rim, from the core-mantle boundary, or from hibonite or spinel, but Δδ17O correlates with the Åk content of the melilite below Åk = 5 mol%: at high Åk (>6 mol%) there is no resolvable change in the Δδ17O values, which scatter around a mean value of ≈7‰.
To shed light on the time interval between the core and the mantle crystallization, Mg isotope ratios of melilite, hibonite and Al-rich spinel were determined. The points fall near a single isochron. The initial ($^{26}$Al/$^{27}$Al) and initial ($^{26}$Mg) are $4.8 \pm 1.0 \times 10^{-5}$ and $1.4 \pm 1.7 \times 10^{-5}$, respectively. The initial ratio is consistent with the initial ratio commonly observed in refractory inclusions of $4.6 \pm 0.4 \times 10^{-5}$.

These results imply that mantle crystallization occurred no more than 0.2 million years after core crystallization. If the O isotopic composition of the core and mantle were in equilibrium with the surrounding gas, the O isotopic composition of this gas drifted from $^{16}$O-rich to $^{16}$O-poor within 0.2 million years. Where this inclusion formed, the O-isotopic environment had changed dramatically within this short time span.

Formation scenario of Tama: The consistency among interpretations based on composition, petrography, the phase diagram and isotopic micro-distribution supports the conclusion that the first material in Tama was a liquid having the core composition and that the mantle formed later. A conceivable scenario of the formation is as follows: (1) The core was crystallized from a liquid droplet at temperatures $>2100$K. After the crystallization of the core, it became embedded in materials which were then melted. A small amount of the core might also have melted eutectically during this event. (3) Mantle melilite crystallized from this liquid and penetrated voids in the core.

As discussed above, the formation of the ultrarefractory core seems best understood in terms of the evaporation of a refractory liquid followed by rapid crystallization. Its O-isotopic composition and the initial $^{26}$Al/$^{27}$Al ratio are about the same as those of other refractory inclusions; thus, it probably formed in the same environment (i.e., at about the same time and place). The chief challenges are to explain the large difference in O-isotopic composition between the core and the bulk of the mantle, and also to explain the gradient in O-isotopic composition and in Åk content of the melilite mantle.

We considered two main models; both start with the core having already formed and both require that the O-isotopic environment had changed dramatically within this short time span. O-isotopic and Mg-isotopic evidence in Tama indicates that refractory inclusions were generated by multiple heating events within a span of 0.2 million years.