DISCOVERY OF RUBINITE, Ca$_3$Ti$^{3+}_2$Si$_3$O$_{12}$, A NEW GARNET MINERAL IN REFRACTORY INCLUSIONS FROM CARBONACEOUS CHONDRITES.

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Introduction: During a nanomineralogy investigation of carbonaceous chondrites, a new Ti$^{3+}$-dominant garnet, named “rubinite,” Ca$_3$Ti$^{3+}_2$Si$_3$O$_{12}$ with the $Ia\bar{3}d$ garnet structure, was identified in five Ca-Al-rich inclusions (CAIs) from the CV3 chondrites Vigaranò, Allende, and Efremovka. Field-emission scanning electron microscope, electron back-scatter diffraction, electron microprobe and ion microprobe techniques were used to characterize the chemistry, oxygen-isotope compositions, and structure of rubinite and associated phases. Synthetic Ca$_3$Ti$^{3+}_2$Si$_3$O$_{12}$ garnet was reported by [1]. Here, we describe the first natural occurrences of rubinite as a refractory mineral in primitive meteorites. The mineral has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2016-110) [2]. The name honors Alan E. Rubin, a cosmochemist at University of California, Los Angeles (UCLA), USA, for his many contributions to cosmochemistry and meteorite research.

Occurrence, Chemistry, Oxygen Isotopes, and Crystallography: Rubinite appears as irregular to subhedral crystals, ~0.5–1 μm in Vigaranò, 1–8 μm in Allende, and 1–20 μm in Efremovka. In Vigaranò, it occurs in the central portion of an ultra-refractory fragment with Zr-panguite, spinel and davisite-diopside, all enclosed within an amoeboid olivine aggregate. In the Allende compound fluffy type A (FTA) CAI AE01-01, it occurs with primary gehlenitic melilité, perovskite, spinel, hibonite, corundum, davisite, grossmanite, diopside, and eringaité, plus secondary anorthite, grossular, and Na-melilité. Rubinite occurs within gehlenitic melilité with perovskite, spinel, and grossmanite in three Compact Type A (CTA) CAIs from Efremovka: E101, E105, and 40E-I (in a compound CAI [3]). It occurs in spinel-poor regions in all four of the Efremovka and Allende CAIs but is in contact with spinel in the Vigaranò inclusion.

In the Efremovka CTAs, spinel is $^{16}$O-rich ($\Delta^{17}$O ~ 24‰); rubinite and perovskite show limited ranges of $\Delta^{17}$O (from ~24 to ~16‰; most analyses range from ~24 to ~20‰); melilité and grossmanite are the most $^{18}$O-depleted minerals ($\Delta^{17}$O range from ~10 to ~4‰ and from ~8 to ~5‰, respectively). In the Allende FTA AE01-01, spinel is $^{16}$O-rich ($\Delta^{17}$O ~ 24‰); rubinite and perovskite show large ranges of $\Delta^{17}$O (from ~21 to ~6‰ and from ~14 to ~2‰, respectively); melilité has yet to be measured.

The mean chemical composition of type rubinite in Allende is (wt%) CaO 32.68, Ti$_2$O$_3$ 14.79, TiO$_2$ 13.06, SiO$_2$ 28.37 Al$_2$O$_3$ 3.82, Sc$_2$O$_3$ 1.80, Na$_2$O 1.01, ZrO$_2$, 0.80, MgO 0.79, V$_2$O$_3$ 0.61, FeO 0.53 Y$_2$O$_3$ 0.07, Cr$_2$O$_3$ 0.05, total 98.38, giving rise to an empirical formula of (Ca$_{2.97}$Na$_{0.06}$)(Ti$_{3.04}$Ti$^{3+}_{0.59}$Sc$_{0.13}$Mg$_{0.10}$V$_{0.04}$Fe$_{0.04}$Zr$_{0.03}$)(Si$_{2.36}$Al$_{0.48}$Ti$^{4+}_{0.16}$)O$_{12}$, where Ti$^{3+}$ and Ti$^{4+}$ are partitioned based on stoichiometry. Efremovka rubinite has a similar composition with a mean empirical formula of (Ca$_{2.97}$Na$_{0.06}$)(Ti$_{3.05}$Ti$^{3+}_{0.59}$Sc$_{0.13}$Mg$_{0.12}$Zr$_{0.03}$Fe$_{0.03}$)(Si$_{2.36}$Al$_{0.48}$Ti$^{4+}_{0.06}$)O$_{12}$. Vigaranò rubinite is much more Y-, Sc-, and Zr-rich, showing an empirical formula of (Ca$_{1.98}$Y$_{0.83}$Mg$_{0.28}$)(Ti$^{3+}_{0.59}$Sc$_{0.05}$Zr$_{0.72}$Mg$_{0.2}$V$_{0.02}$Cr$_{0.00}$)(Si$_{1.64}$Al$_{1.18}$Ti$^{4+}_{0.07}$Fe$_{0.00}$)O$_{12}$. All rubinites are Ti$^{3+}$-rich but a significant amount (11–46%) of the Ti is 4+. The end-member formula of rubinite is Ca$_3$Ti$^{3+}_2$Si$_3$O$_{12}$.

Electron back-scatter diffraction patterns of rubinite can only be indexed using the $Ia\bar{3}d$ garnet structure with a best fit for unit cell dimensions $a = 12.1875$ Å, $V = 1810.27$ Å$^3$, and $Z = 8$ from [1]. The calculated density for this phase is 3.63 g cm$^{-3}$ using the formula for the Allende rubinite given above.

Origin and Significance: Rubinite, Ca$_3$Ti$^{3+}_2$Si$_3$O$_{12}$, is a new member of the garnet group and the Ti$^{3+}$-analog of eringaité Ca$_{2.97}$Sc$_{0.06}$Si$_3$O$_{12}$, goldmanite Ca$_3$V$_2$Si$_3$O$_{12}$, uvarovite Ca$_3$Cr$_2$Si$_3$O$_{12}$, or andradite Ca$_3$Fe$_2$Si$_3$O$_{12}$. Like eringaité [4], rubinite is among the first solid materials in the solar nebula; it formed either as a condensate or through crystallization from an $^{16}$O-rich Ca, Al, and Ti-rich melt under highly-reduced conditions. Subsequently, most rubinite grains in the Allende CAI and some in the Efremovka CAIs experienced O-isotope exchange with an $^{16}$O-depleted external reservoir in the solar nebula [5] and/or during fluid-rock interactions on the CV parent body [6].