

DISCOVERY OF RUBINITE, $\text{Ca}_3\text{Ti}^{3+}_2\text{Si}_3\text{O}_{12}$, 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,” $\text{Ca}_3\text{Ti}^{3+}_2\text{Si}_3\text{O}_{12}$ with the $Ia\bar{3}d$ garnet structure, was identified in five Ca-Al-rich inclusions (CAIs) from the CV3 chondrites Vigarano, 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 $\text{Ca}_3\text{Ti}^{3+}_2\text{Si}_3\text{O}_{12}$ 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 Vigarano, 1–8 μm in Allende, and 1–20 μm in Efremovka. In Vigarano, 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 melilite, perovskite, spinel, hibonite, corundum, davisite, grossmanite, diopside, and eringaite, plus secondary anorthite, grossular, and Na-melilite. Rubinite occurs within gehlenitic melilite with perovskite, spinel, and grossmanite in three Compact Type A (CTA) CAIs from Efremovka: *E101*, *E105*, and *40E-1* (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 Vigarano inclusion.

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

The mean chemical composition of type rubinite in Allende is (wt%) CaO 32.68, Ti_2O_3 14.79, TiO_2 13.06, SiO_2 28.37, Al_2O_3 3.82, Sc_2O_3 1.80, Na_2O 1.01, ZrO_2 , 0.80, MgO 0.79, V_2O_3 0.61, FeO 0.53, Y_2O_3 0.07, Cr_2O_3 0.05, total 98.38, giving rise to an empirical formula of $(\text{Ca}_{2.94}\text{Na}_{0.08})(\text{Ti}^{3+}_{1.04}\text{Ti}^{4+}_{0.59}\text{Sc}_{0.13}\text{Mg}_{0.10}\text{V}_{0.04}\text{Fe}_{0.04}\text{Zr}_{0.03})(\text{Si}_{2.38}\text{Al}_{0.38}\text{Ti}^{4+}_{0.24})\text{O}_{12}$, where Ti^{3+} and Ti^{4+} are partitioned based on stoichiometry. Efremovka rubinite has a similar composition with a mean empirical formula of $(\text{Ca}_{2.97}\text{Na}_{0.06})(\text{Ti}^{3+}_{1.05}\text{Ti}^{4+}_{0.66}\text{Mg}_{0.12}\text{Sc}_{0.09}\text{Zr}_{0.03}\text{V}_{0.03}\text{Y}_{0.01}\text{Fe}_{0.01})(\text{Si}_{2.36}\text{Al}_{0.48}\text{Ti}^{4+}_{0.16})\text{O}_{12}$. Vigarano rubinite is much more Y-, Sc-, and Zr-rich, showing an empirical formula of $(\text{Ca}_{1.89}\text{Y}_{0.83}\text{Mg}_{0.28})(\text{Ti}^{3+}_{0.59}\text{Sc}_{0.50}\text{Zr}_{0.72}\text{Mg}_{0.2}\text{V}_{0.02}\text{Cr}_{0.01})(\text{Si}_{1.64}\text{Al}_{1.18}\text{Ti}^{4+}_{0.07}\text{Fe}_{0.06})\text{O}_{12}$. All rubinites are Ti^{3+} -rich but a significant amount (11-46%) of the Ti is $4+$. The end-member formula of rubinite is $\text{Ca}_3\text{Ti}^{3+}_2\text{Si}_3\text{O}_{12}$.

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 $a = 12.1875 \text{ \AA}$, $V = 1810.27 \text{ \AA}^3$, 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, $\text{Ca}_3\text{Ti}^{3+}_2\text{Si}_3\text{O}_{12}$, is a new member of the garnet group and the Ti^{3+} -analog of eringaite $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$, goldmanite $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$, uvarovite $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$, or andradite $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$. Like eringaite [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].

References: [1] Valldor M. et al. 2011. *Inorganic Chemistry* 50:10107–10112. [2] Ma C. et al. 2017. *Mineralogical Magazine* 81:408. [3] Ivanova M. A. et al. 2017. *Meteoritics & Planetary Science* 52(S1): this meeting. [4] Ma C. 2012. *Meteoritics & Planetary Science* 47(S1):A256. [5] Kawasaki N. et al. 2016. *Lunar and Planetary Science Conference* 47:#1856. [6] Krot A. and Nagashima K. 2016. *Meteoritics & Planetary Science* 51(S1):A614.