DISCOVERY OF RUBINITE, $Ca_3Ti^{3+}{}_2Si_3O_{12}$, 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," $Ca_3Ti^{3+}{}_2Si_3O_{12}$ 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 $Ca_3Ti^{3+}{}_2Si_3O_{12}$ 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 ($\Delta^{17}O$ ~ –24‰); rubinite and perovskite show limited ranges of $\Delta^{17}O$ (from –24 to –16‰; most analyses range from –24 to –20‰); melilite and grossmanite are the most ^{16}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 in $\Delta^{17}O$ (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 $(Ca_{2.94}Na_{0.08})(Ti^{3+}{}_{1.04}Ti^{4+}{}_{0.59}Sc_{0.13}Mg_{0.10}V_{0.04}Fe_{0.04}Zr_{0.03})(Si_{2.38}Al_{0.38}Ti^{4+}{}_{0.24})O_{12}$, where Ti^{3+} and Ti^{4+} are partitioned based on stoichiometry. Efremovka rubinite has a similar composition with a mean empirical formula of $(Ca_{2.97}Na_{0.06})(Ti^{3+}{}_{1.05}Ti^{4+}{}_{0.66}Mg_{0.12}Sc_{0.09}Zr_{0.03}V_{0.03}Y_{0.01}Fe_{0.01})(Si_{2.36}Al_{0.48}Ti^{4+}{}_{0.16})O_{12}$. Vigarano rubinite is much more Y-, Sc-, and Zr-rich, showing an empirical formula of $(Ca_{1.89}Y_{0.83}Mg_{0.28})(Ti^{3+}{}_{0.59}Sc_{0.50}Zr_{0.72}Mg_{0.2}V_{0.02}Cr_{0.01})(Si_{1.64}Al_{1.18}Ti^{4+}{}_{0.07}Fe_{0.06})O_{12}$. All rubinites are Ti^{3+}-rich but a significant amount (11-46%) of the Ti is 4+. The end-member formula of rubinite is $Ca_3Ti^{3+}{}_2Si_3O_{12}$.

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, $Ca_3Ti^{3+}{}_2Si_3O_{12}$, is a new member of the garnet group and the Ti^{3+}-analog of eringaite $Ca_3Sc_2Si_3O_{12}$, goldmanite $Ca_3V_2Si_3O_{12}$, uvarovite $Ca_3Cr_2Si_3O_{12}$, or andradite $Ca_3Fe_2Si_3O_{12}$. 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].

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