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# RARE EARTH ELEMENT AND YTTRIUM MINERAL OCCURENCES IN THE ADIRONDACK MOUNTAINS

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**KEYWORDS:**

***Rare Earth Elements, Yttrium, Lyon Mountain Granite, Iron Deposits, Eastern Adirondack Highlands***

## INTRODUCTION

The rare earth elements (REE), formally called lanthanides, are a set of fifteen chemical elements, from lanthanum (La) to lutetium (Lu). Yttrium (Y) is added to this group because it has similar properties and occurs in the same mineral deposits. These elements are divided into low-atomic number, lanthanum to europium (La-Eu), or light rare earth elements (LREE), and heavy-atomic number, gadolinium to lutetium (Gd-Lu), or heavy rare earth elements (HREE). Even though they are called "rare," they are widely distributed in the Earth's crust and are present in all types of igneous, metamorphic, and sedimentary rocks. Some of the REE have abundances (relative amount of an element in the Earth's crust) comparable or higher than gold, mercury, tungsten, tin, arsenic, copper, cobalt, and zinc (Handbook of Chemistry and Physics, 2016). In geology research, REE are used to understand earth processes such as crystal fractionation, partial melting, magma mixing, and absolute age dating of minerals.

The REE have high-tech industrial applications and are essential for making hybrid cars, computers, smartphones, color TV, lasers, ceramics, and military devices. For this reason, the United States Geological Survey identified the rare earth element dysprosium as one of the most critical elements in the 2010 Critical Materials Strategy

report. Significant igneous REE deposits are often associated with unusual igneous rocks such as carbonatites and peralkaline silicate rocks; chemical weathering is another geological process that may concentrate REE in economic abundances (for details, see *Elements* 2012). In this paper, we discuss the mineralogy, chemical composition, and occurrences of the REE minerals and REE-bearing minerals from the Adirondack Mountains. The mineralogical survey of New York State indicates three types of occurrences as potential sources for the rare earth elements (REE) and yttrium (Y) minerals: (1) Low Ti-Fe oxide (magnetite) – fluorapatite (LTF); (2) Pegmatite; and (3) Metamorphic-hydrothermal veins.

The LTF deposits contain REE- or REE-bearing minerals such as REE-rich fluorapatite, monazite-(Ce), allanite-(Ce), stillwellite-(Ce), and zircon. Allanite-(Ce), fergusonite-(Y), polycrase-(U), and monazite-(Ce) occur in pegmatites and bastnaesite-(Ce), cerian epidote, and kainosite-(Y) are components of the hydrothermal or metamorphic-hydrothermal veins. By far, the most important potential source for the REE in the Adirondack Mountains is fluorapatite from the LTF ores.

***Figure 1:*** *Hand specimen of magnetite (dark)-fluorapatite (light orange colored) ore from Mineville.*

## RARE EARTH ELEMENT MINERALS OF THE ADIRONDACK REGION

*Fluorapatite*, $Ca_5(PO_4)_3F$ (Figure 1), is the most important REE-bearing mineral in New York, both economically and scientifically. It occurs in deposits from eastern Adirondacks (Hammondville, Skiff Mountain, Mineville, and Cheever in Essex County; Palmer Hill, Arnold Hill, Rutgers Mine, and Lyon Mountain in Clinton County). It was first mined in 1852 from Mineville by the Moriah Phosphate Company with the intention of producing fertilizers. The mine initially exploited the outcrop (Figure 2), and the amount of apatite from the surface was greater than it was from the underground works (Maynard 1889).

The phosphate mineral apatite came to the attention of the Professor Ebenezer Emmons, who supervised the American Mineral Company formed in 1853. The company mined mainly apatite for fertilizers and iron as by-product, but because the market did not react very well to their products, the company had to lease their properties and mineral rights to Port Henry Iron Ore Company (Farrell 1996). Initially, fluorapatite was considered only useful for the production of fertilizers, but after 1940, a U. S. Geological Survey report showed that the phosphate was very rich in rare earth elements. Molycorp, a REE producing company, leased the mineral rights and started their recovery from the tailings, but the feasibility studies were unfavorable and the company did not acquire the property. Interest in the REE-bearing apatite was renewed in 1983, and Williams Strategic Metals of Colorado purchased the fluorapatite-rich tailings then re-sold them in 1986 to Rhone-Poulenc, Inc., a French state-owned company (Farrell 1996). Later, Rhodia Inc. of New Jersey became the owner, and today Solvay, a Belgium company, has the surface and mineral ownership.

***Figure 2:*** *Outcrop of the magnetite-fluorapatite ore. The 4 inch GPS device is for scale.*

Mariano and Mariano (2012) suggested "if there is an urgent need for HREEs in North America, the apatite tailings at Mineville, NY, may be the best source" (Figure 3). According to them the tailings embrace 5 million $m^3$ containing 8-9 million kilograms (kg) of $Y_2O_3$ with a grade of 0.12% $Y_2O_3$ and 0.6% REO. Fluorapatite from the eastern Adirondacks iron deposits displays distinctive concentric zoning or dissolution under scanning electron microscopy (SEM) and cathodoluminescense (CL). Backscattered electron images (BSE) highlight four major types of textures: (a) areas of low BSE intensities within brighter apatite grains, or along crystal margins; (b) fractured fluorapatite with tiny secondary monazite-(Ce) and thorite crystals; (c) blobs or rods of quartz in fluorapatite; (d) mantled fluorapatite; (e) monazite-(Ce)- allanite(Ce) ± fluorapatite symplectite. In all of the above mentioned textural situations, the LREE were leached out and recrystallized as REE minerals (monazite, allanite), but yttrium was always retained by fluorapatite.

*Stillwellite-(Ce)*, (Ce,La,Ca) $BSiO_5$, was found at Mineville (Mei et al. 1979) and Cheever, Essex County. The sample from Mineville was collected from the "Old Bed" magnetite-fluorapatite ore body in the area of a fault on the 2100 ft-level. It occurs as 1-2 mm-wide tabular crystals with waxy luster and pink to reddish color. Our analyses show the following REE concentration in the mineral: 20.44 lanthanum, 30.83 cerium, 1.51 praseodymium, 7.07 neodymium, and 1.73 samarium, all in weight percent (wt%). It is low in yttrium and thorium. The stillwellite-(Ce) from Cheever displays the same mineral association, properties, and composition.

*Monazite-(Ce)*, (Ce,La,Nd,Th)$PO_4$, occurs in LTF deposits and pegmatites. Monazite-(Ce) from the LTF deposit is low in xenotime ($YPO_4$) component, but large amounts of lanthanum and neodymium substitute for cerium. Monazite-(Ce) from the Batchellerville pegmatite in Saratoga County displays the following composition: 18.1 cerium, 17.01 thorium, 7.89 lanthanum, 7.12 neodymium, and 1.69 yttrium, all in element wt% (Lupulescu et al. 2012).

*Xenotime-(Y)*, $YPO_4$, was found only from the Mayfield pegmatite.

*Allanite-(Ce)*, $(Ca,Ce)_2(Al,Fe^{2+},Fe^{3+})_3(SiO_4)(Si_2O_7)O(OH)$, is generally not a very spectacular mineral (it is dark colored) and is of no use at this moment for REE extraction. It is, however, common in the pegmatites (Batchellerville, Saratoga County; Roe Spar Bed, Mineville, Hague, Essex County), and in some magnetite-fluorapatite deposits of the Adirondack Mountains. The most remarkable crystals were found by Blake (1858) at Mineville, on the eastern side of the Adirondacks, in small pegmatite dikes cutting the magnetite ore; the crystals were very large: 20-25 cm long, 6-20 cm wide, and 2.5-5 cm thick. Our analyses indicate that the allanite-(Ce) from Mineville contains 10.10 lanthanum, 12.36 cerium, 2.17 neodymium, and 1.68 praseodymium, all in wt%.

*Fergusonite-(Y)*, $YNbO_4$, occurs in intergrowth with allanite-(Ce) at the Roe Spar pegmatite as clusters of crystals 1.5-2.5 inches in length displaying fan-shaped radial sections, adamantine luster, and brown color.

*Uranopolycrase*, $(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$, occurs in the Day (Overlook), Saratoga County pegmatite (Smith and Kruesi 1947) as small, dark greenish to brown-black, tabular crystals associated with quartz, feldspar, and/or schorl. It displays pinacoids and domes and few prisms and pyramidal faces.

*Zircon*, $ZrSiO_4$, is very common, occurring at almost all the pegmatite locations, mainly in the metamict state due to its uranium and thorium content. It is very common in the granitic rocks of the Adirondack Mountains.

*REE-bearing epidote*, $Ca_2(Fe^{3+},Al)_3(SiO_4)_3(OH)$, was found from the Coal Mine vein, Rossie, St. Lawrence County in association with allanite-(Ce). Here, it occurs as acicular radial aggregates of greenish crystals on calcite (Robinson et al. 2001). Another occurrence of

this mineral was described from a metamorphic-hydrothermal vein from Long Lake, Hamilton County (Richards and Robinson 2000).

*Kainosite-*(Y), $Ca_2(Y,Ce)_2Si_4O_{12}(CO_3)H_2O$, occurs as millimeter-sized crystals associated with fluorite, REE-bearing epidote, and quartz (Richards and Robinson 2000). The HREE are predominant in the REE budget.

*Bastnaesite-(Ce),* $Ce(CO_3)F$, was described as fine-grained tiny crystals associated with REE-bearing apatite from Mineville (McKeowan and Klemic 1956) and in association with quartz in a hydrothermal vein cutting the Potsdam sandstone, Trout Brook Valley, Ticonderoga, Essex County (Doll 1983).

***Figure 3:*** *Tailings at Mineville, Essex County.*

## SUMMARY

Most of the REE minerals from the Adirondack Mountains have only scientific significance or could be seen as specimens of Museums and mineral collectors' interest. This is the case for the minerals occurring in pegmatites and hydrothermal-metamorphic veins; they are rare or in the form of silicates and therefore are not properly processed for the REE extraction. The tailings from the previously mined LTF deposits contain fluorapatite that is rich in REEs, significantly the heavier REEs, to be of economic interest. United States Geological Survey started an aeromagnetic survey of the eastern Adirondacks in the fall-winter of 2015. A press release from the United States Geological Survey from December 4, 2015 indicated a 450 $mi^2$ area in Essex and Clinton counties will be investigated by aerial geophysical techniques to map buried geological structures associated with iron and REE deposits (USGS 2015). This geophysical investigation will bring information of the deep buried geological structures in this part of the Adirondacks.

**ACKNOWLEDGEMENT**

The authors gratefully acknowledge a thorough and insightful review by Bruce Selleck.

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