

# Round Top Mountain rhyolite (Texas, USA), a massive, unique Y-bearing-fluorite-hosted heavy rare earth element (HREE) deposit

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**Abstract:** Round Top Mountain in Hudspeth County, west Texas, USA is a surface-exposed rhyolite intrusion enriched in Y and heavy rare earth elements (HREEs), as well as Nb, Ta, Be, Li, F, Sn, Rb, Th, and U. The massive tonnage, estimated at well over 1 billion tons, of the deposit makes it a target for recovery of valuable yttrium and HREEs (YHREEs), and possibly other scarce elements. Because of the extremely fine grain size of the mineralized rhyolite matrix, it has not been clear which minerals host the YHREEs and in what proportions. REE-bearing minerals reported in the deposit included bastnäsite-Ce, Y-bearing fluorite, xenotime-Y, zircon, aeschynite-Ce, a Ca-Th-Pb fluoride, and possibly ancylite-La and cerianite-Ce. Extended X-ray absorption fine structure (EXAFS) indicated that virtually all of the yttrium, a proxy for the HREEs, resided in a coordination in the fluorite-type crystal structure, rather than those in the structures of bastnäsite-Ce and xenotime-Y. The YREE grade of the Round Top deposit was just over 0.05%, with 72% of this consisting of YHREEs. This grade was in the range of the South China ionic clay deposits that supply essentially all of the world's YHREEs. Because the host Y-bearing fluorite is soluble in dilute sulfuric acid at room temperature, a heap leaching of the deposit appeared feasible, aided by the fact that 90%–95% of the rock consists of unreactive and insoluble feldspars and quartz. The absence of overburden, remarkable consistency of mineralization grade throughout the massive rhyolite, proximity (a few km) to a US interstate highway, major rail systems and gas and electricity, temperate climate, and stable political location in the world's largest economy all enhanced the potential economic appeal of Round Top.

**Keywords:** heavy rare earth elements; yttrium-bearing fluorite; yttrifluorite; heap leaching; rhyolite; Round Top; deposit

The rare earth elements (REEs) are essential components of current and emerging 21<sup>st</sup> century technologies. Recent concern about future supplies of all the REEs now has narrowed chiefly to the heavy rare earth elements (HREEs). Essentially all the world's HREEs currently are sourced from the south China ion-adsorption clays. The ability of those deposits to maintain and increase production is uncertain, particularly in light of environmental degradation associated with some mining and extraction operations in the region.

We investigated an yttrium and HREE (YHREE) deposit that has proven to be unique in its mineralogy and impressive in its tonnage. This unconventional deposit presents the potential to become a significant source for YHREEs in the near future.

## 1 Round Top Mountain HREE deposit

### 1.1 Nature and characteristics of the deposit

Round Top Mountain, at Sierra Blanca, west Texas, USA, is a rhyolite laccolith intrusion (a fine-grained ig-

neous rock body related to granite, emplaced as a mushroom-shaped mass between sedimentary rock layers), enriched in rare earths elements, particularly the scarce YHREEs: Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. The rhyolite is also enriched in Be, Ga, Sn, Nb, Ta, U, and Th. The deposit lies some 130 km southeast of El Paso, TX (Fig. 1<sup>[1]</sup>).

Development of a beryllium mine at Round Top in the 1980s was later abandoned. The beryllium deposit lies along part of the lower contact with limestone; the target was  $3 \times 10^5$  tons of 2% BeO mineralization<sup>[1]</sup>. The property now is leased from the General Land Office of the State of Texas by Texas Rare Earth Resources, a US corporation. TRER plans to recover the REEs; it is evaluating simultaneous extraction of lithium, uranium, and beryllium from the rhyolite as well<sup>[1]</sup>.

The Round Top Mountain rhyolite is enormous; the Texas Bureau of Economic Geology estimated the rock mass at 1.6 billion tons<sup>[2]</sup>. The mountain itself is approximately 375 m tall and nearly 2 km in diameter. Measured, indicated, and inferred total REEs (TREEs) exceed  $5 \times 10^5$  t<sup>[3]</sup>. Approximately 72% of the TREEs in the rhyolite are the scarce YHREEs<sup>[3]</sup>.

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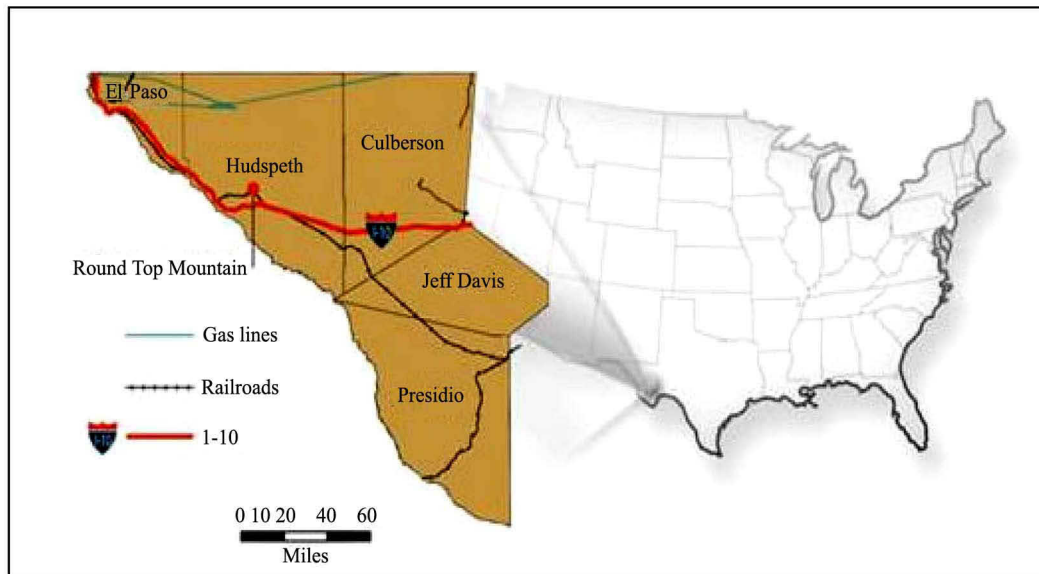


Fig. 1 Location of Round Top Mountain deposit

The deposit is exposed as an erosional remnant that can easily be surface-mined, with essentially no cover to be removed (Fig. 2<sup>[1]</sup>). Although huge in extent, well exposed, easily accessible by rail and US interstate highway, and proximal to electricity and natural gas, the mineralization is both dilute (TREE grade just over 500 ppm) and diffuse (no concentrated zones)<sup>[2,3]</sup>. The ability to economically tap this potential world-class resource hinges on extraction from an ore grade an order of magnitude (one-tenth) or more lower than those in conventional REE mining operations, which typically are in the % range. It is, however, within the range of the HREE ion-adsorption clays of southern China<sup>[4]</sup>. Further, in addition to their *homogeneous distribution* (very little variation in concentration throughout the rhyolite), the REEs are hosted in a matrix that is *extremely fine grained* (generally sub-micron in diameter). Potassium feldspar, plagioclase, and quartz grains comprise the bulk, 90%–95% of the volume, of the rhyolite. Large REE-

containing grains that could be easily beneficiated by such physical means as gravity or magnetic separation are scarce. The REE-bearing minerals are not concentrated in veins within the rhyolite that could be extracted by selective mining.

We have been experimenting in the laboratory at bench scale with direct acid leaching to assess heap leaching as a possible route to low-cost YHREE extraction. Previous studies indicated that very fine grinding and froth floatation concentrates the target YHREEs, but this approach requires a large initial capital expenditure and significant operating complexity and expenses<sup>[3]</sup>. Successful extraction of the YHREEs at Round Top by heap leach would be a breakthrough in REE mining technology.

## 1.2 REE mineralogy at Round Top

The mineralogy of the YREEs and other critical elements is essential to develop an appropriate extraction



Fig. 2 Round Top Mountain, virtually all of which is mineralized rhyolite

protocol. Previous study of the elemental composition of mineral grains by electron microprobe indicates that the REEs are hosted by bastnäsite-Ce, Ce-bearing fluorite, Y-bearing fluorite, xenotime-Y, zircon, aeschynite-Ce, a Ca-Th-Pb fluoride, and possibly ancylite-La and cerianite-Ce<sup>[2,3,5,6]</sup>. It was suspected, but never demonstrated, that most of the REEs were hosted in various fluorine minerals. The relevant microprobe analyses were limited by grain size: only “large” particles, mostly 5–10  $\mu\text{m}$  in dimension, could be examined. Aside from the feldspar and quartz phenocrysts, most of the remaining 5%–10% of the rock volume comprises grains a micrometer or less in diameter. These are not suitable for electron probe microanalysis. The fraction of the REEs in each mineral, or in unidentified phases too small to analyze, was not, and probably could not be estimated. Optical or microprobe point counting of grains is the conventional way to quantify the fraction of an element in different phases. This is not possible due to both the low concentration (for Yb at 50 ppm, one searches through a million grains in an attempt to encounter a single grain of fluorite that is, say, 2% ytterbium) and minuscule grain size (analogous to “invisible” gold) of the critical elements in the bulk rock. Lacking firm knowledge of the mineralogy of the REEs, development of an extraction process is forced to be based on an extensive and expensive program of trial and error.

### 1.3 Research goal

To assist in evaluating heap leaching, our goal was to determine which mineral(s) host the highly prized YHREEs, and in what proportions. For this task we chose synchrotron-based X-ray absorption spectroscopy (XAS) experiments, which provide the opportunity to directly speciate or determine the mode(s) of incorporation of a particular element in a bulk sample.

For this initial study we examined yttrium because it is by far the most abundant YHREE (Table 1) in the Round Top deposit at 221 g/t (or ppm) and provides an accessible K-edge for XAS. Yttrium is markedly similar in its chemical and geochemical behavior to the HREEs, e.g., holmium and dysprosium. In 102 acid leaching experiments (briefly described later), the correlation between % dysprosium extracted (percentage) and % yttrium extracted (percentage) was a remarkable 0.975, significant at better than the 99.9% confidence level. Thus yttrium serves as a valid and robust proxy for the HREE suite at Round Top. Examination of the individual HREEs in the rhyolite proved difficult due to interferences with the X-ray emissions associated with the L-III edges of the HREEs from the K-edge excitations and emissions of the major elements and transition metals in the rhyolite. The excitation energies of the K-edges of the HREEs are beyond those normally available at synchrotron sources.

**Table 1 HREE and Y average concentrations in Round Top Mountain rhyolite**

Elements	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
Concentration/(g/t)	0.2	10.6	3.6	31.7	8.0	32.8	7.1	56.5	8.9	221

Note: Data from Ref. [3]

## 2 Materials and methods

### 2.1 Rhyolite samples

All but one sample were split from a well-mixed >250 kg sample composited from material recovered from a representative set of reverse circulation exploration drill holes into the Round Top Mountain rhyolite. This material assayed at 211 g/t yttrium. Table 2 lists two samples that were sieved to the specified grain size, and a third sample that was a small block cut from a large grain recovered from the drill debris. The remaining 5 samples were size-sorted granular rhyolite that was leached for various periods and temperatures in 8.3 vol.% sulfuric acid. The amount of the initial yttrium remaining in the samples, relative to the respective untreated material (first 2 samples), is listed. All samples, except for the block, were subsequently reduced in a ball mill to <10  $\mu\text{m}$  grain size, and pressed into a standard 25-mm X-ray fluorescence puck with the addition of a cellulose binder and paraffin sealant. The % yttrium remaining (percentage) in the leached solids was determined by X-ray fluorescence analysis of the respective untreated and treated samples, using a PANalytical Epsilon5 energy dispersive spectrometer with a germanium solid-state detector.

### 2.2 X-ray absorption spectroscopy technique

X-ray absorption fine structure (XAFS), a technique of XAS, uses photons of a specific energy (narrowly tuned via a double-crystal monochromator to ~1 eV or less) to couple with a specific electron energy level within the element of interest and generate the emission of the corresponding photoelectron. The emitted photoelectron wave backscatters when it encounters near-neighbor atoms, with resultant positive or negative auto-interference, depending on the phase relation of the outgoing and backscattered wave. Negative interference lowers the

**Table 2 Samples analyzed by XAS**

Sample ID	Grain size	Leach time	Y remaining/wt.%	Temperature
YBLK2TO4	2–4 mm	N/A	100	N/A
YBLK0TO125	<0.125 mm	N/A	100	N/A
ROCK1	Polished block	N/A	100	N/A
YHOT8	2–4 mm	3 d	40	70 °C
YS405D	2–4 mm	5 d	38	Room ~19 °C
YS408322W	2–4 mm	2 weeks	26	Room ~19 °C
YS4083211W	2–4 mm	11 weeks	23	Room ~19 °C
YS01258323D	<0.125 mm	3 d	21	Room ~19 °C

overall photoelectron yield, which depends on the initial and final photoelectron energy states. The phase relation depends on the photoelectron wavelength and the distance(s) between the origin atom and the near-neighbor atom(s). By incremental increase of the photoelectron energy beyond the absorption edge, additional energy is transferred to the photoelectron, increasing its kinetic energy and therefore decreasing its wavelength. In this way, the atom of interest's atomic near neighborhood is probed sequentially by photoelectrons of different wavelengths, each generating a different auto-interference and thus a different photoelectron yield, which is recorded via the yield of characteristic X-rays emitted as the atom returns to its ground state. Thus a single experiment results in a spectrum of photoelectron yield versus X-ray beam photon energy. This pattern can be used as a fingerprint, analogous to an X-ray diffraction pattern, for a specific compound or state (e.g., adsorption) by comparison with known materials, or can with the best data be solved for such structural and electronic parameters as valence, number of neighbors, distances to them, and their elemental identities.

XAS offers certain advantages over X-ray diffraction (XRD). First, because it excites a specific element, it can provide structural information at concentrations far lower than XRD, in the ppm range rather than in the percentage range. Second, effectiveness of XAS is not limited to repetitive (lattice) structures as is XRD, but can analyze sorbed atoms as well. An important advantage of XAS over electron microprobe analysis is that XAS in theory interrogates every atom of, say, yttrium in a bulk, 3-dimensional sample (to the escape depth of the emitted characteristic X-rays), not just those in single grains specifically targeted for analysis and residing at the surface of a sample.

Details of XAS techniques and applications can be found in standard texts<sup>[7-10]</sup>.

### 2.3 XAS experiments

XAS experiments were performed at the Stanford Synchrotron Radiation Lightsource (SSRL), a part of the Stanford Linear Accelerator (SLAC) located in Menlo Park, CA, USA. Data were collected in fluorescence mode on beamline 7-3, using a 30-element germanium detector, and on beamline 9-3 with a 100-element monolith germanium detector. The synchrotron was operated in continuous fill mode, with a current ranging from 500 to 495 mA (on 7-3), and at 100 mA with discrete fill (on 9-3). When appropriate, the beam was detuned 30%. Spectra for yttrium were collected at the K-edge, using Soller slits and a Sr-3 filter to attenuate beam scatter. Data were collected using XAS-Collect software and processed with SIXPack and EXAFSPAK.

### 2.4 Model compounds

A total of 6 specimens of 4 relevant REE model com-

pounds (i.e., known to be present at Round Top) were obtained commercially to compare with the rhyolite samples. These are listed in Table 3.

**Table 3 Model REE compounds for spectral comparison with samples**

Mineral	Elemental formula	Y/wt.%	Collection locality
Y-bearing fluorite	$(Ca_{1-x}Y,HREE_x)F_{2+x}$	1.7	Joseph Mine, Ojo Caliente District, Rio Arriba County, New Mexico, USA
Y-bearing fluorite	$(Ca_{1-x}Y,HREE_x)F_{2+x}$	15.5	Innhavet, Drag, Nordland, Norway
Bastnäsité-Ce	$CeCO_3F$	0.02	Zagi Mine, Pakistan
Bastnäsité-Ce	$CeCO_3F$	0.36	Unknown, Pakistan
Xenotime-Y	$(Y,HREE)PO_4$	37.0	Bahia, Brazil
Fluocerite-Ce	$(Ce,Ln)F_3$	1.1	Unknown, Brazil

Notes: 1. Sample analyses by electron microprobe

## 3 Results and discussion

### 3.1 Spectra

Fig. 3 presents extended X-ray absorption fine structure (EXAFS) spectra for samples and model compounds. To assist in matching samples to model compounds, Fig. 3(a) shows the entire XAFS region as a single "fingerprint" with multiple ridges and valleys<sup>[11]</sup>. In both panels we observed a strong pattern similarity among all the Round Top samples. Some differences are the result of data quality, i.e., one or more close minor peaks being clumped into a single peak or a humped peak due to lower resolution. Likewise, different specimens of each of the model compounds are consistent within that model.

It should be obvious that all the samples closely resemble the spectra of the two Y-bearing fluorite model compounds. There is no resemblance at all to xenotime-Y, and little to bastnäsité-Ce. Thus it appears that virtually all of the yttrium in these samples, which are representative of the deposit, most possibly resides in the fluorite-type crystal structure among the 4 phases examined in the present study. This speculation is reinforced by the samples that were leached in the laboratory in sulfuric acid, a process that removed much of the yttrium from the grains. Xenotime-Y is insoluble in sulfuric acid, and bastnäsité-Ce sparingly soluble or probably insoluble in dilute sulfuric<sup>[12]</sup>. If any of the original yttrium resided in either of these two phases or other insoluble minerals, the little yttrium remaining post-leaching would mostly be in those minerals and yield their respective spectra. This did not occur; the samples with decreasing percentages of remaining yttrium in Fig. 3 still retain only the Y-bearing fluorite spectral signature. This indicates that perhaps 5% or less of the yttrium is not in the lattice of fluorite, i.e., 95% or more of the yttrium and by analogy the HREEs are hosted in the Y-bearing fluorite. Therefore the Round Top mineralogy is extremely

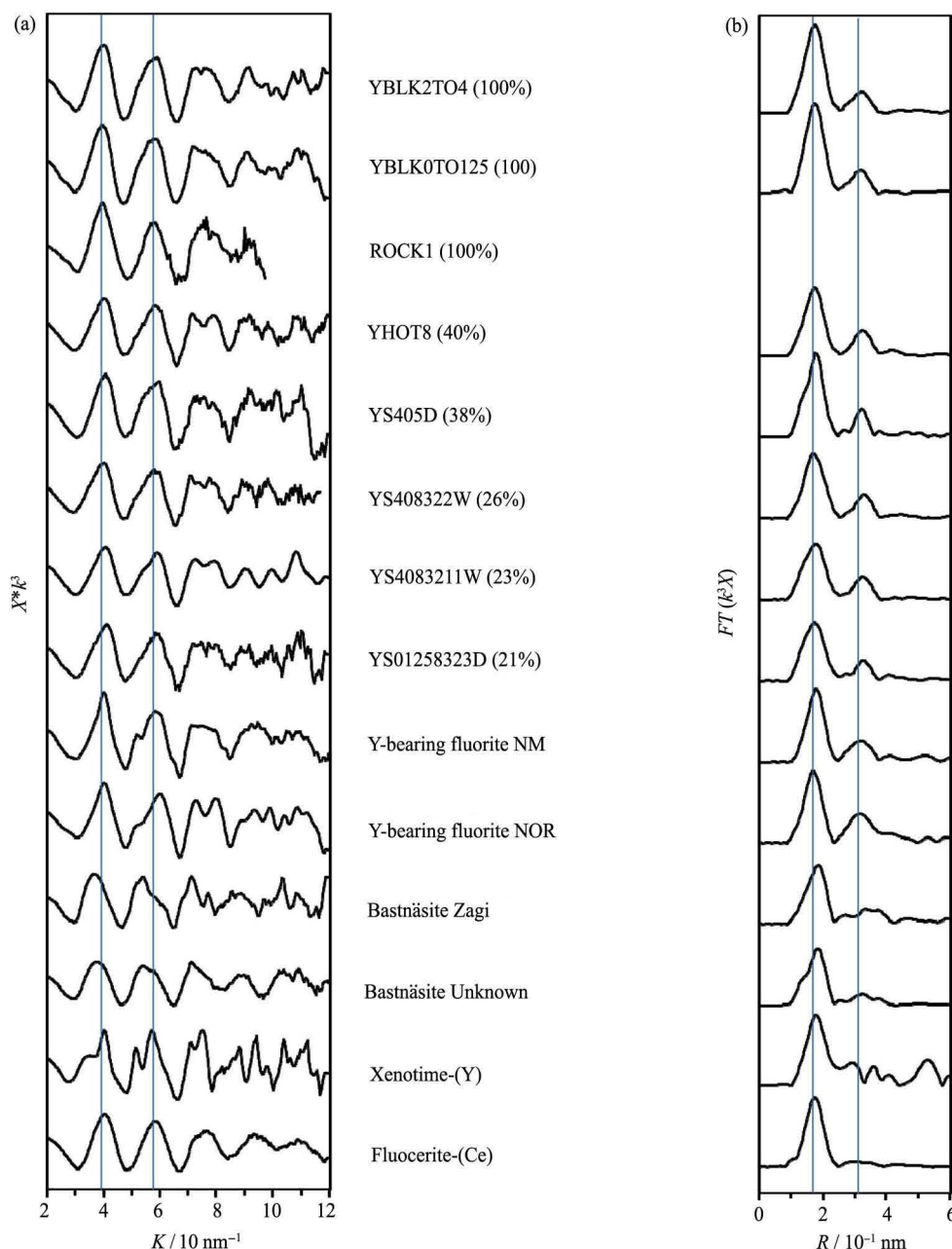


Fig. 3 Spectra background-subtracted, normalized,  $k^3$ -weighted, and plotted in  $k$ -space (a); radial distribution functions (RDF) derived from Fourier transforms of spectra in (a) (distances not corrected for phase shift) (b). No FT given for ROCK1 due to shorter  $k$ -space 3.5-cycle spectrum. YS4083211W and yttrifluorite NOR spectra smoothed to remove excess signal noise.

favorable for extraction of the YHREEs by heap leaching.

Minor differences between the spectra of the two Y-bearing fluorite model compounds can reasonably be attributed to the substitutional nature of this mineral. Therefore there is no specific set of elements in the near-neighbor cation shells surrounding the yttrium atoms. Given this fact, the nearly, but not perfectly, identical spectra of the two Y-bearing fluorites from separate localities is not surprising. Further, minor differences in the sample spectra can be attributed to slightly different materials in the different splits.

### 3.2 Principal components analysis (PCA)

The XAFS spectra of the 8 samples were entered into the Principal Components Analysis program in the SIX-Pack data analysis package. They yielded a single principal component, confirming mathematically that the sample set is monomineralic. Target transformations to each of the 6 model compounds indicated that the Y-bearing fluorite from New Mexico was the best match to the samples. Thus the samples are possibly Y-bearing fluorite.

### 3.3 Least-squares spectral fits

Fig. 4 presents the fits of the Y-bearing fluorite from New Mexico to the two unleached samples and to two leached samples, in which only 38% and 21% of the

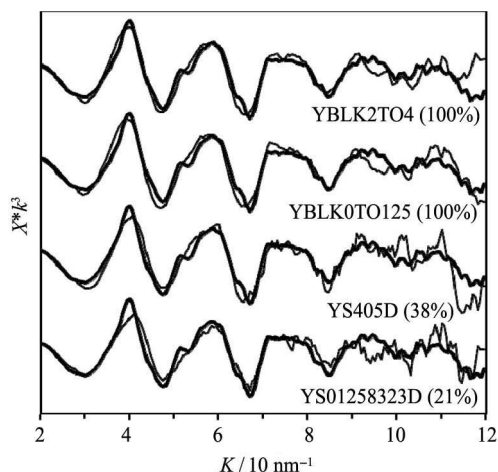


Fig. 4 Fits of the spectrum of Y-bearing fluorite from New Mexico (bold lines) to the spectra of the two unleached samples and to the spectra of two leached samples

original yttrium remains. The fit is seen to be nearly identical in all cases. The differences are comparable to the variation seen between the 2 different Y-bearing fluorite standards themselves. Note that data quality suffers in the leached samples due to their considerably smaller yttrium content. This reinforces our speculation that Y-bearing fluorite is the only host mineral for yttrium in Round Top rhyolite.

## 4 Significance of the Round Top deposit

### 4.1 Y-bearing fluorite: A unique mineralogy

Fluorite is a common mineral. A part of calcium in fluorite can be replaced with rare earth elements to form a solid solution series,  $(Ca_{1-x}REEx)F_{2+x}$ . The degree of substitution is usually slight; it rarely is greater than 0.3 apfu. The Y- or Ce-bearing varieties of fluorite have so-called variety names as “yttrofluorite,” “yttrocrite” and/or “cerfluorite,” but they are not independent mineral species. In November 2006 the Commission on New Minerals and Mineral Names of the International Mineralogical Association discredited yttrofluorite as an independent mineral species. The term is, however, encountered in pre-2006 literature, and remains in use as a mineral variety name, e.g., the mindat.org website<sup>[13]</sup>.

The US Geological Survey’s (USGS) 2002 compendium of hundreds of REE mines, deposits, and occurrences contains no reference to yttrofluorite or Y-bearing fluorite deposits<sup>[14]</sup>. Only passing references to “yttrofluorite” or Y-bearing fluorite are found in such standard technical books as *Rare Earth Minerals* and *Mineralogy and Geology of Rare Earths in China*<sup>[15,16]</sup>.

### 4.2 Economic potential of Round Top Mountain

Y-bearing fluorite may be a favorable economic REE resource because of both its yttrium content and its associated ability to preferentially incorporate the HREEs. Of

equal importance is the solubility of the mineral, which dissolves rapidly in dilute sulfuric acid at room temperature. Sulfuric acid is inexpensive (\$ 100–200 per ton; half that if generated in an on-site plant by combustion of sulfur) and universally available industrial commodity. This simplifies the liberation of YHREEs and suggests a heap leach model for ore processing. Because 90%–95% of the rhyolite rock volume is feldspars and quartz, minerals unreactive to dilute sulfuric acid, acid consumption is minimized. With the YHREEs hosted essentially exclusively in Y-bearing fluorite, we anticipate that very high heap leach recoveries can be achieved.

### 4.3 A unique deposit – or a new exploration target?

The Round Top rhyolite could be a unique deposit, where Y-bearing fluorite is speculated as the main ore mineral of REEs. Nonetheless, given the current and future projected economic value of YHREEs, it is wise to consider that similar deposits could remain undiscovered at the surface or, perhaps more likely, in the subsurface. Because the economic demand for YHREEs is recent, and this Y-bearing-fluorite-hosted YHREE deposit is neither well-known nor yet proved (i.e., in commercial production), there has been no exploration program(s) aimed to locate this target that we know of. Perhaps this study will generate exploration interest for deposits of Y-bearing fluorite in the near future.

## 5 Conclusions

X-ray absorption spectroscopy suggested that virtually all the yttrium, and therefore by proxy the HREEs, in the Round Top Mountain rhyolite deposit was hosted in Y-bearing fluorite. The deposit was thus unique. Because fluorite dissolved in dilute sulfuric acid at room temperature, it appeared favorable that Y and HREEs could be recovered at Round Top by inexpensive heap leaching. Since the yttrium, and by analogy, the HREEs were hosted apparently exclusively in Y-bearing fluorite, heap leach recoveries likely would be very high.

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