

# Microprobe Mapping of Rare Earth Element Distribution in Round Top Yttrofluorite Deposit

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## Abstract

The electron microprobe maps the spatial distribution of elements in a rock at a sub-mineral-grain scale to provide a basis for understanding mineralization processes and to determine optimal strategies for extraction of valuable target elements. Round Top Mountain (near the town of Sierra Blanca, Hudspeth County, west Texas, USA) is a peraluminous rhyolite laccolith that is homogeneously mineralized at over 500 ppm rare earths, more than 70% of which are yttrium and heavy rare earths (YHREEs). The massive deposit is exposed at the surface as a mountain some 2 km in diameter and 375 m in height. Round Top Mountain also contains Li, Be, U, Th, Nb, Ta, Ga, Rb, Cs, Sn, and F. The valuable YHREEs are hosted in yttrofluorite, which is soluble in dilute sulfuric acid. Texas Mineral Resources Corporation proposes to surface mine, crush, and heap leach the deposit. The distribution of YHREEs, and that of other trace elements, is remarkably homogeneous at outcrop drill hole scale. Here we document that YHREE mineralization appears pervasive through the rhyolite at a millimeter scale. Back scattered electron (BSE) and characteristic X-ray maps reveal the fine grain size and apparently random and dispersed spatial distribution of the yttrofluorite that hosts Round Top's valuable YHREEs. The yttrofluorite grains do not appear to cluster at special mineralized locations, e.g., in pores or along cracks in the rhyolite. The same is apparently true of such other potentially valuable minerals as cassiterite and uranium species. These findings confirm that the distribution of YHREEs in Round Top Mountain rhyolite is homogeneous through different orders of magnitude of scale, i.e., from outcrop (as seen in the companion work in this volume) to sub-thin section. The material thus is ideal for a heap leach operation where homogeneous feedstock is crucial to consistent and economic operation. The findings also confirm and explain why mechanical separation would prove very difficult and expensive due to the astronomical number of yttrofluorite grains in even a golf-ball-size piece of Round Top rhyolite.

#### **Keywords**

Heavy Rare Earth Elements, Yttrofluorite, Electron Microprobe, Micromapping, Round Top

## **1. Introduction**

The invaluable electronic, optical, and chemical properties enabled by compounds incorporating the rare earth elements (REEs) are prime drivers of new and emergent technologies. Advanced REE-based materials are fundamental to, for example, optical communication fibers, numerous types of lasers, the powerful permanent magnets found in the motors of hand tools and generators of wind turbines, various metal super-alloys, and catalysts for petroleum refining. Such additional future applications as widespread use of high-strength scandium-doped aluminum alloys depend on large, reliable supplies of specific REEs that are not currently available [1] [2] [3].

Because some 90% or more of the global REE supply is sourced from China, there are concerns in the rest of the world about the stability and security of the REE supply chain [4] [5]. Growing domestic REE needs for a fast-expanding economy in China could limit the amounts of raw rare earths and rare-earth-containing products exported into the global trade [6]. The geologic extent of REE reserves and resources might be not be sufficient to ensure supply at reasonable cost in the future as REE applications expand [7]. The REE supply chain is also being challenged by possible mining curtailment due to growing concerns in China about environmental pollution from REE extraction [8]-[14]. Finally, geopolitical uncertainties in a world of shifting interests and government relationships represent an unpredictable challenge to a robust and uninterrupted international supply chain.

The most vulnerable REEs are the scarce heavy rare earths (HREEs), Gd to Lu, and typically including Y, herein labelled as YHREEs [1] [8]. These are almost exclusively sourced from the south China ion adsorption clays, and extracted by *in situ* caustic leaching [9] [10]. There is growing concern and regulation of artisanal and often illegal mining of these deposits due to the extensive environmental damage that often accompanies extraction [11] [12] [15].

In response to potential and actual shortages or high costs of specific REEs, there is a search for new traditional deposits, as well as for exploitation of non-conventional deposits, and efforts at recycling [16] [17] [18] [19].

A potential supplementary source of YHREEs is yttrofluorite ( $(Ca_{1-x}Y,HREE_x)F_{2+x}$ , isometric), a variety of the common mineral fluorite ( $CaF_2$ , isometric) in which trivalent (3+) Y and HREEs substitute for bivalent  $Ca^{2+}$  to the extent of from 5% to 30% [20]. At present Round Top Mountain, near the town of Sierra Blanca in Hudspeth County, west Texas, USA, is the only documented site of extensive yttrofluorite mineralization [21] [22].

The mountain is a laccolith, a mushroom-shaped igneous intrusion formed by magma squeezed up toward the surface that then spread out between older flat-lying rock units. The rock type at Round Top is rhyolite, a fine-grained relative of granite; it is 36 Ma (million years) in age as determined by radiometric dating [23]. The overlying weaker sedimentary rocks have gradually eroded, leaving most of the laccolith exposed as a mountain nearly 2 km in diameter and over 375 m high [24] [25].

REEs are present in the rhyolite in excess of 500 ppm [26]. In contrast to most igneous REE deposits, at Round Top YHREEs are 72% of the total REEs (TREEs). Additional incompatible elements (those whose charge and size restrict their incorporation in most common rock-forming minerals) also are present in the rhyolite: Be, Li, Sn, Rb, Cs, Ga, Nb, Ta, U, and Th [26].

After performing extensive laboratory tests, Texas Mineral Resources Corporation has proposed to extract the YHREEs *via* a heap leach with dilute  $H_2SO_4$  [27] [28] [29]. The YHREE host yttrofluorite was found to be soluble in dilute sulfuric acid, a relatively inexpensive and widely available industrial chemical. The company also anticipates that they would be able to recover such byproduct elements as Li and U, also hosted in acid-soluble minerals.

In a companion paper in this volume (*Remarkably Consistent Rare Earth Element Grades at Round Top Yttrofluorite Deposit*) we documented the unusual homogeneity of the mineralization grade of the deposit at the scale of a set of exploratory drill holes that sampled roughly half of the exposure of massive Round Top Mountain [30]. In this current contribution we examine the rhyolite at a much finer scale to understand the microscopic distribution of the acid-soluble yttrofluorite that hosts the primary target YHREEs. We also examine the micro-distribution of potentially valuable byproduct elements.

Our *primary purpose* in creating and interpreting these maps is to delineate the distribution of the YHREE host mineral yttrofluorite at the microscopic level. This can help in the design of a heap leach that maximizes dissolution of the mineral and release of the YHREEs to the pregnant leach solution, without excessive cost of sulfuric acid. Likewise, one would like to maximize recovery of such valuable byproduct elements as U, Li, Be, and others. For example, if microprobe maps indicate that a particular element is present chiefly in an insoluble mineral, one would realize that it cannot be effectively recovered by the acid leach. Our *secondary purpose* is to provide insights to better understand the mineralization process, which would help in exploration for similar deposits elsewhere.

# 2. Materials and Methods

### 2.1. Rhyolite Sample Source and Preparation

For various mechanical and chemical laboratory studies TMRC produced a large composite sample by mixing several hundred kg of aliquot material recovered from >100 reverse circulation drill holes scattered across much of Round Top

Mountain. We chose at random, subject to the selected pieces being large enough (about 2 - 3 cm), 15 rhyolite fragments from that material, to be cut and ground for fashioning into petrographic thin sections. The thin sections were ground down to the standard 30- $\mu$ m thickness and mirror-polished (0.05- $\mu$ m gamma aluminum oxide final step) for examination with the electron probe microanalyzer. The polished thin sections were cleaned in an ultrasonic bath followed by an ethanol rinse immediately before carbon coating. Under rough-pump vacuum a minuscule layer of carbon was sputtered onto the surface of the sections to provide electrical conductivity to drain electrons received from the microprobe beam.

### 2.2. Electron Microprobe Mapping

Electron probe microanalysis (EPMA) was performed on a Cameca SX-50 (upgraded to SX-100 capability) instrument with 4 wavelength dispersive spectrometers (WDS). Image scans of a total of 16 elements (Y, Dy, Yb, F, U, Th, Nb, Sn, Zr, Rb, Ca, Na, K, Fe, Al, Si) plus back scattered electron (BSE) images were collected on multiple thin sections. Characteristic X-ray mapping was performed in WDS mode by continuous stage raster across a  $2 \times 2$  mm field at a  $512 \times 512$ pixel resolution, or more than 250,000 individual analyses for each element on each map. Beam conditions were 20 KeV accelerating voltage and 200 or 250 nA current. These specific conditions are given at the bottom of each map image.

Time for each run, typically using all 4 spectrometers, ranged from 1.5 to 12 hours, depending on the concentrations in the element set being analyzed. Low-concentration minor and trace elements required longer analysis times than the high-concentration major and rock-forming elements. Dwell time per pixel was 140 msec for minor and trace element scans, and 20 msec for major element scans.

Na was analyzed using the K-a line on a TAP diffracting crystal; Al using the K-a line on a TAP crystal; K using the K-a line on a PET crystal; Fe using the K-a line on a LIF crystal; F using the K-a line on a TAP crystal; Si using the K-a line on a TAP crystal; Sr using the L-a line on a TAP crystal; Rb using the L-a line on a TAP crystal; Sn using the L-a line on a TAP crystal; Nb using the L-a line on a TAP crystal; Dy using the L-a line on a LIF crystal; Yb using the L-a line on a TAP crystal; Dy using the L-a line on a LIF crystal; Yb using the M-a line on a TAP crystal; U using the M-a line on a TAP crystal; U using the M-a line on a PET crystal; Th using the M-a line on a PET crystal; and Zr using the L-a line on a TAP crystal. LIF is lithium fluoride, PET is pentaerythritol, and TAP is thallium acid phthalate. Spectrometers were peaked and optimized to the specific emission lines using appropriate Astimex and Cameca microanalysis standards.

Gray scales of images were manually adjusted to best depict mineral and elemental features of particular interest. Adjustment of gray scale is useful when studying and interpreting a particular map, especially for establishing background signal. In the maps in the following section we have chosen an appropriate gray scale that best presents the salient features of interest.

## 3. Results and Discussion

#### **3.1. Optical Views: Major Minerals**

**Figure 1** presents, for reference, several blocks of Round Top Mountain rhyolite and two photomicrographs of the rhyolite taken in reflected light. Pinkish color of some material is caused by incipient or partial oxidation of magnetite ( $Fe_3O_4$ , isometric) grains. Large geometric forms in photomicrographs are feldspar phenocrysts with albite (NaAlSi<sub>3</sub>O<sub>8</sub>, triclinic) cores and K-spar (orthoclase, KAl-Si<sub>3</sub>O<sub>8</sub>, monoclinic) rims. Quartz (SiO<sub>2</sub>, trigonal) is present as gray-to-clear material in the groundmass surrounding the large phenocrysts. These three common rock-forming minerals comprise 90% - 95% of the rhyolite.

The fine-grained groundmass, which contains the REEs and other potentially valuable elements, typically ranges in size from perhaps 20  $\mu$ m to sub-micron grains. The groundmass has proven difficult to study by conventional petrographic optical microscopy with standard polarized transmitted light due to multiple scattering at grain boundaries, creating hazy images. Here we use reflected light to discern the major rhyolite mineralogy.

### 3.2. Electron Microprobe Maps: Major Elements—Iron

Figure 2 presents, *left*, the backscattered electron (BSE) image of a  $2 \times 2$  mm portion of a typical thin section of Round Top Mountain rhyolite. In a BSE image the brightest areas are those from which the *most* electrons from the



**Figure 1.** *Left:* Four blocks of Round Top rhyolite, largest 5 cm in length. Pink samples result of oxidation of iron minerals. *Right:* Phenocrysts of albite (NaAl-Si<sub>3</sub>O<sub>8</sub>, triclinic) overgrown by K-spar (orthoclase, KAlSi<sub>3</sub>O<sub>8</sub>, monoclinic), approximately 200  $\mu$ m in both reflected-light photomicrographs. Quartz (SiO<sub>2</sub>, trigonal) seen as gray-to-clear material in the groundmass. Black in lower photo (pink sample) is magnetite (Fe<sub>3</sub>O<sub>4</sub>, isometric).

# BSE - Backscattered Electron Image Iron High z (heavy) element areas are brightest 1.6% iron oxide as Fe<sub>2</sub>O<sub>3</sub> in Round Top rhyolite 2 mm × 2 mm FOV (Field of View) Mineral is magnetite (Fe<sub>3</sub>O<sub>4</sub>)



**Figure 2.** *Left:* BSE image of  $2 \times 2$  mm area of petrographic thin section of Round Top Mountain rhyolite. Bright areas correspond to minerals containing higher-Z elements. *Right:* X-ray map of same area with detector optimized to count photons of only a specific Fe emission wavelength. Brightest areas have highest Fe content. Note correspondence of these areas to bright areas in BSE map. Mineral is magnetite, Fe<sub>3</sub>O<sub>4</sub>, which also commonly is observed in hand specimens and in optical microscope examination of the rhyolite. Note square form of some white areas, reflecting the common cubic crystal habit of this member of the isometric crystal system. Gray areas correspond to other minerals with lower Fe content.

bombarding source beam of electrons are expulsed from the sample and collected at a ring of overhead detectors. High-Z (Z = atomic number) elements expel more electrons than low-Z elements. Thus the brightest areas represent minerals that are composed of or incorporate high-Z elements. For multi-element minerals, the BSE brightness is determined by the average Z of the material. For reference, the igneous-rock-forming minerals in rhyolite contain chiefly low-Z elements, e.g., O, Si, Al (aluminosilicates), plus varying amounts of K, Na, Ca, etc.

## 3.3. Electron Microprobe Maps: Major Elements—Potassium, Silicon, and Aluminum

**Figure 3** shows the distribution of the three major minerals that comprise 90% - 95% of Round Top Mountain rhyolite: **albite, quartz,** and **orthoclase or K-spar**. All three are common rock-forming minerals. Both feldspars contain nearly the same amounts of Si and of Al and thus appear as single shades of gray on their respective elemental maps. The difference between the two minerals is apparent in the K map: black (no K) for the Na-rich albite cores and white for the K-spar (high potassium) rims. The BSE image of the K-spar (KAlSi<sub>3</sub>O<sub>8</sub>) is brighter than



**Figure 3.** Left: BSE image of  $2 \times 2$  mm area of petrographic thin section of Round Top Mountain rhyolite, and X-ray maps of same area for K, Si, and Al. Bulk rhyolite is approximately 74% SiO<sub>2</sub>, 13% Al<sub>2</sub>O<sub>3</sub>, and 4% K<sub>2</sub>O. Examples of the three major minerals are identified both by their shape (feldspars) and by their elemental compositions. Black areas on X-ray maps indicate that a particular element is not present in that region. Note, for example, how Si here is black at loci of Fe in **Figure 2**, or how K map exhibits the most black since it is the least abundant of the 3 elements displayed.

that of the albite (NaAlSi<sub>3</sub>O<sub>8</sub>) due to the higher Z of K than that of Na, giving a higher *average* Z to that mineral.

# 3.4. Electron Microprobe Maps: Minor Mineral—Cryolite

**Cryolite** (Na<sub>3</sub>AlF<sub>6</sub>, monoclinic) occurs as a minor mineral at Round Top, present at levels up to a few percent reported in some samples. The identification and distribution of cryolite is illustrated in **Figure 4** [24] [25] [31]. This particular sample displays several large grains in addition to dispersed smaller crystals. The formation of cryolite is associated with significant amounts of fluorine in the residual magma. This particular thin section contained more than the typical amount of cryolite characteristic of the Round Top Mountain deposit.

In the past, cryolite was sought as a flux for electrolytic aluminum production and therefore had significant commercial value. That market has been superseded by the industrial production of synthetic sodium hexafluoroaluminate.

# 3.5. Electron Microprobe Maps: Yttrofluorite

The next two X-ray maps indicate the distribution of YHREEs in two samples of Round Top rhyolite. In **Figure 5**, ten corresponding (identical position on map)



**Figure 4.** *Left*: Sodium map. *Right:* Fluorine map. *Top right*: Al map. Cryolite (Na<sub>3</sub>AlF<sub>6</sub>, monoclinic) is observed in the pixel areas where bright gray levels of Na, F, and Al superimpose. Cryolite is a common minor mineral at Round Top. Dull gray in Na map shows outlines of albite feldspar cores (compare to **Figure 3**).



**Figure 5.** *Left:* Yttrium map. *Top right:* Ytterbium map; *Bottom right:* Dysprosium map. Note strong correlation of Y and Yb locations, indicating their presence together in a mineral, here yttrofluorite. Dy map, with a lower intensity brightness level, shows similar pattern on careful inspection.

grains enriched in Y and Yb are relatively easy to discern; several additional fainter spots are possible grains. The Dy map is fainter and fewer correspondences are obvious. (Large, hazy gray areas, seen on close, enlarged inspection, correspond to magnetite grains. An Fe emission line tails off to the Dy emission line, an interference that leads to the apparent, but false, presence of a small amount of Dy). Note that the composition of yttrofluorite is quite variable because it involves substitution of Y and each of the HREEs for the  $Ca^{2+}$  cation in the fluorite lattice. The levels and proportions of these substitutions differ and are independent of each other. Thus one yttrofluorite grain can have, for example, more Y and less Dy than another grain.

**Figure 6** presents a typical electron probe microanalysis (EPMA) of the REE content of an yttrofluorite grain. The relative concentrations in this EPMA analysis are reasonably similar to the overall bulk HREE content of Round Top rhyolite, as seen in **Table 1**.

**Figure 7** is intended to permit visualization of the spatial intersections of Y, Ca, and F X-ray maps. The overlapping areas correspond to yttrofluorite grains. Between 10 and 20 yttrofluorite grains occur in each **Figure 5** and **Figure 7**. That number of grains is typical of the 15 thin sections that were studied and mapped (at least one  $2 \times 2$  mm area on each). Most grains were under 10 µm in 2-dimensional size. For the following inquiry, we choose a conservative 10 grain figure of merit as the minimum number of target yttrofluorite grains per  $2 \times 2$  mm



**Figure 6.** Wavelength dispersive (WDS) X-ray emission spectrum of an yttrrofluorite grain, using a synthetic LiF (lithium fluoride) diffracting crystal. Horizontal scale is  $\sin\theta \times 10^5$ , angle of diffracting crystal; vertical scale is relative intensity, based on number of emitted characteristic X-ray photons detected. Labels, above actual ragged spectrum, identify element and specific electronic transition (L*a*, L*β*). Relative height of peak corresponds roughly to concentration level of the element relative to neighboring elements, for a given transition, but over the entire scan range sensitivity of the detection system changes. L*a* peaks as a group always exhibit higher intensities than L*β* peaks.



**Figure 7.** X-ray map of a different sample than **Figure 5**. *Left*: Yttrium map. R*ight*: Calcium map: *Top right*: Fluorine map. Circles on Ca map delineate Ca bright spots that correspond to bright spots on Y map. (More corresponding spots of lesser intensity are found on careful inspection of the two maps). Several correspondences are highlighted on the F map; more also are seen by close inspection. At least 12 and perhaps 20 yttrofluorite grains are present.

Table 1. Average REE content at Round Top Mountain<sup>a</sup>.

Element	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
ppm	217	20.3	79.8	10.4	28.5	10.4	0.17	10.3	3.5	31.0	7.8	32.4	7.1	56.4	8.8

<sup>a</sup>: Data from NI 43-101 Preliminary Economic Assessment [27].

area in the rhyolite, or 2.5 grains per square mm. Next we assume that the EPMA sampled to a maximum depth of 5  $\mu$ m (penetration of electron beam) and that sampled grains at the surface did not extend below that depth in size. A 1-mm (1000- $\mu$ m) cube of the rhyolite can be considered to comprise 200 such 5- $\mu$ m-thick "layers" and thus the cube contains 200 × 2.5, or 500 yttrofluorite grains. Viewed from a mining processing standpoint, each crushed chunk for the anticipated TMRC heap leach, with a nominal crush size of ~1 - 1.5 inches (~25 - 38 mm), would contain, rounded off, on the order of 10 to 25 million yttrofluorite grains.

#### 3.6. Electron Microprobe Maps: Other Elements-Rubidium

**Rubidium** has a number of specialized industrial and scientific applications but overall its market as a commodity is limited in value. For example, the US currently does not produce any rubidium, but has been importing its needs from a single pegmatite mine in Canada, which is now closed and exporting stockpile supplies. Some Rb, and its partner element Cs, have been recovered in leaching experiments with dilute sulfuric acid performed on Round Top Mountain rhyolite.

**Figure 8** indicates that most of the Rb, and presumably the Cs, in the rhyolite substitutes for K in the orthoclase feldspar. Since the feldspars are largely insoluble in dilute sulfuric acid, the source of most of the leached Rb is presumed to be the annite-type mica that is an accessory mineral dispersed throughout the rhyolite [24] [25] [31] [32]. The small, white spots on the Rb map are presumed to be grains of annite mica, with a higher Rb content than the K-spar.

# 3.7. Electron Microprobe Maps: Other Elements—Uranium and Thorium

**Uranium** is an important potential byproduct at Round Top, one that is saleable with a reasonably long-term and transparent marketplace demand. Much of the U is recovered in bench-scale leach tests with dilute sulfuric acid. **Thorium**, however, is also released in that process. This mildly radioactive element has only a small current market; the promising thorium nuclear power reactor is not yet a reality so a market for Th fuel has not developed. Thorium is seen as a penalty in mining since it is regulated as a radioactive waste in many venues and therefore by legislation it requires proper isolation and secure storage.

In **Figure 9** the U and Th bright spots coincide, indicating residence in similar host minerals. The figure informs us that U and Th will leach together since they reside in the same host minerals. Other optical microscopy and electron probe microanalysis studies have identified a number of U-Th minerals in the Round Top rhyolite [24] [25] [27] [31]. Note that as is typical for Round Top mineralization, the distribution of U- and Th-containing minerals is both disperse and random.

# 3.8. Electron Microprobe Maps: Other Elements—Tin and Zirconium

**Tin** and **zirconium** also are potential valuable byproducts at Round Top. **Figure 10** shows that these two minor elements are dispersed in the rhyolite in their chief mineral hosts, cassiterite  $(SnO_2, tetragonal)$  and zircon  $(ZrSiO_4, tetragonal)$ . These minerals have been identified in prior studies by optical microscopy and electron probe microanalysis. The zircons also contain zirconium's highly valued cousin, hafnium, which assays in the bulk rhyolite rock at a level of nearly 80 ppm.

Unfortunately, neither of these minerals is soluble in the dilute sulfuric acid that would be used at Round Top Mountain to recover the YHREEs. Extraction would require mechanical beneficiation with expensive fine grinding to release the cassiterite and zircon from their locked positions in the groundmass of the rhyolite. Preliminary laboratory studies suggest that fine grinding of the spoils after the acid heap leach could be feasible. The leaching damages the integrity of



**Figure 8.** *Left*: Rb X-ray map. *Right*: K X-ray map. Most of the Rb is seen to be substituting for K in the K-spar, light areas surrounding dark albite feldspar phenocryst cores. Several small brighter areas are present on the Rb map. These most likely are grains of annite  $(KFe^{2+}_{3}AlSi_{3}O_{10}(OH)_{2})$ , monoclinic) or related mica in which Rb has been concentrated.



**Figure 9.** *Left*: Uranium X-ray map. *Right*: Thorium X-ray map. Not surprisingly, the distributions of U and Th in the rhyolite are seen to largely coincide. The half-dozen brightest grains closely overlap, as do several less intense bright spots.

the rhyolite and could result in lower costs to reach a fine particle size by grinding.

# 3.9. Electron Microprobe Maps: Other Elements—Niobium and Tantalum

**Niobium** and its close geochemical relative **tantalum** are both enriched in the Round Top Mountain rhyolite. They are found chiefly in the mineral solid



**Figure 10.** *Left:* Tin X-ray map. *Right:* Zirconium X-ray map. The four bright Sn spots do not coincide with any of the Zr bright areas. (Careful measurement of the location of the Sn spot on the right side of the map shows it does not overlap either of the two large Zr areas).

solution of columbite ((Fe,Mn)Nb<sub>2</sub>O<sub>6</sub>)—tantalite ((Fe,Mn)Ta<sub>2</sub>O<sub>6</sub>), both orthorhombic. Nb is an important alloy in high strength metals and "coltan" ore is widely sought to extract Ta for use in the capacitors essential for cell phones and other electronic devices. Despite the relatively high value of these elements, **Figure 11** suggests that extraction of the columbite—tantalite grains would be extremely difficult. The fine grain size and the dispersed and random distribution of the material would require expensive grinding to create particles that free the target mineral. As with the cassiterite and zircon, post-leach grinding and release might be economically feasible if the acid leach attack sufficiently weakens the rhyolite and favorably lowers its crushing strength.

#### 3.10. Significance

BSE and characteristic X-ray maps reveal the fine grain size and apparently random and dispersed spatial distribution of the yttrofluorite that hosts Round Top's valuable YHREEs. The yttrofluorite grains do not appear to cluster at special mineralized locations, e.g., in pores or along cracks in the rhyolite. This supports the model of a pervasive late magmatic stage mineralization effected by a supercritical fluid phase [22] [25] [31].

The microprobe maps indicate that mechanical separation of the minuscule yttrofluorite grains would require breaking down the rhyolite to a sub-millimeter scale. Such an operation would be inefficient and prohibitively expensive.

Random and dispersed distributions, and generally small grain sizes, also characterize the occurrences of such other valuable minerals as cassiterite, zircon, and uranium species. Considerable amounts of uranium are recovered by sulfuric acid leaching, but little tin and zirconium. These elements would require fine



**Figure 11.** Niobium and tantalum X-ray map. These two elements occur together at Round Top in the mineral solid solution columbite—tantalite. Distribution of grains appears random and disperse. Only Nb was actually mapped; Ta is included by association.

grinding for release and extraction from the rhyolite.

### **3.11. Future Directions**

Mapping of additional elements by electron microprobe would complement the current study. This could add data to the current mineralization model. Also, mapping of larger areas, but at coarser scale, would provide additional insight into the distribution of the major minerals, *i.e.*, quartz, albite, K-spar, annite and magnetite. This would assist in understanding the earlier phases of magma cooling and mixing processes.

We currently are deriving detailed mineralogical maps from these X-ray maps using a combination of multivariate statistical analysis and GIS (geographic information system) techniques. This approach, using a published software tool, automates the presentation of the relationship between mineralogical composition and rock texture [33].

A comparison study of crush strengths of the rhyolite pre- and post-leaching would suggest whether the acid corrosion weakens the rock sufficiently to render crushing and milling to a fine grain sizes economically feasible. If that should prove to be the case, it would be possible to evaluate the economics of recovery of cassiterite, columbite-tantalite, and zircon.

## 4. Conclusions

These findings confirm that the distribution of YHREEs in Round Top Mountain rhyolite is homogeneous through different orders of magnitude of scale, *i.e.*, from

outcrop (as seen in the companion work in this volume) to sub-thin section. The material thus is ideal for a heap leach operation, where homogeneous feedstock is crucial to consistent and economic operation. The findings also confirm and explain why mechanical separation would prove very difficult and expensive due to the astronomical number of yttrofluorite grains even in a golf-ball-size piece of Round Top rhyolite.

Microprobe mapping has proved important to our understanding of rock processing on a bulk scale. It helps to explain why some elements leach effectively from the rhyolite and others do not. That knowledge can guide optimization of the recovery process, a change in technical approach to recovery, or abandonment of the pursuit of a potential byproduct target element.

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## Disclosure

N.E.P. serves on the Board of Directors of TMRC. He is not and has never been an employee of TMRC, nor has he received any compensation from the research contracts that supported this research. M.P., who managed the UTEP Microprobe Laboratory and performed the analyses, declares no potential conflicts. She received no compensation for participating in the project. L.M.N. declares no potential conflicts and received no compensation for project participation. D.G. is the CEO of TMRC and serves on its Board of Directors. The funding sponsor, TMRC, had no role in the decision to publish the results.

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