Preliminary Report: Raman Spectral Analysis of Poverty Gulch Project Black Sand Minerals

Prepared by Austin Behmer for Charles P. Watson and Carl Lane

Purpose:

The potential resources of the Poverty Gulch Project (PGP) include titanium, zirconium, and Rare Earth Elements (REEs). These valuable elements are found in various minerals, each with different properties that will affect the beneficiation process required for concentration. Identification of these minerals is vital to the future mining operation of the PGP. Namely, what type of equipment is required and the design of processing centers.

Introduction to Raman Spectroscopy:

Raman spectroscopy is a material identification technique which utilizes the Raman scattering effect. When light hits a material, it interacts with its electrons and then scatters the light back out. The energy exchange between the incident light and the electrons of the material can be elastic or inelastic. An elastic energy exchange results in scattered light having the same wavelength as the incident ray. This is known as Rayleigh scattering and comprises over 99% of the light that will be emitted by the material. When light is scattered at higher or lower wavelengths than the incident light it is known as Raman scattering. Materials, such as minerals, have characteristic Raman spectra that have been cataloged in databases. Thus, by obtaining the Raman spectra for a material, it is possible to identify it by matching that data with cataloged spectra. Raman spectra are plotted with an X-axis that represents the Raman shift and a Y-axis that represents the intensity/counts. The Raman shift is the change in wavelength of the scattered light, measured in wavenumbers (cm⁻¹). This shift corresponds to the vibrational energy levels of the molecules in the sample. The intensity/counts show the intensity of the scattered light, measured in counts. This indicates the number of photons detected at each Raman shift, reflecting the strength of the vibrational modes.

Raman Spectroscopy

Materials and Methods:

Sediment from PGP samples 1A 20'-25', 15B 70'-85', 22 15'-20', and 42A 65'-70' were separated into finer material through -20 Mesh, washed to remove organics and fine sediment, panned to heavy mineral sand, and finally dried at 250°F for 30 minutes. The heavy mineral sand was then separated into magnetics and non-magnetics using ceramic block magnets. Visual analysis, selection for Raman scans, and identification was done using a 10-20x magnification binocular microscope.

Raman spectra are obtained using a Renishaw Confocal Raman Microscope provided by the Keck Spectral Imaging Facility at the University of California, Davis. This microscope uses a 785 nanometer (nm) laser with 5x, 20x, and 50x magnification. The microscope allows for varying laser power levels of 1%, 10%, 25%, 50%, and 100%. For the purposes of this study, a power level of 50% is used at 50x magnification. Calibration is done using a silicon (Si) standard slide provided by the facility. Raman spectra is obtained for the Si, with a standard spectrum peak of 520.4 nm and calibrated to within \pm 0.2 nm. Obtained Raman spectra are processed using the optical spectroscopy software Spectragryph Version 1.2.16.1 developed by Dr. Friederich Menges. Mineral identification is done using sample databases provided by the RRUFF Project via work done at the University of Arizona. The databases and sample data are uploaded onto the software and automatically compared. This comparison yields possible material matches with ratings (shown as percentages) that indicate the confidence level in the match. The RRUFF Project website (*RRUFF.info*) also hosts extensive reference plots, which are not compatible with the Spectagryph software, that are used for spectral comparison and identification (RRUFF). The reference plots are required for peak comparison beyond 1200 cm⁻¹ (the limit for the databases compatible with Spectragryph).

Raman Identification of Source Minerals for Titanium, Zirconium, and REEs

Titanium

Ilmenite



Image Credit: Georgia State University (Left), sandatlas.org (middle), collinsdictionary.com(right)

Physical Properties of Ilmenite

- Chemical Formula: FeTiO₃
- **Density:** 4.70-4.79 g/cm³
- Hardness: 5-6 on Mohs scale
- Magnetic Properties: Weakly magnetic
- Crystal Habit: Tabular or thick tabular, often granular or massive
- Luster: Metallic to submetallic
- Crystal System: Trigonal

Description and Formation

Ilmenite, with the chemical formula FeTiO₃, is the primary ore of titanium, a metal crucial for various industrial applications including aerospace, medical devices, and pigments. Ilmenite typically forms in igneous and metamorphic rocks, particularly associated with gabbro, anorthosite, and other mafic intrusive rocks (Farjana et al., 2021).

Ilmenite is also prevalent in heavy mineral sands, coastal deposits formed by the accumulation of dense minerals through the action of waves and currents. These sands are significant sources of ilmenite and other valuable minerals such as zircon and rutile (Gosen et al., 2019).

The beneficiation process of ilmenite involves several stages. Initially, the ore undergoes physical separation techniques like gravity and magnetic separation to concentrate the ilmenite. Further processing is then used to extract titanium dioxide (TiO₂), the primary commercial product derived from ilmenite (Bulatovic, 2010; Khalloufi et al., 2021).

Occurrences

Ilmenite has over 1000 reported occurrences in the United States (*Mindat.org*) and is mined from heavy mineral sand deposits on the east coast. It is also widely distributed across the globe, with significant deposits found in the heavy mineral sands of Australia, India, and South Africa (USGS, 2021).

Raman Identification



Fig 1. Images of sampled ilmenite crystals taken at 50x. A) Ilmenite 1. B) Ilmenite 2. C) Ilmenite 3.

Ilmenite was identified in the magnetic and weakly magnetic portions of all PGP samples. It appears as black to dark gray, subhedral, subangular-subrounded crystals with metallic to vitreous luster. Sampled ilmenites are roughly 200-400 micrometers (μ m) in diameter (Fig. 1).

Reference spectra (Fig.2A) were consistent across the observed RRUFF catalog. They display a defining major peak at roughly 680 cm⁻¹, and more minor peaks at 370 cm⁻¹ and 220 cm⁻¹ (Fig.2A dashed lines). Ideal matching spectrum was produced for Ilmenite 1 (Fig.2B). Once a Raman spectral identification was confirmed, the visual appearance of this crystal was used in further selection. This led to further Raman spectral identification of ilmenites (Fig.2C).

Visually ilmenite was initially difficult to distinguish between magnetite and hematite. The dark color, concentration in magnetics, and surface alterations made positive identification tenuous at best. However, with the obtained Raman spectrum for ilmenite, it is typically distinguishable from hematite and magnetite (Fig. 3). Visual and Raman identification of these minerals can be complicated by solid solutions between minerals or simply inclusions of one into the other (Fig. 4)



Fig. 2. Ilmenite Reference Spectra and Sample Ilmenite from PGP. (Dashed lines indicate major peaks used for identification). **A)** Ilmenite reference via RRUFF Raman Spectral Database, Ilmenite Ref.1 (Top, Orange), Ilmenite Ref. 2 (Bottom, Red). **B)** Sampled PGP ilmenite, Ilmenite 1 (Top, Blue), and Ilmenite Ref. 1 (Bottom, Orange). **C)** Spectra from three ilmenites from PGP Samples, Ilmenite 1 (Top, Blue), Ilmenite 2 (Middle, Red), and Ilmenite 3 (Bottom, Light Blue).



Fig. 3. Stacked Spectrum of Sampled Ilmenite on Ilmenite, Magnetite, and Hematite Reference Spectra. Sampled ilmenite, Ilmenite 1 (Top, Blue), ilmenite reference, Ilmenite Ref.1 (Top Middle, Orange), magnetite reference, Magnetite 1 (Bottom Middle, Red), and hematite reference, Hematite Ref. 1 (Bottom, Light Blue).



Fig. 4. Stacked Spectrum of Sampled Mineral Solid Solution on Reference Spectra. (Dashed lines indicate major peaks used for identification). Sample spectra with peaks associated with magnetite, hematite and ilmenite, Magnetite-Hematite-Ilmenite 1 (Top, Blue) over magnetite reference spectrum, Magnetite Ref. 1 (Top Middle, Orange), hematite reference spectrum, Hematite Ref. 1 (Bottom Middle, Red), and ilmenite reference spectrum, Ilmenite Ref. 1 (Bottom, Light Blue)

Rutile



Rutile Image Credit: Mindat.org

Physical Properties of Rutile

- Chemical Formula: TiO₂
- **Density:** 4.23-4.25 g/cm³
- Hardness: 6-6.5 on Mohs scale
- Magnetic Properties: Non-magnetic
- Crystal Habit: Prismatic, acicular, often in radiating aggregates
- Luster: Adamantine to submetallic
- Crystal System: Tetragonal

Description and Formation

Rutile (TiO₂) is a titanium dioxide mineral and one of the most important sources of titanium. It typically forms in high-temperature and high-pressure metamorphic rocks such as eclogites and amphibolites, as well as in igneous rocks like granite and pegmatites (Anthony et al., 2001). Rutile is also a major constituent of heavy mineral sands, where it is mined as an important source of titanium (Bulatovic, 2010; Gosen et al., 2019).

The beneficiation process of rutile involves physical separation techniques such as gravity and magnetic separation to concentrate the mineral. Subsequent processing steps, including chlorination and smelting, are employed to extract titanium dioxide (TiO₂), which is used extensively in the production of pigments, coatings, and other industrial applications (Khalloufi et al., 2021).

Associated and Solid Solution Minerals

Rutile is commonly associated with minerals such as quartz, hematite, magnetite, ilmenite, and zircon. It often occurs with titanite (sphene), anatase, and brookite, which are other polymorphs of TiO₂ (Triebold et al., 2007). Rutile can also form solid solutions with niobium and tantalum oxides, where these elements partially substitute for titanium in the crystal structure (Frost et al., 2007).

Occurrences

Rutile has over 1000 reported occurrences in the United States (Mindat.org) and is mined from heavy mineral sand deposits on the east coast. Rutile is also widely distributed globally, with significant deposits in the heavy mineral sands of Australia, South Africa, and India (USGS, 2021).

Raman Identification



Fig 5. Images of sampled rutile crystals taken at 50x. A) Rutile 1. B) Rutile 2. C) Rutile 3.

Rutile was identified in the nonmagnetic portion of all PGP samples. It appears as small subangular crystals (semi-prismatic/cubic crystal faces). It has an earthy to waxy luster and is roughly 200-300 μ m in diameter (**Fig.5**). Its color varies between sampled crystals from dark reds to pastel pinks, reds, and greens. Every rutile scanned produced an ideal rutile Raman spectrum with sampled peaks corresponding to reference peaks at 235 cm⁻¹, 438 cm⁻¹, and 610 cm⁻¹ (**Fig.6**).



Fig. 6. Rutile Reference Spectra and Sampled Rutile Spectra. (Dashed lines indicate major peaks used for identification). **A)** Rutile Reference Spectra via RRUFF database, Rutile Ref. 1 (Top Blue), Rutile Ref. 2 (Bottom, Red). **B)** Sampled rutile, Rutile 1 (Blue). **C)** Stacked sampled rutile on reference spectrum, Rutile 1 (Top, Blue), Rutile 2 (Top Middle, Orange), Rutile 3 (Bottom Middle, Red), Rutile Ref. 1 (Bottom, Light Blue).

Titanite



Titanite Image Credit: Mindat.org

Physical Properties of Titanite

- Chemical Formula: CaTiSiO₅
- **Density:** 3.48-3.60 g/cm³
- Hardness: 5-5.5 on Mohs scale
- Magnetic Properties: Non-magnetic
- Crystal Habit: Wedge-shaped crystals, often elongated or tabular
- Luster: Adamantine to resinous
- Crystal System: Monoclinic

Description and Formation

Titanite, also known as sphene, is a calcium titanium silicate mineral (CaTiSiO₅) found in a variety of igneous and metamorphic rocks such as granites, diorites, syenites, gneisses, and schists. It forms under various temperatures and pressures, typically during the crystallization of granitic magmas or high-grade metamorphism (Deer et al., 2013).

Associated Minerals

Titanite is commonly associated with minerals such diopside, chlorite, epidote, apatite, allanite, magnetite, ilmenite, and amphiboles (Klein, 2002).

Rare Earth Elements (REEs) in Titanite

Titanite can incorporate various REEs into its crystal structure, enhancing its economic potential, particularly in regions where REEs are in high demand. The REEs commonly found in titanite include cerium (Ce), neodymium (Nd), and lanthanum (La), which substitute for calcium within the crystal lattice. The incorporation of REEs occurs due to the similar ionic radii and charge of these elements compared to calcium (Hughes et al., 1997).

Mining and Economic Importance

While titanite is not typically mined as a primary ore on a commercial scale, it has garnered interest for its REE content in certain geological settings. In some regions, titanite is extracted as a byproduct during the mining of other titanium and iron-rich minerals such as ilmenite, rutile, and magnetite (Klein, 2002) The economic viability of extracting REEs from titanite depends on the concentration and accessibility of these elements within the ore body.

Occurrences

Titanite has over 1000 reported occurrences in the United States and is widely distributed globally (Mindat.org)

Significant occurrences of titanite include:

- The Alps, Europe
- Bancroft, Ontario, Canada
- The Adirondack Mountains, New York, USA
- The Ural Mountains, Russia
- Localities in Norway and Austria

Raman Identification

Titanite is a major component of the non-magnetic heavy mineral sands. It is yellow, vitreous, and semitransparent. It forms wedge and diamond shapes and is found in large quantities across all the PGP samples. Its long axis can range from 200 to over 800 μ m in length (Fig. 7). Its short axis ranges from 50 to 400 μ m in width (Fig. 7). Major Raman peaks associated with Titanite occur at a shift between 1100 cm⁻¹ and 2200 cm⁻¹ (Fig. 8). Sampled titanite crystals match the reference spectra in peak pattern and shift (Fig. 8)



Fig. 7. Images of Sampled Titanite Crystals taken at 50x. A) Titanite 1. B) Titanite 2.



Fig. 8. Titanite Reference Spectra and Sampled Titanite Spectrum. Boxes indicate same spectral range for each plot. Dashed lines indicate major peaks used for identification. **A)** Titanite reference spectrum via the RRUFF Spectral Database. **B)** Sampled titanite spectrum, Titanite 1 (Top, Orange), Titanite 2 (Bottom, Light Blue).

Zirconium

Zircon



Zircon Image Credit: Mindat.org

Physical Properties of Zircon

- Chemical Formula: ZrSiO₄
- **Density:** 4.6-4.7 g/cm³
- Hardness: 7.5 on Mohs scale
- Magnetic Properties: Non-magnetic
- Crystal Habit: Prismatic, often with dipyramidal terminations
- Luster: Adamantine to vitreous
- Crystal System: Tetragonal

Description and Formation

Zircon (ZrSiO₄) is a zirconium silicate mineral and a major source of zirconium, which is used in various industrial applications, including ceramics, refractory materials, and nuclear reactors. Zircon typically forms in igneous rocks, particularly granites and syenites, and is a common accessory mineral in sedimentary and metamorphic rocks (Hoskin & Schaltegger, 2003). Due to its high resistance to weathering, zircon often accumulates in placer deposits and heavy mineral sands (Gosen et al., 2014).

The beneficiation process of zircon involves several stages, including gravity separation, electrostatic separation, and magnetic separation, to concentrate the zircon mineral. Subsequent processing steps are used to extract zirconium, which is then purified for various industrial uses (Bulatovic, 2010).

Associated and Solid Solution Minerals

Zircon is commonly associated with minerals such as quartz, ilmenite, rutile, monazite, and xenotime. It can contain trace amounts of uranium, thorium, and rare earth elements, which can substitute for zirconium in the crystal structure (Triebold et al., 2007; Hoskin & Ireland, 2000).

Occurrences

Zircon has over 1000 reported occurrences in the United States (*Mindat.org*) and is mined from heavy mineral sand deposits on the east coast. Zircon also is widely distributed globally, with significant deposits in the heavy mineral sands of Australia, South Africa, and India (USGS, 2021).

Raman Identification



Fig 9. Image of sampled zircon crystal at 50x magnification. A) Zircon 1. B) Zircon 2. C) Zircon 3.

Zircon is abundant in the non-magnetic heavy mineral sands across all PGP samples. They are euhedral semitransparent long prisms with bipyramidal terminations on both ends. They are clear to faint pink in color with a vitreous to pearly luster. They have a long axis that ranges in length from 200 to over 800 μ m, and a short axis that ranges from 50 to 150 μ m in width (Fig. 9). Reference zircon spectra show two major peak ranges. One between 150 cm⁻¹ and 600 cm⁻¹ and the other between 1200 cm⁻¹ and 1700 cm⁻¹ (Fig. 10A). Sampled zircon crystals showed corresponding peak patterns and locations. Notably, the intensities of the peaks in the 150 cm⁻¹ and 600 cm⁻¹ range are lower in the sampled zircons relative to the reference spectra (Fig. 10A,B). Peak intensity normalization was done to compare the lower range

peak locations of the sampled zircons to the reference. Matching peaks are observed near 200 cm⁻¹, 310 cm⁻¹, 355 cm⁻¹, 440 cm⁻¹, and 640 cm⁻¹ Raman shifts (Fig. 11).



Fig. 10. Zircon Reference Spectrum from RRUFF Spectral Database and Sampled Zircons. Boxes indicate peak ranges used for identification. **A)** Zircon reference spectrum, Zircon Ref. 1. **B)** Sampled zircon crystals, Zircon 1 (Top, Orange), Zircon 2 (Middle, Red), and Zircon 3 (Bottom, Green)



Fig. 11. Stacked Sampled Zircons Over RRUFF Database Reference Spectrum. (Dashed lines indicate major peaks used for identification). Sampled zircons, Zircon 1 (Top, Blue), Zircon 2 (Top Middle, Orange), Zircon 3 (Bottom Middle, Red), and zircon reference, Zircon Ref. 1 (Bottom, Light Blue).

Rare Earth Element (REE) Bearing Minerals: NOT YET IDENTIFIED Possible Rare Earth Element Bearing Minerals of the PGP Samples *Monazite*



Monazite Image Credit: Mindat.org

Physical Properties of Monazite

- Chemical Formula: (Ce, La, Nd, Th)PO₄
- **Density:** 4.6-5.4 g/cm³
- Hardness: 5-5.5 on Mohs scale
- Magnetic Properties: Weakly magnetic
- Crystal Habit: Prismatic to tabular crystals, often granular or massive
- Luster: Resinous to vitreous
- Crystal System: Monoclinic

Description and Formation

Monazite is a phosphate mineral that is a significant source of rare earth elements (REEs), particularly cerium (Ce), lanthanum (La), neodymium (Nd), and thorium (Th). It typically forms in igneous and metamorphic rocks, such as granites, pegmatites, and gneisses. Monazite can also be found in sedimentary environments, particularly in placer deposits, where it accumulates due to its resistance to weathering and high density (Deer et al., 2013).

Associated and Solid Solution Minerals

Monazite is commonly associated with minerals such as zircon, xenotime, apatite, and allanite. It can form solid solutions with other phosphate minerals, incorporating significant amounts of REEs due to the similar ionic radii and charge of these elements (Gupta & Krishnamurthy, 2005).

Mining and Economic Importance

Monazite is mined primarily for its REE content. The extraction process typically involves physical separation techniques such as gravity and magnetic separation to concentrate the monazite from ore, followed by chemical processing to extract the individual REEs. Monazite is particularly valued for its thorium content, which can be used in nuclear applications, as well as for its REEs, which are critical for various high-tech industries (Orris & Grauch, 2002).

Occurrences

Monazite has over 600 reported occurrences in the United States and is actively mined at the Mountain Pass Mine in California (*Mindat.org*). Proposed rare earth mineral mining projects inside the United States include the Round Top Rare Earths and Critical Minerals Project (Texas), the Bokan-Dotson Ridge Project (Alaska), and the Bear Lodge Project (Wyoming) (*Thediggings.com*).

Significant occurrences of monazite include:

- The coastal sands of Brazil and India
- The alluvial placers of Australia
- Mountain Pass, California, USA
- The central and southern African regions

Bastnäsite



Bastnäsite Image Credit: Mindat.org

Physical Properties of Bastnäsite

- Chemical Formula: (Ce, La, Nd)(CO₃)F
- **Density:** 4.9-5.2 g/cm³
- Hardness: 4-4.5 on Mohs scale
- Magnetic Properties: Weakly magnetic
- Crystal Habit: Tabular to prismatic crystals
- Luster: Vitreous to resinous
- Crystal System: Hexagonal

Description and Formation

Bastnäsite is a carbonate-fluoride mineral that is a primary source of light rare earth elements (LREEs), including cerium (Ce), lanthanum (La), and neodymium (Nd). It typically forms in carbonatites, hydrothermal veins, and alkaline igneous complexes. Bastnäsite is often associated with other REE minerals and is a significant ore in REE mining operations (Castor & Hedrick, 2006).

Associated and Solid Solution Minerals

Bastnäsite is commonly found with minerals such as monazite, xenotime, fluorite, barite, and parisite. It can form solid solutions with other REE carbonates, which allows it to accommodate a range of REEs in its structure (Zheng, 2003).

Mining and Economic Importance

Bastnäsite is extensively mined for its rich REE content. The mining process involves crushing the ore, followed by beneficiation techniques such as flotation, gravity separation, and magnetic separation to concentrate bastnäsite. Chemical processing is then used to extract the REEs. Bastnäsite is a critical mineral for the production of REE-based materials used in various high-tech applications, including electronics, magnets, and renewable energy technologies (Castor & Hedrick, 2006).

Occurrences

Bastnäsite has over 100 reported occurrences in the United States and is actively mined at the Mountain Pass Mine in California (*Mindat.org*). Proposed rare earth mineral mining projects inside the United States include the Round Top Rare Earths and Critical Minerals Project (Texas), the Bokan-Dotson Ridge Project (Alaska), and the Bear Lodge Project (Wyoming) (*Thediggings.com*).

Significant occurrences of bastnäsite include:

- Mountain Pass, California, USA
- Bayan Obo, Inner Mongolia, China
- The Khibiny Massif, Russia
- The Bear Lodge Mountains, Wyoming, USA

Raman Spectra of Reference REE Bearing Minerals and of Possible REE Bearing Sampled Minerals

Reference Raman spectra of all common REE bearing minerals show a major peak range between 1000 cm⁻¹ and 2000 cm⁻¹. The Raman shifts in this range are typically of far higher intensity and display clearly defined peaks as opposed to the lower peak ranges (Fig. 12, 13, 14). The difficulties determining exact REE bearing minerals via Raman spectra are due to the variation in spectra among the same mineral, such as monazite (Fig. 12), in conjunction with the shared major peak range of the others (Fig. 12, 13, 14).



Fig. 12. Multiple Reference Spectra for the REE Bearing Mineral Monazite Showing Variations in Peak Locations and Intensity. Dashed lines indicate major peak range for monazite exists between 1000 cm⁻¹ and 2000 cm⁻¹.



Fig. 13. Raman Spectra of the REE Bearing Minerals Allanite-(Ce), Bastnasite-(Ce), Cerianite-(Ce), and Cerite-(Ce) (Top to Bottom). Dashed lines indicated shared major peak range among all minerals between 1000 cm⁻¹ and 2000 cm⁻¹.



Fig. 14. Raman Spectra of the REE Bearing Minerals Fluorapatite, Loparite-(Ce), Parisite-(Ce), and Sahamalite-(Ce) (Top to Bottom). Dashed lines indicate major peak range is shared among all minerals between 1000 cm⁻¹ and 2000 cm⁻¹.

Several sampled crystals display major peaks of high intensity in the 1000 cm⁻¹ to 2000 cm⁻¹ range (Fig. 15, 16). However, when these peak locations and patterns are compared to the reference REE bearing mineral spectra, no exact match has yet been found. Slight variances in peak locations, number of peaks, and their relative intensities, results in partial matches and mismatches between the samples and reference spectra.



Fig. 15. Sampled Spectra of Possible Rare Earth Minerals (REM). REM 1-3, display peaks in the range of 1000 cm⁻¹ to 1800 cm⁻¹ (limit of scan for these samples). Dashed lines indicate range of major peaks.



Fig. 16. Sampled Spectra of Possible Rare Earth Minerals (REM). REM 4-6, display peaks in the range of 1000 cm⁻¹ to 1800 cm⁻¹ (limit of scan for these samples). Dashed lines indicate range of major peaks.

Other Identified Minerals

Almandine: Fe₃Al₂(SiO₄)₃



Fig. 17. Stacked Raman Spectra of Sampled Almandine, Almandine 1 (Top, Blue) on Almandine Reference Spectrum from the RRUFF Spectra Database, Almandine Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Anatase: TiO₂



Fig. 18. Stacked Raman Spectra of Sampled Anatase, Anatase 1 (Top, Blue) on Anatase Reference Spectrum from the RRUFF Spectra Database, Anatase Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Diopside: CaMg(SiO₃)₂



Fig. 19. Stacked Raman Spectra of Sampled Diopside, Diopside 1 (Top, Blue) on Diopside Reference Spectrum from the RRUFF Spectra Database, Diopside Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Dravite: NaMg3Al6(BO3)3Si6O18(OH)4



Fig. 20. Stacked Raman Spectra of Sampled Dravite, Dravite 1 (Top, Blue) on Dravite Reference Spectrum from the RRUFF Spectra Database, Dravite Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Epidote: Ca2(Al, Fe³⁺)₃(SiO₄)₃(OH)



Fig. 21. Stacked Raman Spectra of Sampled Epidote, Epidote 1 (Top, Blue) on Epidote Reference Spectrum from the RRUFF Spectra Database, Epidote Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Goethite: FeO(OH)



Fig. 22. Stacked Raman Spectra of Sampled Goethite, Goethite 1 (Top, Blue) on Goethite Reference Spectrum from the RRUFF Spectra Database, Goethite Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Hematite: Fe₂O₃



Fig. 23. Stacked Raman Spectra of Sampled Hematite, Hematite 1 (Top, Blue) on Hematite Reference Spectrum from the RRUFF Spectra Database, Hematite Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Magnetite: Fe₃O₄



Fig. 24. Stacked Raman Spectra of Sampled Magnetite, Magnetite 1 (Top, Blue) on Magnetite Reference Spectrum from the RRUFF Spectra Database, Magnetite Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Orthoclase/Microcline: KAlSi₃O₈ (Both orthoclase and microcline share this formula as they are polymorphs.)



Fig. 25. Stacked Raman Spectra of Sampled Microcline/Orthoclase on Microcline and Orthoclase Reference Spectrum from the RRUFF Spectra Database. Dashed lines indicate major peaks used for identification. Sampled microcline/orthoclase, Microcline/Orthoclase 1 (Top, Blue). Reference spectrum, Microcline Ref. 1 (Middle, Orange), and Orthoclase Ref. 1 (Bottom, Red)

Spessartine: Mn₃Al₂(SiO₄)₃



Fig. 26. Stacked Raman Spectra of Sampled Spessartine, Spessartine 1 (Top, Blue) on Spessartine Reference Spectrum from the RRUFF Spectra Database, Spessartine Ref. 1 (Bottom Orange). Dashed lines indicate major peaks used for identification.

Summary

The heavy mineral sands of PGP contain abundant titanium, zirconium, and REEs. The primary titanium ore mineral, ilmenite, is present in the weakly-magnetic and magnetic portions. The titanium ore mineral, rutile, and the zirconium ore mineral, zircon, are present in the non-magnetic portion. The source mineral for the REEs has not been positively identified. It is possible that REEs may be incorporated into the abundant titanite, zircon, or other minerals in the PGP heavy mineral sands. Future work, possibly including X-ray fluorescence (XRF), can determine the elemental composition of these minerals and determine to what level, if any, REEs are incorporated into their crystal structure. This elemental analysis will allow for a more focused Raman study to identify the source mineral(s) of the REEs of the PGP heavy mineral sands.

References

Anthony, J. W., Bideaux, R. A., Bladh, K. W., & Nichols, M. C. (2001). *Handbook of Mineralogy*. Mineralogical Society of America.

Bulatovic, S. M., (2010). Handbook of Flotation Reagents: Chemistry, Theory and Practice. Elsevier.

Castor, S. B., & Hedrick, J. B. (2006). Rare Earth Elements. In *Industrial Minerals and Rocks* (7th ed., pp. 769-792). SME.

- Deer, W. A., Howie, R. A., & Zussman, J. (2013). *An Introduction to the Rock-Forming Minerals*. Mineralogical Society of America.
- Farjana, S. H., Mahmud, P., & Huda, N. (2021). Life Cycle Assessment for Sustainable Mining. *Elsevier*.
- Frost, R. L., et al. (2011). Raman Spectroscopy of Bastnäsite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 78(4), 1182⁻¹186.
- Gosen, B. S., Hou, B., Song, T. (2019). Heavy mineral sands resources in China. Society of Economic Geologists, 22, 581-593.
- Gupta, C. K., & Krishnamurthy, N. (2005). Extractive Metallurgy of Rare Earths. CRC Press.
- Hoskin, P. W.O., & Ireland, T. R. (2000). Rare earth element chemistry of zircon and its use as a provenance indicator. *Geology*, 28(7), 627-630
- Hoskin, P. W. O., & Schaltegger, U. (2003). The Composition of Zircon and Igneous and Metamorphic Petrogenesis. *Mineralogical Society of America*, 27-62.
- Hughes, J. M., Bloodaxe, E. S., Hanchar, J. M., & Foord, E. E. (1997). Incorporation of rare earth elements in titanite: Stabilization of the A2/a dimorph by creation of antiphase boundaries. *American Mineralogist*, 82, 512-516.
- Khalloufi, M. E., Drevelle, O., & Soucy, G. (2021). Titanium: An Overview of Resources and Production Methods. *Minerals*, *11*, 1425.
- Klein, C. (2002). The Manual of Mineral Science (22nd ed.). John Wiley & Sons, Inc., 641.
- Orris, G. J., & Grauch, R. I. (2002). Rare Earth Element Mines, Deposits, and Occurrences. US Geological Survey Open-File Report 02, 89.

- Triebold, S., von Eynatten, H., Luvizotto, G. L., & Zack, T. (2007). Deducing source rock lithology from detrital rutile geochemistry: an example from the Erzgebirge, Germany. *Chemical geology*, *244*(3-4), 421-436.
- USGS. (2021). Mineral Commodity Summaries 2021. U.S. Geological Survey.
- Zheng, Z., & Greedan, J. E. (2003). Rare Earth Elements and Materials. *Encyclopedia of Physical Science and Technology*, 3.