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Characterization of the Rare-Earth Mineralogy at the Pea Ridge Deposit, Missouri

By C. W. Whitten and R. J. Yancey

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	mm	millimeter
gal	gallon	µm	micrometer
in	inch	mt	metric ton
kg	kilogram	oz/st	ounce per short ton
km	kilometer	pct	percent
m	meter	ppm	part per million

CHARACTERIZATION OF THE RARE-EARTH MINERALOGY AT THE PEA RIDGE DEPOSIT, MISSOURI

By C. W. Whitten[1] and R. J. Yancey[2]

ABSTRACT

Iron ore deposits in south-central Missouri have emerged as a possible resource for the rare-earth elements. The Pea Ridge Iron Mine is one such deposit. Rare-earth minerals at the Pea Ridge Iron Mine are contained in breccia pipes consisting primarily of silicon oxides and feldspars. These pipes extend up through the magnetite ore body and appear to be alterations and replacement of earlier hematite. The mineralogy of these pipes is very complex and varied, which could complicate the concentration and extraction of the rare-earth minerals.

This U.S. Bureau of Mines report represents a study by characterization of the mineral phases to assess the amenability and development of concentration and extraction techniques. Previous characterization of rare-earth minerals has been mainly by transmitted light microscopy. This method along with reflected light microscopy, scanning electron microscopy, and X-ray diffraction was used to identify and characterize the rare-earth and associated minerals.

The minerals identified were the major ore minerals, magnetite and hematite; the rare-earth phosphates, monazite and xenotime; the rare-earth silicate, allanite; the minor associated minerals, cassiterite, pyrite, and apatite; and the gangue minerals, feldspar, quartz, and actinolite.

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INTRODUCTION

Located 95 km southwest of St. Louis, the Pea Ridge Deposit is part of the southeast Missouri Iron Metallogenic Province. Structurally, the iron deposit is within St. Francois igneous terrain on the northern flank of the Ozark Dome. A distinct magnetic anomaly at the location was documented by an airborne magnetometer survey in 1950. Subsequent surveys and drilling led to the development of the deposit, with milling operations coming on line in February 1964.

The ore deposit at Pea Ridge Iron Mine is generally viewed as a residual liquid injection of a phosphatic, iron-rich differentiate from deep silicic magma. The major core minerals are magnetite and hematite in association with quartz, amphibole, feldspar, apatite, fluorite, barite, pyrite, and a variety of other minor minerals. Intruding porphyritic rhyolite, the dike-like ore body, dips nearly vertical and strikes north 60° east. In plain view, it is somewhat crescent shaped with concavity to the south. The size and spatial relationship of mineralized zones vary vertically, with an approximate maximum length of 900 m and a width of 200 m. The iron-rich injection extends to an unknown depth, and both it and the host rock rhyolite are Precambrian.[3]

Breccia pipes containing rare-earth minerals, apatite, fluorite, barite, and at some locations gold mineralization (0.2 ppm), which relates to 0.006 oz/st, extend vertically in the northern convex portion of the deposit and are present northward in the host rock for an unknown distance. The breccia pipe swarm has individual pipes varying from a few meters to over 35 m in diameter through the mine workings (figs. 1-2). The cross-cutting relationship of the breccia pipes to both the magnetite ore body and host rhyolite indicates a late magmatic pyroclastic event followed by a hydrothermal mode of mineral deposition. The pipes are the primary source of rare-earth minerals at the mine.

Pea Ridge Iron Mine rare-earth mineralization may be of economic importance because the average tenor is ~12 pct rare-earth oxides (REO) with an estimated 600,000 mt in reserve. The average grade of the major rare-earth ore bodies are ~7.5 pct at Mountain Pass, CA (bastnasite), 8 pct in the carbonate iron ore rocks of Bayan Obo, China, and ~2 pct in the placer-type deposits along the coasts of India.[4]

The workability of this ore body is presently the main emphasis of the rare-earth research project being conducted by the U.S. Bureau of Mines.

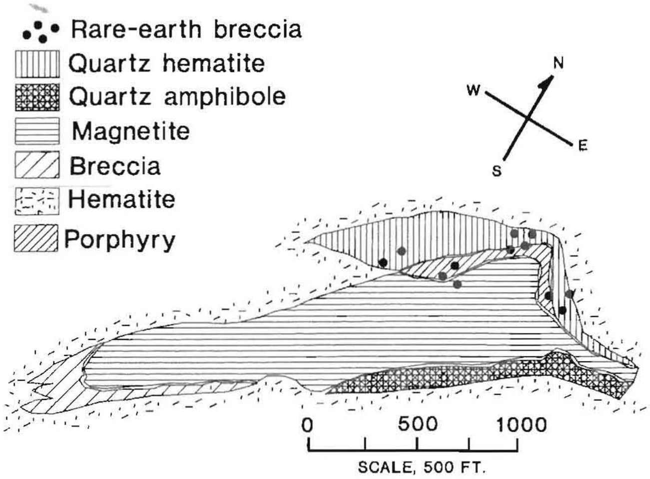

Figure 1.—Map of 2,275-ft level at Pea Ridge.

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[3] Emery, J. Geology of the Pea Ridge Iron Ore Body. Ore Deposits of the United States, 1933-1967, AIME, NY, 1968, pp. 359-369.

[4] Mahadevan, T. M. Rare-Earth Resources. Mater. Sci. Forum, v. 30, 1987, pp. 18-20.

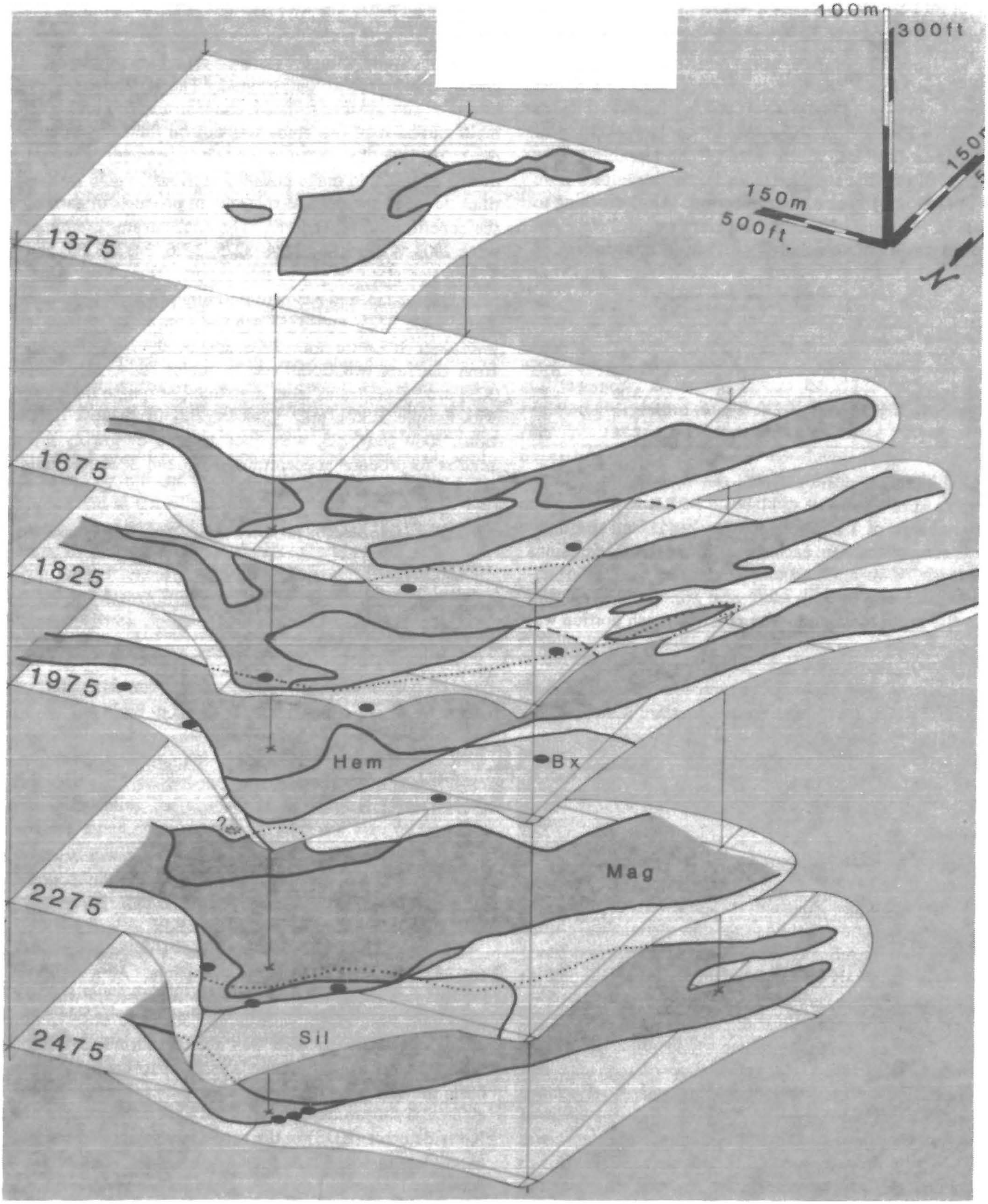

Figure 2.—Vertical three-dimensional map of Pea Ridge breccia pipes. (Courtesy of Missouri Geological Survey)

DESCRIPTION OF MATERIAL

Two types of samples were received from the Pea Ridge Iron Mine. The first sample consisted of a 55-gal drum of a low-grade material. This was labeled Pea Ridge rare earth PRRE 102. The second sample consisted of 11 separate samples, which were of considerable higher grade than the first sample (table 1). Both samples were >6 in (150 mm) in size when received. After crushing to <0.75 in (19 mm) in size, the separate samples were put through a roll mill to achieve <0.25 in (6 mm) in size.

Table 1.—Partial chemical analysis

Sample	Elemental, wt pct			
	Fe	Ce	La	Y
PRRE 102 . .	0.81	0.53	0.54	0.28
PRRE 103 . .	4.59	4.69	3.09	.51
PRRE 104 . .	5.05	4.90	3.16	.63
PRRE 105 . .	4.43	4.23	2.75	.61

One-kilogram portions from the separate high-grade samples were combined and labeled PRRE 103. Using an initial charge of 1 kg, both the low-grade and the high-grade composites were each stage ground to achieve minus 400 mesh. Two hundred and fifty grams of -0.25-in material was added to each successive grind until ~100 g of plus 400 mesh remained. The plus 400-mesh portion was screened into three size fractions (plus 40, plus 200, and minus 200), and samples from each were mounted for future microscopic analysis. This procedure was repeated yielding PRRE 104. It was repeated a third time with the final grind to minus 200 mesh and labeled PRRE 105.

For this study, samples were classified into three categories: raw, crushed, and ground. The ground category has three subcategories: head, concentrate, and tail. The main emphasis of this study was not on the raw samples due to the lack of availability and brittle behavior exhibited during attempts to make polished sections. Table 2 identifies the head sample and subsequent products of each of the beneficiation procedures. The concentrates examined were 2903, 3069, 3095, 3224, 3225, 3226, 3232, 3233, and 3234. For clarification in this report, 2903, 3069, 3224, 3225, 3232, 3233, and 3234 are flotation products. Samples 2903, 3069, 3225, and 3233 are the concentrates from a phosphate flotation with 2908 and 3070 being the tails from the first two flotations. Samples 3224, 3232, and 3234 are concentrates from a sulfide-phosphate flotation, with sample 3235 a tail. Concentrates from these flotations, 3069 and 3225, were then treated by gravity separation to produce concentrates 3095 and 3226 and tails 3096 and 3227, respectively.

Table 2.—Identification numbers of samples and products

Sample	Crushed	Ground head	Concentrate	Tail
PRRE 102 . .	2901	2902	2903	2908
PRRE 103 . .	3040	3149	3069, 3095	3070, 3096
PRRE 104 . .	3152	3228	3224, 3225, 3226	3227
PRRE 105 . .	3231	3236	3232, 3233, 3234	3235

DESCRIPTION OF PROCEDURES USED

Optical methods were used to identify and characterize minerals of the Pea Ridge Deposit and their intergrowths with one another. Polished sections were studied with reflected light, and polished grain thin sections were studied in both reflected and transmitted light. The two major rare-earth minerals encountered in this study (monazite and xenotime) have very similar physical properties making correct identifications difficult. Reflected light microscopy was used to make preliminary identification of the rare-earth minerals. The reflectance of monazite and xenotime is ~15 pct, while the gangue phases reflectance is ~5 to 8 pct and the metallic phases are in the range of 18.6 for ilmenite to 44.4 for chalcopyrite. Reflectance was not the only property used in the identifications, but was the initial identifying criterion. The scanning electron microscope (SEM) was used to make the determination of the mineral and to analyze semiquantitatively the elemental composition of phases. Transmitted light microscopy and X-ray diffraction were also utilized.

The small size of most of the grains studied made mineral identifications difficult to impossible. As a result of this phenomenon, transmitted light microscopy was not used unless the grains were large enough to observe the different properties. This was not the normal course of the study. X-ray diffraction was used to determine the basic mineral phases present after beneficiation. Minor elemental substitutions determined with energy dispersive X-ray detector (EDS) in the rare-earth minerals were not identified as specific minerals other than monazite or xenotime.

The mounted samples were coated with carbon, examined, and photographed with a Hitachi[5] S-570 SEM. The SEM has an Everhart-Thornly secondary electron detector,[6] a GN solid-state backscatter electron detector, Kevex 8000 EDS, and a Peak wavelength dispersive (WDS) unit attached.

The EDS and WDS units were utilized in combination to determine semiquantitatively the elemental abundances of the phases in the mineral samples. The EDS system was used for the identification of all elements with masses greater than sodium. The WDS system was used for identification of carbon, oxygen, and fluorine. A five-point process was used for semiquantitative analysis of energy dispersive spectrums. This includes atomic peak identification, detection of extraneous peaks, Gaussian deconvolution of the rare-earth overlapped peaks, and ZAF computer program correction with the ASAP computer program modifier. No reduction of the WDS data was done.[7]

DISCUSSION OF RESULTS

The rare-earth phosphates, monazite ($CeLaPO_4$) and xenotime (YPO_4) are by far the most abundant rare-earth element (REE) bearing minerals present. However, monazite is present in much greater concentrations than xenotime. This observation is verified by both the chemical and SEM analysis. The best examples of monazite and xenotime were found as large euhedral crystals in the raw sample and as large liberated fragments, 1 to 4 mm, in the coarser crushed samples. Physical colors of the rare-earth minerals range from brown-black to red-brown. Reflected light microscopy indicated there were two phases present in the red-brown fragments based on the internal reflections observed. Monazite shows red and blue reflections, and xenotime has a slight yellow internal reflection with the red and blue. SEM analysis shows the xenotime is locked in the monazite, indicating a disseminated texture of the xenotime in the monazite (fig. 3). Along with the xenotime, chalcopyrite and hematite are included in the monazite. Examination of the brown-black particles with reflected light yielded virtually no yellow internal reflections, indicating the absence of xenotime (fig. 4). SEM analysis again confirms this. There are also varying degrees of colors between these two, and the amount of xenotime decreased as the dark color became more pronounced. In many instances, xenotime was also associated with zircon (fig. 5) as inclusions in the quartz. This was a valuable aid in distinguishing between the two rare-earth minerals.

To a much greater extent, the monazite and xenotime were identified as being associated with the gangue, specifically quartz or alkali feldspar. Intergrowths with these minerals are manifested in several basic types. The most common textures observed are space-filling crystal growths in brecciated materials and simple mutual boundary intergrowths with feldspar and quartz (fig. 6). Also noted are mottled or embayment types of intergrowths. In several instances, an argument can be made for vein-like replacement texture in some of the gangue minerals (fig. 7). The sizes of the locked particles vary greatly depending upon the size of associated gangue particle, 1 mm to submicron for the monazite-xenotime. The monazite-xenotime particles range down in size to 37 μm with the majority >74 μm.

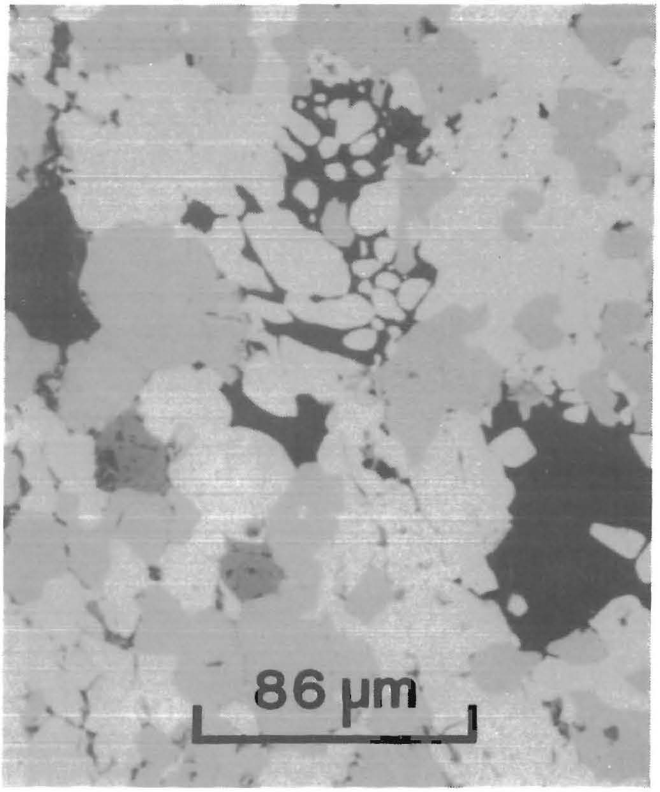

Figure 3.—Xenotime (gray), monazite (white), quartz (dark gray), and holes (black).

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[5] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

[6] Goldstein, J., D. E. Newbury, P. Echlin, D. C. Joy, C. Flori, and E. Lifshir. Scanning Electron Microscopy and X-ray Microanalysis. Plenum, 1981, p. 147.

[7] KEVEX Corp. (Santa Cruz, CA). Energy Dispersive X-ray Microanalysis: An Introduction. 1983, p. 48.

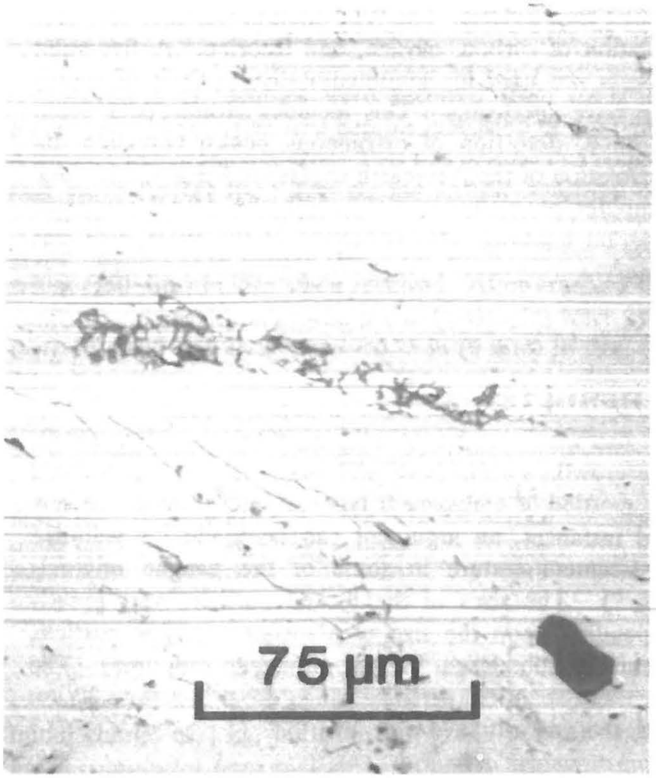

Figure 4.—Xenotime absent monazite (white), vein of hematite, and quartz (black).

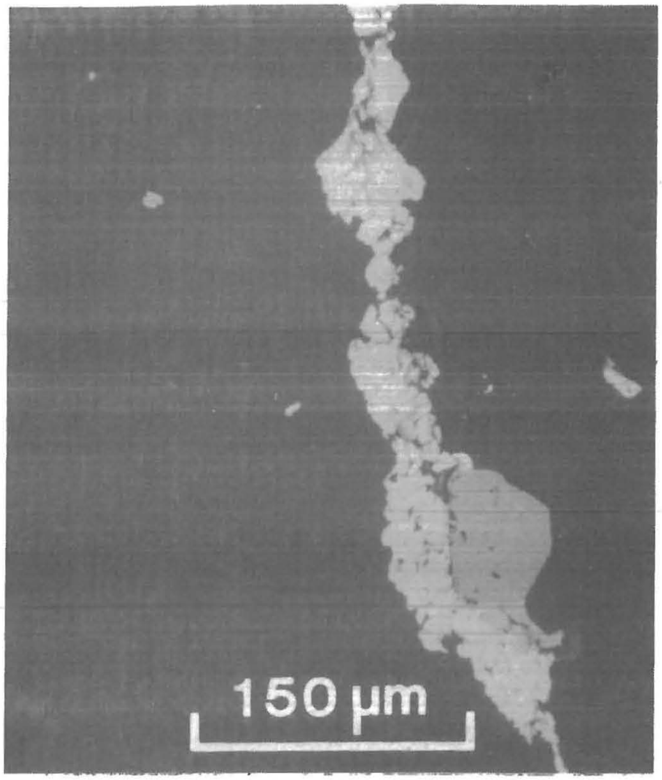

Figure 5.—Xenotime (white) with zircon (gray) in quartz (black).

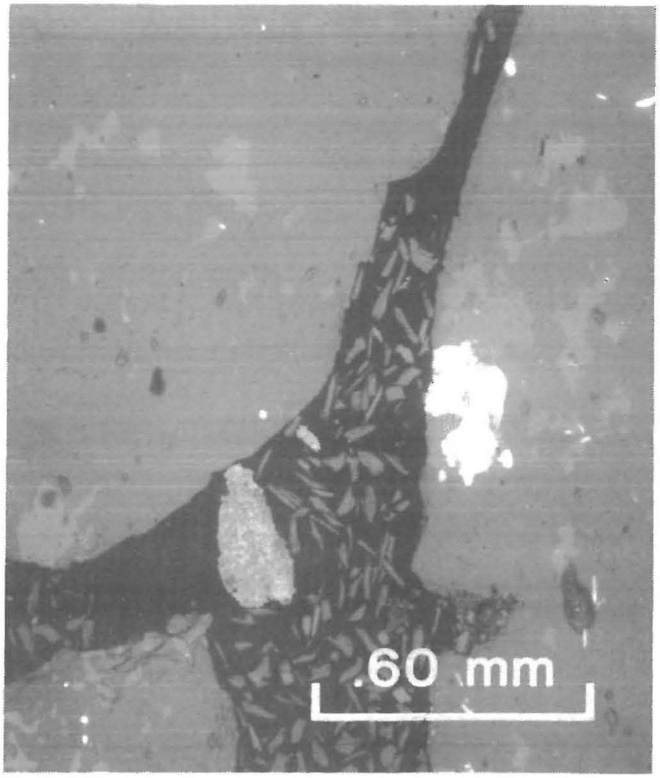

Figure 6.—Monazite (white) in quartz (dark gray) and apatite (light gray).

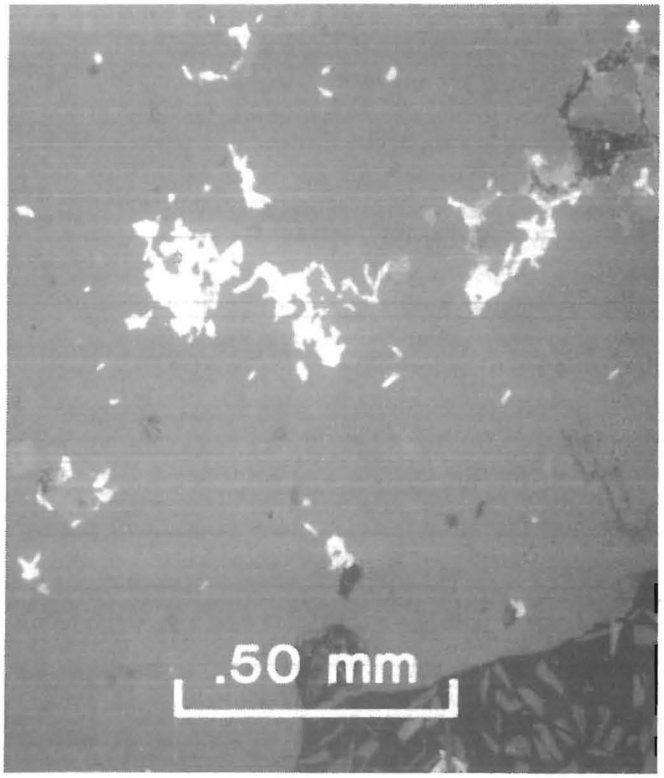

Figure 7.—Xenotime (white) in fracture fill in quartz (dark gray) and apatite (light gray).

Although quartz is harder than the rare-earth minerals, monazite 5.5 and quartz 7, grinding to a mesh of minus 200 produces liberation of the rare earths. There are still middling particles, which consist of gangue, either quartz or feldspar, that have rare-earth values present in a solid solution and are in association with rare-earth minerals (fig. 8). These fine-grained relationships indicate that it will be very difficult to treat by the usual methods of beneficiation. The overall percentage of these grains is small, <5 pct, based on visual observations and should be considered as rare-earth minerals during beneficiation and examined further if a concentration method is warranted.

Of less common occurrence are monazite-xenotime particles that were associated with calcite. The boundaries of the calcite indicate that formation was that of open-space filling first, with the quartz forming second, then the rare-earth minerals (fig. 9). Present in these particles is an appreciable concentration of thorite. The thorite formed as small inclusions in the monazite, and thorite is also present as a substitution in small concentrations in the monazite. The size of the individual thorite grains is commonly as small as 0.1 μm and the largest is about 1 μm. A fine grind of minus 400 mesh will still leave most, if not all, of the thorite grains locked with the monazite or xenotime. To a large extent, when thorite or thorium is present, calcium is also present either as $CaPO_4$ or $CaCO_3$ inclusions or calcium as a substitution in the monazite.

Other rare-earth values include allanite and REE's substituted for calcium in apatite ($CaPO_4$). The calcium phosphate contains up to 0.5 pct substituted REE's. The phosphate concentrate produced at Pea Ridge contains ~5 pct REO. The higher total REO is attributed to the monazite disseminated throughout the apatite.

Also, present in the rare-earth minerals are veinlets of pyrite and hematite and locked particles of chalcopyrite and hematite. These textures appear throughout the whole range of monazite and xenotime particles (fig. 10). Other minerals of secondary importance identified in the crushed ore samples were casserite, apatite, barite, and galena. The identification of sulfides, pyrite, chalcopyrite, and galena, suggests a bulk sulfide flotation to separate them from the rare-earth minerals. The gangue, mainly silicates, suggests a silicate flotation separation technique can be employed. And finally, a phosphate flotation could possibly be employed to separate and concentrate the rare earths from the previously mentioned undesirables such as nonsulfide iron-bearing minerals, sulfides, and silicates.

Because the relative specific gravities of the rare-earth minerals are somewhat higher than the relative specific gravities of the major gangue minerals, a gravity separation to concentrate the rare earths would appear to be feasible. Owing to the presence of magnetite, a magnetic separation is also a possibility as a cleaner step to one of the previously mentioned beneficiation methods.

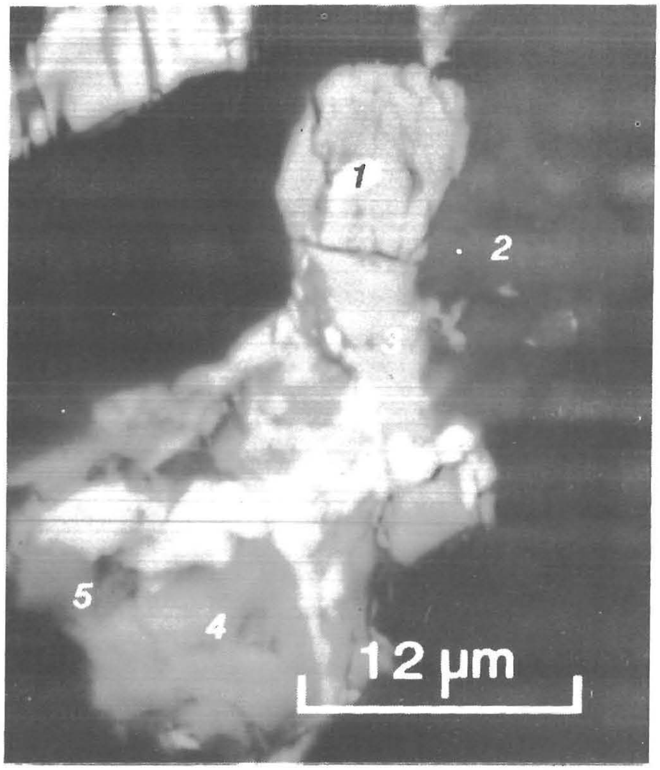

Figure 8.—Middling particle: (1) thorite, (2) alkali feldspar, (3) monazite, (4) alkali feldspar—heavy rare-earth substitutions, and (5) alkali feldspar—light rare-earth substitutions.

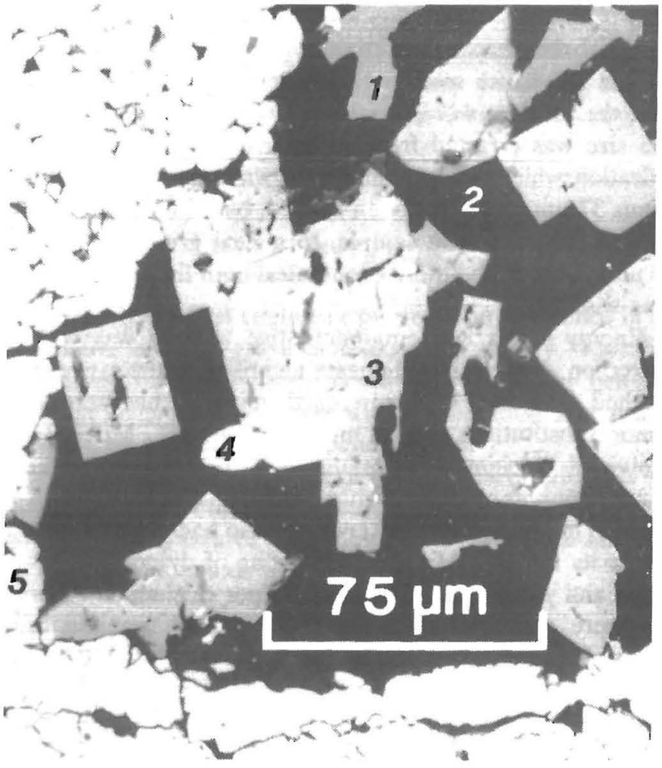

Figure 9.—(1) Xenotime, (2) quartz, (3) calcite, (4) thorite, and (5) monazite.

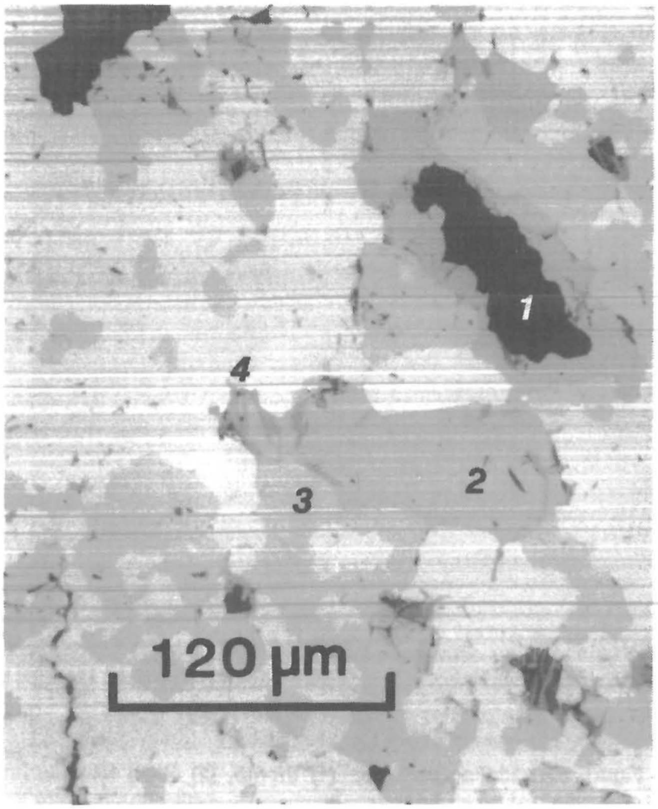

Figure 10.—(1) Quartz, (2) chalcopyrite, (3) xenotime, and (4) monazite.

All of the proposed methods are based on a sample particle size much smaller than 0.25 in (6 mm). Therefore, the samples were ground to minus 400 mesh. The fine size was dictated from preliminary mineral characterization, which indicated liberation was not achieved until minus 37 µm. This has been revised, based on a study of a more representative sample, to a final grind of minus 74 µm. This will be more economical both financially and time wise.

Energy dispersive semiquantitative analysis was conducted on all the mineral phases identified in the raw and crushed samples. Both rare-earth minerals had several minor substitutions in the mineral matrices. Monazite contained calcium, neodymium, and praseodymium in minor amounts with samarium, yttrium, and thorium in trace to minor amounts. Xenotime also had substitutions within its matrix. Minor substitutions of dysposium, erbium, and ytterbium with trace to minor calcium and thorite were detected. The thorite contained uranium in varying concentrations (table 3).

Table 3.—Elemental substitutions, percent

	Monazite	Xenotime	Thorite
P	25.33	19.04	3.97
U	ND	ND	3.47
Lu	ND	1.39	ND
Ca	.65	ND	1.02
La	23.7	ND	1.85
Ce	32.77	ND	3.25
Nd	9.30	ND	ND
Sm	1.44	.61	ND
Th	1.53	.73	46.08
Pr	3.15	ND	ND
Si	1.94	1.02	18.90
Y	ND	53.4	11.99
Gd	ND	1.51	ND
Dy	ND	6.84	3.08
Ho	ND	1.58	ND
Er	ND	6.23	1.60
Tm	ND	1.04	ND
Yb	ND	7.42	2.09

ND Not detected.

The elemental substitutions in these rare-earth minerals are found throughout all the samples. These substitutions do not interfere with the basic separation techniques proposed. The presence of thorite does, however, propose a different set of concerns. The thorite, which usually contains uranium, has to be stockpiled because the world's consumption does not equal present production.

The study of minor constituents is aided by a prior beneficiation process, it allows the examination of these minerals due to their concentration either in the concentrate or the tailings. The ground head samples, 2902, 3149, 3228, and 3236, all have very much the same composition. The gangue is quartz and alkali feldspar at a ratio of ~8 to 1, respectively. The size of the quartz particles ranges from 0.5 to 30 µm; whereas, the feldspar is somewhat smaller, 0.5 to 15 µm.

There are several other minerals and phases present not yet specifically mentioned. These phases are not abundant. These minerals are barite ($BaSO_4$), rutile ($FeTiO_2$), and covelite (CuS). The presence of these minerals, coupled with the previously identified minerals, again indicates a flotation of either sulfides and/or phosphates should be explored. If a gravity method was to be employed, barite would concentrate with the rare-earth minerals and could present a problem if present in appreciable amounts. Barite is present at an approximate concentration of 4 pct. At this time, it is not concentrated enough to pose a problem.

The absence of fluorite in the samples analyzed is quite noticeable because fluorite is present in the breccia pipes at Pea Ridge. The only fluoride analyzed for was in the apatite to discern whether it was fluoro-apatite. The fluoride concentration in the apatite was ~0.1 wt pct.

Based on an assumption that the pyrite was gold bearing in the rare-earth samples, a sulfide flotation was conducted in an attempt to concentrate the gold values. Microscopic analysis was unable to identify any gold occurrences. The examination of these concentrates did provide information concerning the rare-earth minerals. There were rare-earth minerals with pyrite rims, inclusions of pyrite, and simple interlocking particles of pyrite and rare-earth minerals (fig. 11). These particles account for only ~2 pct of the total constituents based on visual observations. A loss of rare earths due to a bulk sulfide flotation would be negligible compared with the total rare earths available. A finer grind would probably separate these grains, but apparently would not be economically feasible.

The gravity concentrates did not yield much additional information to that already gathered. The basal cleavage of the xenotime was more noticeable and aided greatly in distinguishing rare-earth minerals. The abundance of the thorite in this concentrate was to be expected as was the concentration of the ilmenite, hematite, and magnetite network particles.

The tails, samples 2908, 3070, 3096, 3227, and 3235, yielded the usual gangue of quartz, alkali feldspar, and actinolite. A spinel with makeup of aluminum, magnesium, silicon, and iron was identified in four of the samples. Most of these particles were present in the low-grade tailing sample 2908. The amenability of a silicate separation is, at most, a distant possibility because the concentration of the rare earths is low when compared with the gangue minerals.

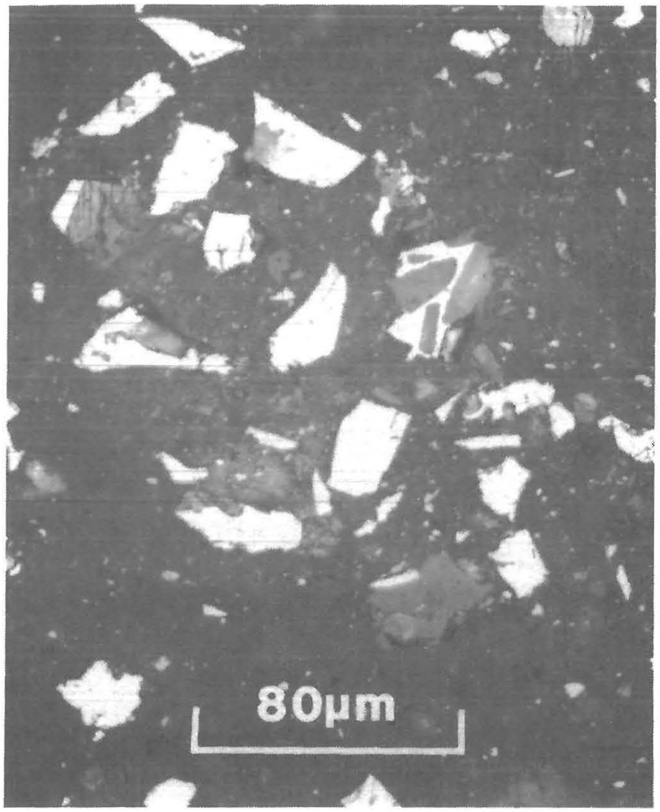

Figure 11.—Pyrite (white) and rare-earth minerals (light gray).

CONCLUSIONS

Mineralogical considerations on beneficiation processes are liberation, mineral speciation, and associations.

The size of the rare-earth minerals, 4 mm to 37 µm, indicates liberation will be achieved with a grind to minus 200 mesh. Speciation of sulfides and silicates along with the iron mineralization suggests flotation as a physical means for separation and concentration. This, coupled with a cleaner flotation of the rare-earth minerals as a phosphate to produce a marketable concentrate, is probably the first route to explore. The difference in the relative specific gravities indicates a gravity separation method for beneficiation could be a secondary beneficiation scheme. A combination of flotation and gravity could be a possibility for beneficiation.

Elemental composition of the rare-earth minerals was touched upon lightly. A more in-depth analysis would give a much clearer indication of the separation and concentration methods to be pursued.

*U.S. Government Printing Office: 1990 — 511-010/40007