USGS
science for a changing world

Chemistry of Selected Core Samples, Concentrate, Tailings, and Tailings Pond Waters: Pea Ridge Iron (-Lanthanide-Gold) Deposit, Washington County, Missouri

By Richard I. Grauch, Philip L. Verplanck, Cheryl M. Seeger, James R. Budahn, and Bradley S. Van Gosen

Open-File Report 2010–1080

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2010

Contents

Figures

Tables

Chemistry of Selected Core Samples, Concentrate, Tailings, and Tailings Pond Waters: Pea Ridge Iron (-Lanthanide-Gold) Deposit, Washington County, Missouri

By Richard I. Grauch, Philip L. Verplanck, Cheryl M. Seeger, James R. Budahn, and Bradley S. Van Gosen

Introduction

The Minerals at Risk and for Emerging Technologies Project of the U.S. Geological Survey (USGS) Mineral Resources Program is examining potential sources of lanthanide elements [rare earth elements (REE)] as part of its objective to provide up-to-date geologic information regarding mineral commodities likely to have increased demand in the near term. As part of the examination effort, a short visit was made to the Pea Ridge iron (-lanthanide-gold) deposit, Washington County, Missouri in October 2008. The deposit, currently owned by Wings Enterprises, Inc. of St. Louis, Missouri (Wings), contains concentrations of lanthanides that may be economic as a primary product or as a byproduct of iron ore production. The specific objectives of the day and a half visit to the mine site and subsequent work were to: (a) meet with the owner (Jim Kennedy, president of Wings); (b) assess the availability of information, (c) obtain a few samples for analyses; and (d) begin a decision process regarding further studies of the deposit and its geologic setting. This report tabulates the results of chemical analyses of the Pea Ridge samples and compares REE contents for world class lanthanide deposits with those of the Pea Ridge deposit. The data presented for the Pea Ridge deposit are preliminary and include some company data that have not been verified by the USGS nor by the Missouri Department of Natural Resources, Division of Geology and Land Survey (DGLS), Geological Survey Program (MGS). The inclusion of company data is for comparative purposes only and does not imply an endorsement by either the USGS or MGS.

Setting

The Pea Ridge deposit is a member of the diverse class of iron oxide copper-gold deposits (IOCG deposits, Williams and others, 2005). It is one of several iron deposits located in southeastern Missouri (figure 1) within the Middle Proterozoic, volcano-plutonic complex of the St. Francois terrane. Host rocks of the iron ore body are altered rhyolite tuff (Nuelle and others, 1992). The deposit area includes the following mappable units: amphibole-quartz rock, heterolithic breccia, pseudobreccia, magnetite, hematite, silicified rock, lanthanide-bearing breccia pipes, mafic dikes, and aplite dikes (Seeger and others, 2001; Seeger, 2004, Nuelle and others, 1992). There are four mapped lanthanide-bearing breccia pipes (X11, V12, X13, V14), which cross-cut the magnetite-hematite ore body and its altered rhyolite host rock (fig. 1). The pipes contain a variety of lanthanide-bearing minerals, including the principal ore minerals monazite and xenotime. Mineral paragenesis and alteration zones are described by Sidder and others (1993). Gold, tin, and silver are unevenly distributed in the breccia pipes and in both the hematite and silicified zones (Husman, 1989).

Mine production ceased in 2001 and the underground workings currently are flooded (2009). The property has two large tailings lakes flanked by extensive waste and tailings piles, most of which have been revegetated, along with several smaller ponds and wetlands. There also are several small, dry

tailings ponds and a variety of ore stockpiles. Altogether there are approximately 180 acres (73 hectares) of waste and tailings (Jim Kennedy, oral commun., 2008).

The size of the lanthanide resource has not been determined. The REE-bearing breccia pipe dimensions are open downward. A copy of an internal company memo, provided by Jim Kennedy (electronic commun., October, 2008), dated 11-22-88 by Larry J. Tucker (retired Pea Ridge mine superintendent) indicates that there is a combined, probable reserve for pipes X11 and X13 of approximately 250,000 metric tons of mineralized rock, grading about 13 percent REE. The reserves were calculated for the volume between levels 2275 and 2675 using a density of 2,000 pounds per 9 cubic feet (lb/ 9 ft$^{3)}$ [approximately 3.56 grams per cubic centimeter (g/cm^3)]. The level numbers represent the depth in feet of the level below the collar of the mine shaft. Whitten and Yancey (1990) report that there are about 600,000 metric tons of REE mineralization with an average grade of approximately 12 percent rare earth oxide. It is not clear what data were used to determine the estimate of 600,000 metric tons. However, a similar, but not equal, value of 600,000 short tons occurs as a note on another internal company memo, provided by Jim Kennedy (electronic commun., October, 2008), dated 10-25-89 by Larry J. Tucker; supporting calculations for the estimate are missing. The tailings contain additional lanthanide resources, primarily because of inclusions of fine-grained, REE-bearing minerals, principally monazite and xenotime, within apatite. The apatite also contains minor amounts of REE in its structure and occurs in variable concentrations throughout the iron ore body (Vierrether and Cornell, 1993).
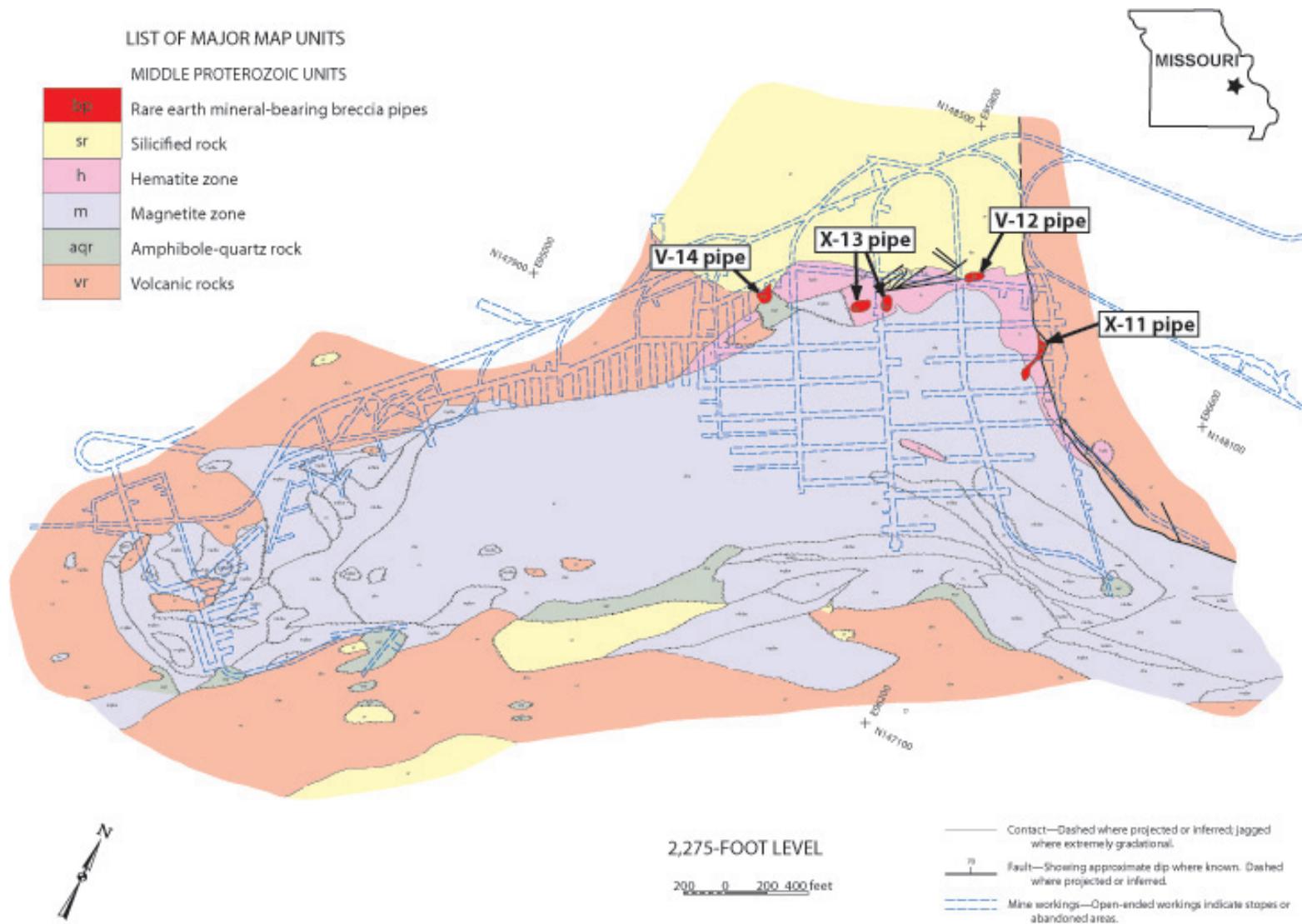
Figure 1. Location and generalized plan map of level 2275 showing location of the four lanthanide-bearing breccia pipes [Modified from Seeger (2004) and Seeger and others (2001)].

Methods

Sampling

Nine samples of core were collected in the Pea Ridge Mine-core shed. Eight of those were from diamond drill hole DDH 14, level 2275 and one from DDH 26, Block 962 (table 1). One core sample (DDH 6, level 2475) was collected from the DGLS McCracken Core Library in Rolla, Missouri. Gamma radiation from Th and U associated with lanthanide ore minerals was used as a guide to sampling high-grade lanthanide samples. Visual inspection guided the selection of representative samples of iron ore and waste material. A final sample was collected from a drum of slightly radioactive material labeled "pulps". The partially destroyed label appears to indicate that the pulps originated on the 2475 level (this level identification seems reasonable as level 2475 was one of the main focal points for lanthanide and gold exploration in the 1980s, which involved core and hammer drilling).

Surface waters were collected from two small pools on the waste and tailings pile and from the largest of the tailings lakes on the mine property (fig. 2 and 3). The three water samples were not filtered. Aliquots for cation determinations were acidified with ultrapure nitric acid.

Two samples of crushed rock from the waste and tailings pile and one from the tailings lake were given to the USGS by Wings. The samples were collected as part of a recent effort by Wings to evaluate the tailings piles, stock piles, and tailings lake. One of the samples is from one of several cores of tailings lake sediments and the other two samples are from trenches cut across the waste and tailings piles.

Analyses

Analytical data contained in this report were produced in-house by the USGS Central Region Mineral Resources Science Center Analytical Chemistry Project, which is administered by the Mineral Resources Program, and externally by SGS Laboratories (formerly XRAL) of Toronto, Canada. Descriptions of the SGS Laboratories' analytical methods, including detection limits can be found at: *http://minerals.cr.usgs.gov/projects/analytical_chem/references.html*.

The 10 core samples, pulp sample, and 3 samples of tailings and waste provided by Wings were analyzed by the SGS Laboratories "55 element ICP-AES-MS sodium peroxide sinter" method (Inductively Coupled Plasma-Atomic Emission Spectroscopy-Mass Spectrometry). Additionally, the pulp and core samples were analyzed by SGS Laboratories' ICP major element analysis using lithium metaborate fusion method, by the USGS utilizing their Instrumental neutron activation by long count method (Budahn and Wandless, 2002), and by the USGS using a short irradiation instrumental neutron activation technique. The latter procedure is similar to that presented in Suzuki and Hirai (1987). The core samples were analyzed for Re and Te by Paul Lamothe (USGS) utilizing a four-acid digestion followed by ICP-MS analysis.

The tailings samples also were analyzed by the USGS wave-length dispersive X-ray fluorescence method (Taggart and Siems, 2002). Densities of the core samples were determined in the USGS Petrophysics Laboratory based on the weight and volume of the sample. Sample weights were determined using an analytical balance. Sample volumes were determined using the buoyancy method, which is based on Archimedes' principle (Hunt and others, 1979).

Analyses of the three water samples were completed in-house. Calcium, magnesium, potassium, sodium, sulfate, and silica and selected trace elements (aluminum, iron, and manganese) were

determined using a Perkin Elmer Optima 3000™ inductively coupled plasma atomic-emission spectrometer (ICP-AES$_{aq}$; Briggs, 2002). Trace elements were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS$_{aq}$) using a method developed by the U.S. Geological Survey (Meier and others, 1994; Lamothe and others, 2002). This method is used to directly determine the elements in the water samples without need for any preconcentration or dilution. Alkalinity (as HCO$_3^-$) was determined using an Orion 960™ autotitrator and standardized H$_2$SO$_4$ (Barringer and Johnsson, 1989).

The analyses listed in tables 1 (solids) and 2 (water) include all of the data returned from the various laboratories. As a result, there are several cases where there is more than one determination for a given element. The preferred method and value (indicated in the table - green shading in the electronic form and gray shading in the printed form) generally are based on the method that provides the best precision and accuracy and a dissolution procedure that is most appropriate for the matrix of the sample being analyzed.

Figure 2.   Small pool on tailings pile, Pea Ridge Mine, site of water sample 08MO01. Note orange alteration above and below water level and well-developed grasslands on reclaimed tailings in background. (P.L. Verplanck standing on the bank).

Figure 3.   Tailings lake, Pea Ridge Mine, site of water sample 08MO03 (C.M. Seeger, J. Kennedy, and A.N. Mariano (left to right), P.L. Verplanck kneeling far right).

Results

Core and Pulp

Lanthanide-plus-Y distribution patterns for pipe X11 samples (PR-1 through PR-9) generally are similar to each other (fig. 4). The exceptions are the Y-controlled downward turn of the patterns of the two REE+Y-rich samples (PR-5, PR-9) and sample PR-10. The latter sample contains at least 85 percent diopside and has a distinctly different pattern, displaying a more positively inclined slope on the heavy REE side of the pattern than those of the other samples. The pulp sample (PR-11), which we think was generated from the X11 pipe, has a pattern and concentration that is intermediate between the two high-grade samples and the iron ore and gangue samples. Our data compare favorably with published work and data generated for the previous mine owners. Composite assays of REE+Y+Th concentrations for each of the four breccia pipes are listed in table 3. Derivative REE+Y patterns are compared to our pipe X11 data in figure 5 (company data in table 3 are from an internal, hand-written, memo by Larry Tucker dated 10/25/89, copy provided by Jim Kennedy (electronic commun., October, 2008). The company assays were performed predominantly by Skyline Labs Inc., of Tucson, Arizona (assay reports provided by Doe Run Mining Company to MGS as part of a cooperative research and mapping program). A REE pattern for grab samples from pipe X13 also is shown in figure 5 (data from Nuelle and others, 1992). The patterns are all similar, especially in consideration of the probable use of different analytical techniques. Our data and those of Nuelle and others (1992) are consistent with, but

do not confirm, the REE distributions and concentrations used by Larry Tucker in his calculation of reserves [internal, hand-written, memo by Larry Tucker dated 11/28/88, copy provided by Jim Kennedy (electronic commun., October, 2008)].

Our density data (table 1) for samples PR-5 and PR-11 (3.83 g/cm^3 and 3.40 g/cm^3 respectively) are consistent with, but do not confirm, the value of approximately 3.56 g/cm^3 used by Tucker in his reserve calculation for lanthanide ore (Tucker memo of 11/28/88). Magnetite ore, samples PR-7 and PR-8 (table 1), have densities of 4.44 g/cm^3 and 4.93 g/cm^3, respectively, which are consistent with the value of 2,000 lb/7ft^3 (approx. 4.58 g/cm^3) used by Tucker in his calculations for magnetite ore reserves at the Pea Ridge Mine (Larry J. Tucker, electronic commun., September 25, 2009).

Table. 3 Composite REE+Y concentrations in percent of the four lanthanide-bearing pipes of the Pea Ridge deposit.

[%, percent; na, not analyzed]
[Data from internal company memo by Larry J. Tucker, dated 10-25-89 (Jim Kennedy, electronic communication, October, 2008)]

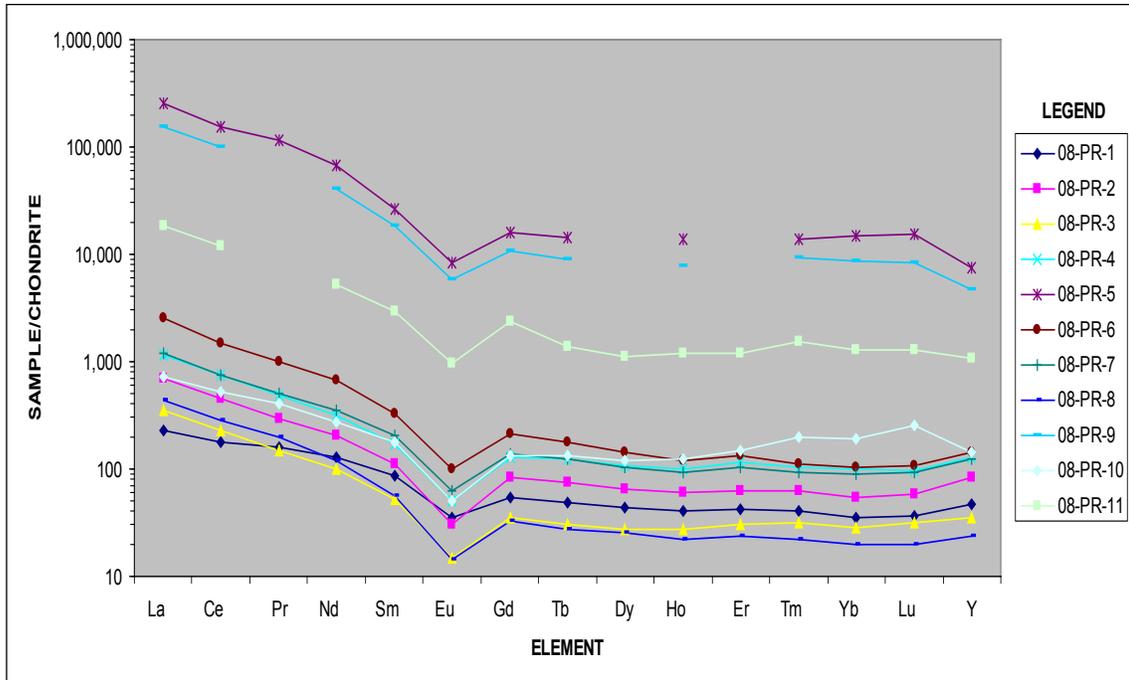| Breccia pipe	X-11	V-12	X-13	V-14
Element				
La	4.45	2.70	2.95	2.05
Ce	8.00	4.50	4.95	4.05
Pr	0.68	na	0.41	0.34
Nd	2.15	na	1.50	1.10
Sm	0.42	na	0.33	0.24
Eu	0.03	na	0.03	0.02
Gd	0.15	na	0.18	0.08
Tb	na	na	na	na
Dy	0.19	na	0.18	0.09
Ho	0.03	na	0.03	0.01
Er	0.09	na	0.09	0.04
Tm	na	na	na	na
Yb	0.16	na	0.12	0.06
Lu	0.02	na	0.01	na
Y	0.70	0.69	0.67	0.36
Th	0.63	na	0.23	0.41

Figure 4. Chondrite normalized REE+Y distribution patterns of core and pulp samples. In this figure and subsequent figures showing REE+Y distribution patterns, the gaps in the patterns are the due to reported qualified concentration values for individual elements (that is values reported as greater than) or to the absence of reported values for individual elements. Chondrite values are from Wakita and others (1971).

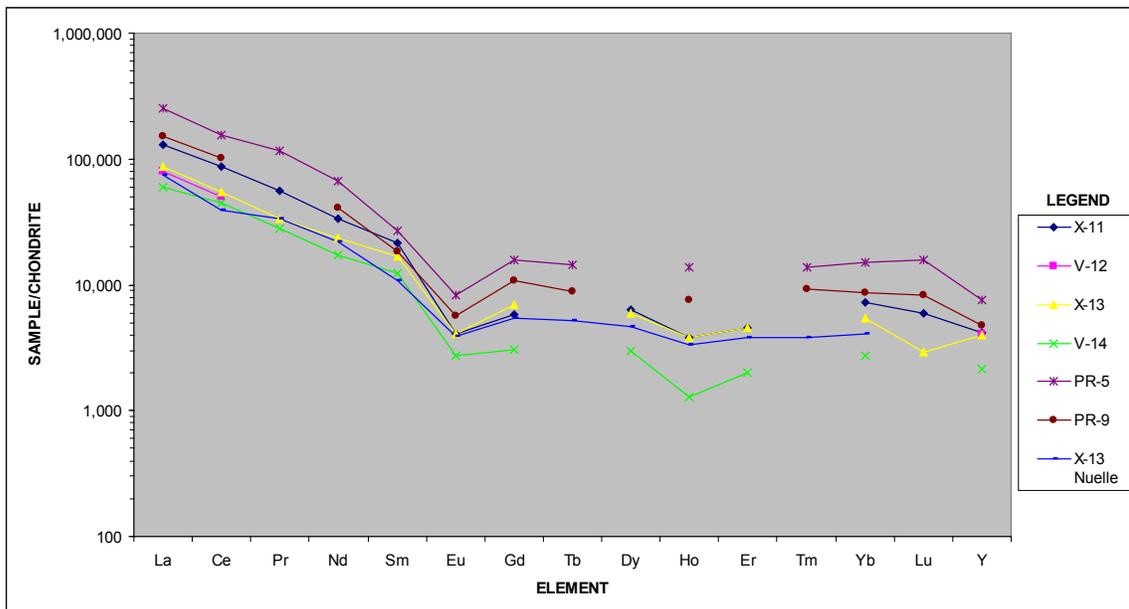**Figure 5.** Chondrite normalized REE+Y distribution patterns of samples from the four lanthanide-bearing breccia pipes of the Pea Ridge deposit. Data for X-11, V-12, X-13, V-14 from memo by Larry Tucker dated 11/28/88; data for X-13-Nuelle from Nuelle and others, 1992; data for other samples from table 1 [see tables 1 and 3 for sample descriptions]. Chondrite values are from Wakita and others (1971).

Tailings

The REE+Y patterns (fig. 6) for the three tailings samples are similar to our Fe-rich samples. The elevated concentrations of REE and Y agree with the data of Vierrether and Cornell (1993), which led them to suggest a REE recovery circuit for the tailings. The circuit is based on the experimental development of a recovery scheme for breccia pipe ores (Whitten and Yancey, 1990) and successful production of phosphate concentrates by the Pea Ridge Iron Ore Company.
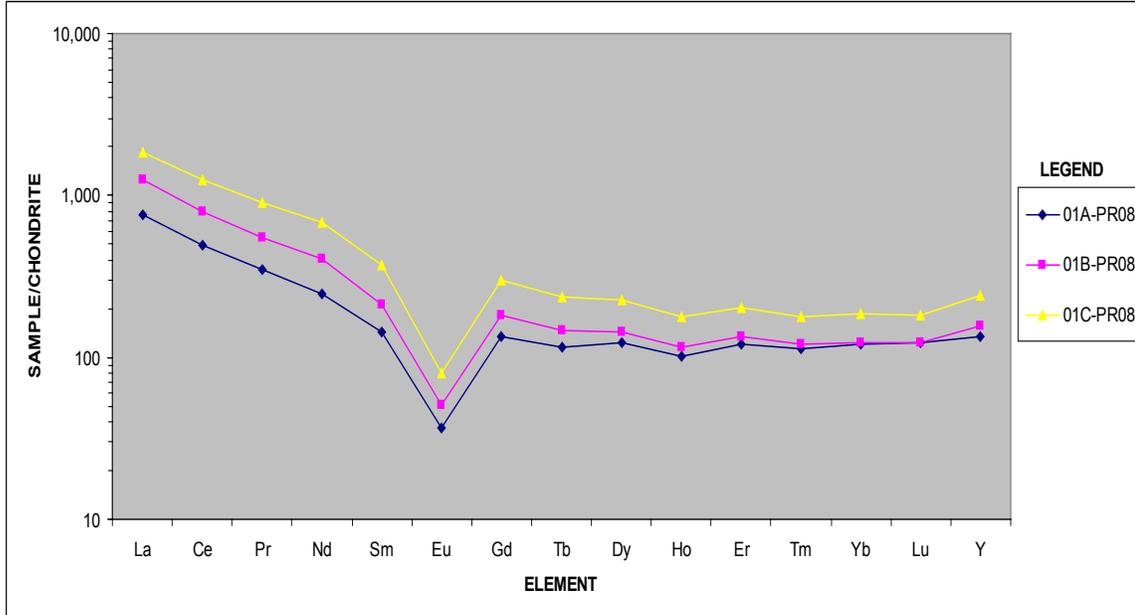

Figure 6. Chondrite normalized REE+Y distribution patterns of three tailings samples from the Pea Ridge deposit. Data from table 1. Chondrite values are from Wakita and others (1971).

Water from Tailings Lake and Pools

The REE+Y patterns of the three water samples (table 2) are similar to each other (fig. 7) and are much flatter than the patterns of the core and tailings samples. The samples from the small pools have lower pH than the lake sample and higher REE+Y concentrations, suggesting a pH affect on the concentration. Two processes may be responsible for this observation: (1) increased dissolution of the REE+Y bearing minerals in the tailings with decreasing pH; and (2) loss of dissolved REEs with increasing pH. Experimental data of Oelkers and Poitrasson (2002) show increasing solubility rates of monazite as a function of decreasing pH below neutrality. Their data and that of Schmidt and others (2006) indicate that both monazite and xenotime tend to dissolve incongruently, which could account for the flattened REE+Y patterns of the water as compared to the rock samples. Some of the difference in total REE concentrations between these three samples also may be a function of partitioning of REEs from the aqueous to the solid phase with increasing pH. Verplanck and others (2004) showed that as pH increased from pH 4 to 6, REEs tend to sorb onto iron precipitates, thus lowering the dissolved concentration of REEs. The low pH in the pools probably is because of the oxidation of sulfide minerals, which are unevenly dispersed in several of the units in the mine (Nuelle and others, 1992).
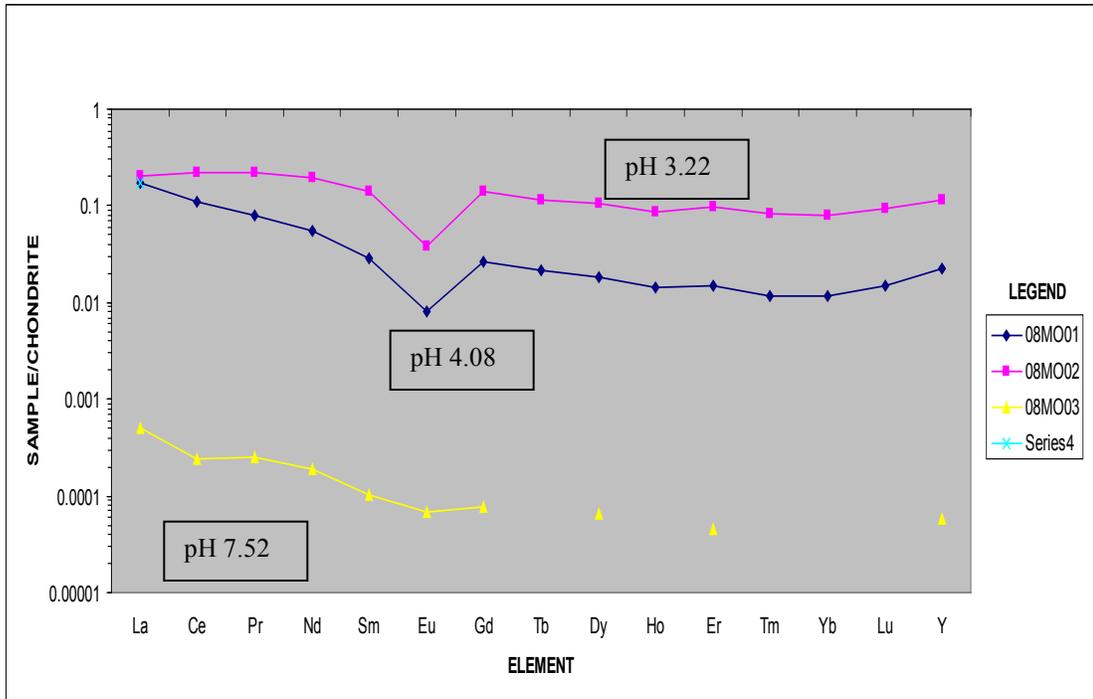
Figure 7. Chondrite normalized REE+Y distribution patterns of three water samples from Pea Ridge tailings lake and pool. Data from table 2. Chondrite values are from Wakita and others (1971).
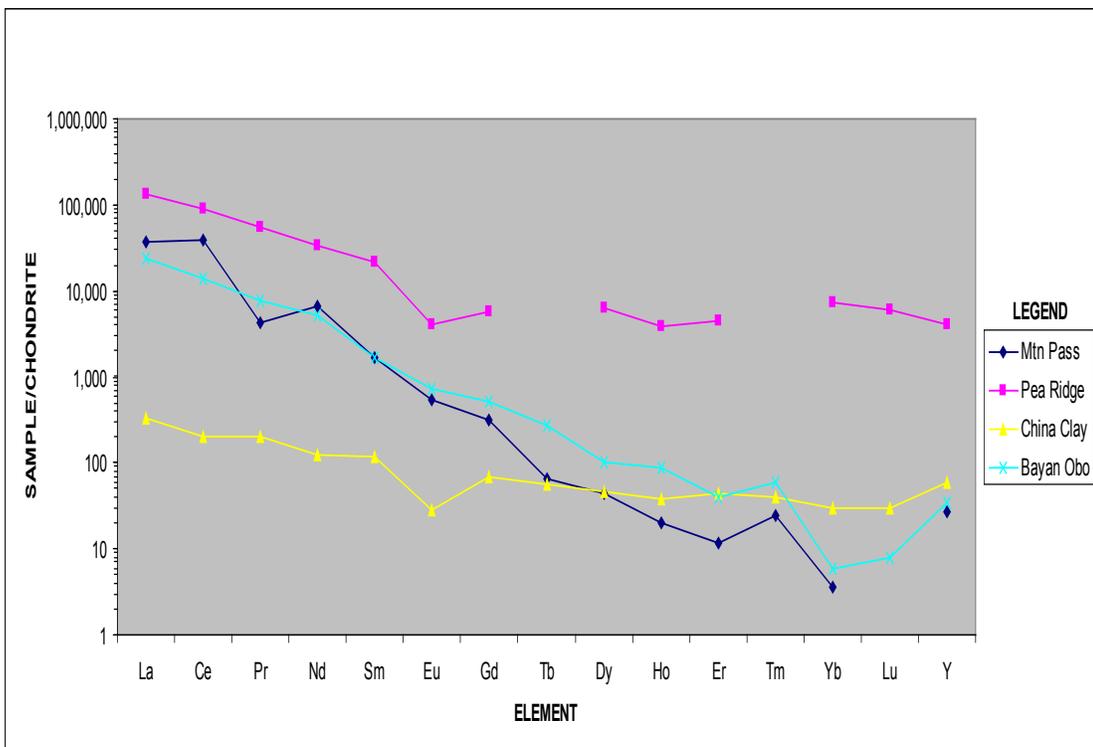

Figure 8. Chondrite normalized REE+Y distribution patterns of world-class lanthanide deposits and the Pea Ridge deposit. Data from table 4. Chondrite values are from Wakita and others (1971).

Comparison to World Class Lanthanide Deposits

With increased demand for REE+Y, anticipated greater need for middle to heavy REE, and decreasing REE exports from China, there is a need to find additional REE+Y resources and to evaluate deposits in terms of the REE distribution in the ore. The grade and tonnage values presented in this report (table 4) are for comparative purposes only; they are **not** compliant with any of the currently (Feb., 2010) accepted reporting standards such as the Canadian Standards of Disclosure for Mineral Projects (National Instrument 43-101) (http://www.msc.gov.mb.ca/legal_docs/legislation/notices/ni43101.pdf) and the Australasian Joint Ore Reserves Committee Code (JORC Code) (http://www.jorc.org/jorc_code.asp). The grade and tonnage values for the individual REE and Y are calculated from tonnage values of the entire deposit and published concentrations of individual elements in either mill feeds (Mountain Pass Rare Earth Deposit), hand samples (Bayan Obo Fe-Nb-REE deposit, China Clay Type Lanthanide Deposits), or drill pulps and hand samples (Pea Ridge deposit).

Two of the World's largest lanthanide deposits are the Bayan Obo Fe-Nb-REE deposit, Inner Mongolia, China and the Mountain Pass Rare Earth deposit, California. They contain approximately 48 million and 2.6 million metric tons of REE+Y oxides, respectively (Berger and others, 2009; Castor and Nason, 2004; Castor, 1991). However, these deposits are dominated by the light REE (table 4). The group of deposits known as China Clay Type Lanthanide Deposits often are cited as the largest known source of low-cost, heavy REE+Y (Grauch and Mariano, 2008). Collectively, the China Clays contain an estimated minimum of 1 million metric tons of REE+Y oxides (Clark and Shuhui Zheng, 1991). Despite its much smaller known reserve of REE+Y oxides (72,000 metric tons), the Pea Ridge deposit apparently contains more of the heavy REE and Y than the Mountain Pass deposit (table 4). The differences in REE+Y distribution between the four deposits are shown in figure 8. The flatter patterns for the China Clay and Pea Ridge deposits reflect their relative enrichment in heavy REE+Y.

Table 4. REE+Y oxide concentrations in metric tons of three world-class lanthanide deposits and the Pea Ridge deposit.

Deposit Oxide	Bayan Obo	Mountain Pass	China Clay	Pea Ridge
La_2O_3	15,267,052	872,120	193,001	18,275
Ce_2O_3	23,720,328	1,279,918	311,762	32,298
Pr_2O_3	1,734,339	106,337	40,529	2,862
Nd_2O_3	6,083,552	288,040	135,197	9,474
Sm_2O_3	616,088	21,939	38,165	1,963
Eu_2O_3	99,822	2,710	3,430	158
Gd_2O_3	247,460	5,420	29,699	808
Tb_2O_3	23,884	413	4,282	nd
Dy_2O_3	56,584	878	22,994	903
Ho_2O_3	12,594	103	4,918	137
Er_2O_3	14,270	155	14,401	430
Tm_2O_3	3,376	52	2,059	nd
Yb_2O_3	2,364	52	10,755	662
Lu_2O_3	490	nd	1,627	88
Y_2O_3	117,798	3,355	187,181	3,942
sum	48,000,000	2,581,490	1,000,000	72,000

Mountain Pass deposit

Estimated reserves of 29 million metric tons of ore at 8.9 percent RE_2O_3 with a 5 percent cutoff (Castor and Nason, 2004 (p. 70).

REE distribution calculated from data in Castor (2008) for RE_2O_3 in concentrate (assumes REE +Y distribution in the concentrate is similar to that in the ore).

Bayan Obo deposit

800 million metric tons of ore at 6 percent RE_2O_3, Berger and others (2009).

REE distribution based on the average of three highly mineralized carbonatite samples from the east ore deposit (Xiao-Yong Yang and others, 2009).

China Clay deposits

Estimated minimum of 1 million metric tons contained RE_2O_3 (Clark and Shuhui, 1991).

REE distribution based on a single ore sample, Grauch and Mariano (2008) and unpublished data.

Pea Ridge deposit

600,000 metric tons of reserves with an average tenor of 12 percent RE_2O_3 (Whitten and Yancy, 1990).

REE distrubution is based on the average of composite assays of samples from four breccia pipes, memo by Larry J. Tucker dated 10-25-89 (Jim Kennedy, electronic communication, October, 2008).

Conclusions

Analytical data for a limited number of hand samples from the Pea Ridge deposit are consistent with, but do not confirm, some of the company data used in calculations of lanthanide and magnetite ore grade and reserves. The Pea Ridge lanthanide resource is high grade and enriched in heavy REE+Y as compared to world class lanthanide deposits such as Bayan Obo (China), Mountain Pass (California), and the South China Clay Type Lanthanide Deposits (southern China). However, the open-ended, probable REE+Y reserve of Pea Ridge is smaller in comparison to the others.

Acknowledgements

References Cited

Barringer, J.L., and Johnsson, P.A., 1989, Theoretical considerations and a simple method for measuring alkalinity and acidity in low-pH waters by gran titration: U.S. Geological Survey Water-Resources Investigations Report 89-4029, 35 p.

Berger, V.I., Singer, D.A., and Orris, G.J., 2009, Carbonatites of the world, explored deposits of Nb and REE—Database and grade and tonnage models: U.S. Geological Survey Open-File Report 2009-1139, 17 p. and database. (Also available at http://pubs.usgs.gov/of/2009/1139/).

Briggs, P.H., 2002, The determination of twenty-seven elements in aqueous samples by inductively coupled plasma-atomic emission spectrometry, in Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02-223, chapter F, 11 p. (Also available at http://pubs.usgs.gov/of/2002/ofr-02-0223/F0203ICPAES_M.pdf).

Budahn, J.R., and Wandless, G.A., 2002, Instrumental neutron activation by long count, in Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02-223, chapter X, 13 p. (Also available at http://pubs.usgs.gov/of/2002/ofr-02-0223/X14INAALong_M.pdf).

Castor, S.B., 1991, Rare earth deposits in the southern Great Basin, in Raines G.I., Lisle R.E., Shafer, R.W., and Wilkinson W.H., eds., Geology and ore deposits of the Great Basin I: Geological Society of Nevada Symposium Proceedings, Reno, p. 523-528.

Castor, S.B., 2008, The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California: The Canadian Mineralogist, v. 46, p. 779-806.

Castor, S.B., and Nason, G.W., 2004, Mountain Pass Rare Earth Deposit, California, in Castor, S.B., Papke, K.G. and Meeuwig, R.O., eds., Proceedings of the 39th Forum on the Geology of Industrial Minerals: Nevada Bureau of Mines and Geology Special Publication 33, p. 68-81.

Clark, A.L., and Shuhui Zheng, 1991, China's rare earth potential, industry and policy, *in* Siribumrungsukha, B., Arrykul, S., Sanguansai, P., Pungrassami, T., Sikong, L., and Kooptarnond, K., eds., Proceedings of International Conference on Rare Earth Minerals and Minerals for Electronic Uses, January 23-25, 1991: Prince of Songkla University, Hat Yai, Thailand, p. 577-601.

Grauch, R.I. and Mariano, A.N., 2008, Ion-adsorption type lanthanide deposits [abs]: Society of Mining, Metallurgy and Exploration Annual Meeting and Exhibit Preliminary Program, p. 40.

Hunt, G.R., Johnson, G.R., Olhoeft, G.R., Watson, D.E., and Watson, K., 1979, Initial report of the petrophysics laboratory: U.S. Geological Survey Circular 789, 74 p

Husman, J.R., 1989, Gold, rare earth element, and other potential by-products of the Pea Ridge iron ore mine, Washington County, Missouri (Contribution to Precambrian Geology No. 21): OFR-89-78-MR, 18 p.

Lamothe, P.J., Meier, A.L., and Wilson, S.A., 2002, The determination of forty-four elements in aqueous samples by inductively coupled plasma-mass spectrometry, *in* Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey: U.S. Geological Survey Open-File Report 02-223, chapter H, 13 p. (Also available at http://pubs.usgs.gov/of/2002/ofr-02-0223/H21&23OFR99-151_M.pdf).

Meier, A.L., Grimes, D.J., and Ficklin, W.H., 1994, Inductively coupled plasma-mass spectrometry—A powerful analytical tool for mineral resource and environmental studies [abs], *in* Carter, L.M.H., Toth, M.I., and Day, W.C., eds., U.S. Geological Survey Research on Mineral Resources—1994, Part A—Program and Abstracts, Ninth V.E. McKelvey Forum on Mineral and Energy Resources: U.S. Geological Survey Circular 1103-A, p. 67-68.

Nuelle, L.M., Day, W.C., Sidder, G.B., and Seeger, C.M., 1992, Geology and mineral paragenesis of the Pea Ridge Iron Ore Mine, Washington County, Missouri — Origin of the rare-earth-element- and gold-bearing breccia pipes: U.S. Geological Survey Bulletin 1989 A-C, p. A1-A11.

Oelkers, E.H., and Poitrasson, F., 2002, An experimental study of the dissolution stoichiometry and rates of a natural monazite as a function of temperature from 50 to 230 °C and pH from 1.5 to 10: Chemical Geology, v. 191, p. 73-87.

Schmidt, C., Rickers, K., Bilderbeck, D.H., and Rong Huang, 2006, In situ synchrotron-radiation XRF study of REE phosphate dissolution in aqueous fluids to 800 °C: Lithos, v. 95, p. 87-102.

Seeger, C.M., Nuelle, L.M., Day, W.C., Sidder, G.B., Marikos, M.A., and Smith, D.C., 2001, Geologic maps and cross sections of mine levels at the Pea Ridge Iron Mine, Washington County, Missouri: U.S. Geological Survey Miscellaneous Field Studies Map MF-2353, 5 sheets, 6 p. (Also available at *http://greenwood.cr.usgs.gov/pub/mf-maps/mf-2353/*).

Seeger, C.M., 2004, Geology and mineralogy of rare earth element-bearing breccia pipes, Pea Ridge Mine, Missouri, *in* Seeger, C.M., ed., Proceedings of the 38th Forum on the Industrial Minerals: Missouri Department of Natural Resources, Geological Survey and Resource Assessment Division, Report of Investigations No. 74, p. 247-259.

Sidder, G.B., Day, W.C., Nuelle, L.M., Seeger, C.M., and Kisvarsanyi, E.B., 1993, Mineralogic and fluid-inclusion studies of the Pea Ridge iron-rare-earth-element deposit, southeast Missouri: U.S. Geological Survey Bulletin 2039, p. 205-216.

Suzuki, S., and Hirai, S., 1987, Instrumental neutron activation analyses of vehicle exhaust particulates as environmental reference material: Analytical Sciences, v. 3, p. 193-197.

Taggart, J.E., Jr., and Siems, D.F., 2002, Major element analysis by wavelength dispersive X-ray fluorescence spectrometry, *in* Taggart, J.E., Jr., ed., Analytical methods for chemical analysis of geologic and other materials: U.S. Geological Survey: U.S. Geological Survey Open-File Report 02-223, chapter T, 9 p. (Also available at http://pubs.usgs.gov/of/2002/ofr-02-0223/T16WDXRF_M.pdf).

Verplanck, P.L., Nordstrom, D.K., Taylor, H.E., and Kimball, B.A., 2004, Rare earth element partitioning between iron oxyhydroxides and acid mine waters: Applied Geochemistry, v. 19, p. 1339-1354.

Vierrether, C.W., and Cornell, W.L., 1993, Rare-earth occurrences in the Pea Ridge tailings: U.S. Bureau of Mines Report of Investigations 9453, 10 p.

Wakita, H., Rey, P., and Schmitt, R.A., 1971, Abundances of the 14 rare-earth elements and 12 other trace elements in Apollo 12 samples — Five igneous and one breccia rocks and four soils: Proceedings of Second Lunar Science Conference, The MIT Press, p.1319-1329.

Whitten, C.W., and Yancey, R.J., 1990, Characterization of the rare-earth mineralogy at the Pea Ridge deposit, Missouri: Bureau of Mines Report of Investigations 9331, p. 9.

Williams, J.P., Barton, M.D., Johnson, D.A., Fontboté, Lluís, deHaller, Antoine, Mark, Gordie, Oliver, H.S., and Marshik, Robert, 2005, Iron oxide copper-gold deposits — Geology, space-time distribution, and possible modes of origin, *in* Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P., eds., Economic Geology 100th Anniversary Volume: Society of Economic Geologists, Littleton, Colo., p. 371-405.

Xiao-Yong Yang, Wei-Dong Sun, Yu-Xu Zhang, and Yong-Fei Zheng, 2009, Geochemical constraints on the genesis of the Bayan Obo Fe-Nb-REE deposit in Inner Mongolia, China: Geochimica et Cosmochimica Acta, v. 73, p. 1417-1435.