

Overview of Rare Earth Element Investigations in Acid Waters of U. S. Geological Survey Abandoned Mine Lands Watersheds

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ABSTRACT

The geochemistry of rare earth element (REE) variations in acid waters is being studied as part of the U. S. Geological Survey Abandoned Mine Lands Initiative in two pilot watersheds, upper Animas, Colorado and Boulder, Montana. The following objectives are under investigation: (1) comparison of acid mine waters and naturally acidic springs, (2) determination of whether the dominant control on REEs in acid waters is source-related or post-dissolution process-related, (3) determination of the role of iron and aluminum colloid formation on the REE patterns, (4) address the utility of REE geochemistry in acid waters as an analogue for the actinides, and (5) produce a Standard Reference Water Sample for REEs. Results demonstrate that the REE concentrations in acid waters increase with decreasing pH but tend to be two to three orders of magnitude lower than ore elements such as Cu and Zn. REE patterns are generally convex-up for waters in the upper Animas, and they are nearly flat with a negative europium anomalies for waters in the Boulder basin. These results reflect predominantly source-related signatures. Natural acid springs are frequently, but not consistently, characterized by a negative Ce anomaly that may be process-related. Field and laboratory experiments indicate that dissolved REEs are affected by iron and aluminum colloid formation but sorption or coprecipitation with aluminum at pH values greater than 4.5 is stronger than with iron. Uranium and thorium, however, show a tendency to be removed from solution more strongly at lower pH (3-4) values, consistent with expected differences in oxidation state and a stronger affinity for iron precipitation.

INTRODUCTION

Rare earth element (REE) geochemistry is a powerful tool for identifying geochemical processes (Brookins, 1989). This has been demonstrated in many petrologic studies but is just beginning to be applied to aqueous systems. REEs have been used as geochemical tracers because of their unique, coherent chemical behavior. The REEs are a suite of fourteen metals from atomic number 57 (La) to 71 (Lu) that have similar chemical and physical properties. There are, however, small differences in geochemical behavior because with increasing atomic number there is a systematic decrease in ionic radius. The REEs are trivalent with the exception of Ce (also 4+) and Eu (also 2+); therefore, the behavior of Ce and Eu relative to the other REEs can

potentially be used as a probe of redox conditions of an environmental system (Loveland, 1989).

Elucidation of the geochemical behavior of REEs in a weathering environment has been hindered by the very low aqueous concentrations, which generally are less than one microgram per liter ($\mu\text{g/L}$) in surface and ground waters. With the advent of inductively coupled plasma-mass spectrometry (ICP-MS) the determination of REE concentrations in waters has become more routine. Concentrations of REEs are usually normalized to a reference standard, such as chondrite or North American Shale Composite (NASC), or to a sample of interest. By normalizing the REE concentrations, the characteristic zigzag pattern due to the increased stability of the even masses is eliminated, and

subtle variations in the REE pattern can be recognized.

Recent studies have demonstrated the use of REE geochemistry in the interpretation of water-rock interactions (Smedley, 1991; Fee and others, 1992; Johannesson and others, 1997). Relatively few studies have investigated the behavior of REEs in an acidic weathering environment (Auque and others, 1993, 1994; Johannesson and others, 1994; Johannesson and Lyons, 1995; Gimeno and others, 1996; Johannesson and others, 1996), and none of these studies have sampled mined areas. Previous investigations have revealed a general decrease in REE concentrations with pH increase, a characteristic convex-up NASC-normalized pattern, and no consistency with respect to Ce anomalies. Interpretations focus on whether these features are source-related (Smedley, 1991; Sholkovitz, 1995) or process-related (Sholkovitz, 1995; Johannesson and others, 1996; Byrne and Sholkovitz, 1996). One of the main interests has been the effect of iron and aluminum colloids on REEs in rivers, estuaries, and seawater, but there has been no direct study of the effect of colloid formation on REE fractionation between aqueous phase and colloidal phase.

As with most elements, the REE concentrations of stream waters may be controlled by water-rock processes along the subsurface flow path as well as the in-stream environment. These processes include dissolution and precipitation of minerals, oxidation and reduction reactions, and adsorption and desorption reactions with secondary minerals or colloidal particles. In most igneous rocks, the dominant rock type in the study areas, the REEs primarily occur within accessory phases, including apatite, zircon, monazite, allanite, titanite, and epidote. Release of the REEs from these minerals is complex owing to the occurrence of accessory phases as inclusions in major mineral phases. Also, some accessory phases are extremely resistant to weathering. Once released from the primary mineral phase, REEs may be sequestered by secondary mineral phases. Detailed mineralogical data including mineral occurrences, compositions, and morphology are needed to unravel this aspect of acidic weathering environments. This part of the

study is in progress and will not be discussed in this overview.

The U. S. Geological Survey (USGS) Abandoned Mine Lands (AML) watersheds are well-suited to investigate the many processes that potentially control the REE geochemistry of acid waters because of the numerous acid water sources and the interdisciplinary approach to watershed characterization. REE geochemistry is being used to try to differentiate between natural and anthropogenic sources of acid waters and metals, as well as to determine processes controlling the fate and transport of metals entering the fluvial system.

This paper is an overview of our investigations into the REE geochemistry of the acidic weathering environment, including water-rock interaction and in-stream processes. Results from field and laboratory investigations are reported. In addition, two new Standard Reference Water Samples were produced to evaluate and control analytical measurements. Such a reference sample has not previously been available.

METHODS

Spring, stream and mine water samples were collected during low flow in the AML pilot watersheds, the upper Animas River basin, Colo. and the Boulder basin, Mont. Water temperature, pH, specific conductance, and Eh were determined on site. The Eh and pH were measured by placing electrodes in a flow-through-cell through which the sample was pumped with a portable peristaltic pump (Ball and others, 1976). The pH electrode was calibrated on site with pH buffers, 1.68, 4.01, 7.00, and 10.00, that bracketed the sample pH value and were equilibrated to the sample temperature. Water samples were filtered through a 142-millimeter (mm)-diameter, 0.1-micrometer (μm)-pore-size filter for major, minor, and trace element analyses. At the USGS Boulder, Colo. facility concentrations of REEs, Zn, U, and Th were determined by ICP-MS (Garbarino and Taylor, 1995) and concentrations of SO_4 were determined by ion chromatography.

At a subset of sampling sites, 2- to 4-liters of unfiltered, unacidified water were collected for

the iron oxidation experiments. These samples were stored at room temperature, and after 6 months, precipitates were concentrated and filtrates were collected using tangential-flow ultrafilters with a nominal cut-off of 10,000 molecular-weight. Filtrates were analyzed by ICP-MS for selected major and trace elements. Precipitates were digested following procedures outlined by Hayes (1993) and analyzed for major and trace elements by ICP-MS. Mineral identification was determined at Ohio State University with X-ray diffraction.

Two well-characterized, acid mine water samples were selected for new Standard Reference Water Samples. Sample PPREE1 is from the Paradise portal, upper Animas River basin, Colorado, and sample SCREE1 is from Spring Creek in the West Shasta mining district of northern California. Fifty liters of each sample were collected and filtration began within three hours of collection in a USGS mobile laboratory truck. Two parallel, 0.1- μm , acid-cleaned, all-plastic plate filters with 293-mm and 142-mm diameters were used, and filtrates were composited into a 50-L acid-washed carboy. Filtration was completed within 1 hour, and the pH of the reference waters was adjusted to less than 2 with concentrated HNO_3 .

At the USGS laboratory in Boulder, Colorado, each reference water was split into 250-milliliter aliquots using a ten position, Teflon cone splitter. The aliquots were capped, sealed with parafilm, and numbered sequentially. Seventeen participating laboratories were sent two aliquots of each reference water with no laboratory receiving sequential numbers. Samples spanning the entire range of numbers were analyzed to allow for recognition of sampling biases.

RESULTS AND DISCUSSION

Standard Reference Water Samples

Seventeen international laboratories, including four USGS facilities, participated in a “round-robin” analysis to determine the “most probable values” (MPVs) for the REEs (table 1). MPVs were determined using a robust statistical

Table 1. Most probable values (MPV) with median absolute deviation (MAD) for two Standard Reference Water Samples. All values in micrograms per liter.

Element	PPREE1		SCREE1	
	MPV	MAD	MPV	MAD
La	80.4	5.9	9.85	0.73
Ce	161.2	7.7	24.6	2.2
Pr	21.2	1.3	4.29	0.28
Nd	92.3	5.7	22.1	0.9
Sm	20.3	1.5	6.71	0.31
Eu	5.95	0.48	1.47	0.07
Gd	23.8	1.7	8.21	0.65
Tb	3.65	0.33	1.34	0.07
Dy	22.0	0.7	8.10	0.34
Ho	4.43	0.09	1.61	0.06
Er	11.9	0.4	4.35	0.21
Tm	1.48	0.05	0.582	0.023
Yb	8.20	0.13	3.39	0.17
Lu	1.12	0.03	0.452	0.014

treatment that is insensitive to outliers (Peart and others, 1998).

In general, there was good agreement in the REE determinations among the participating laboratories. For PPREE1 and SCREE1, 87 and 83 percent, respectively, of the individual laboratories’ results overlap the MPVs. The percent uncertainty for the individual REE concentrations varies from 2 to 9 percent. The REE reference waters are available upon request.

Identifying Source-Water Signatures

Within the upper Animas River watershed in Colorado numerous naturally-occurring acid springs and acid mine waters contribute metals to the streams. One goal of the AML initiative is to define the current baseline conditions in the watersheds and differentiate between natural and mining contributions of metals to the streams. A number of different techniques are being assessed to reach this goal, including identifying source-water signatures using REE geochemistry.

Two subbasins in the Animas basin with different geological characteristics, including bedrock composition and types of alteration and mineralization, were chosen to investigate techniques for identifying source-water signatures. Prospect Gulch (fig. 1) lies within the

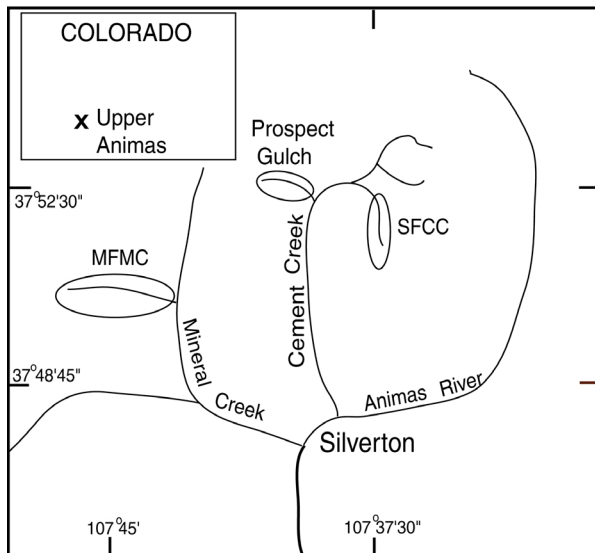


Figure 1. Map of upper Animas River basin. MFMC = Middle Fork Mineral Creek, SFCC = South Fork Cement Creek.

Silverton Caldera, and the bedrock consists primarily of the Burns Formation, a volcanic unit of rhyodactitic flows and tuffs. Alteration ranges from propylitic in the southern part of the basin to quartz-sericite-pyrite and quartz-alunite in the northern part (Bove and others, 1998). The second subbasin, Middle Fork Mineral Creek (MFMC), is located west of the Silverton Caldera and is underlain by the San Juan Formation, thickly-bedded, reworked volcanoclastic deposits that have been intruded by quartz monzonite porphyries. The volcanic rocks surrounding the largest porphyry are altered to varying degrees from quartz-sericite pyrite to propylitic (Ringrose and others, 1986).

In Prospect Gulch, five mine waters (pH 2.4 to 3.6) and four springs (pH 3.3 to 5.7) were sampled during August and September 1997. The REE patterns (fig. 2) display a middle REE enrichment with a maximum at Eu or Gd. Overall, the springs and the mines have similar patterns with the exception of one spring sample, which has a negative Ce anomaly.

During September 1995 five mine waters (pH 3.1 to 5.7) and five springs (pH 3.1 to 6.8) were sampled in the MFMC. The REE patterns display a greater range in shape than the samples from Prospect Gulch. The mine waters have two types of patterns (fig. 3), two samples display a

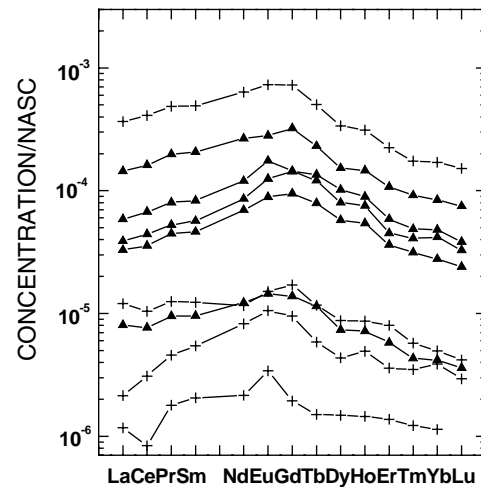


Figure 2. Rare earth element diagram of waters from Prospect Gulch. Concentrations normalized to NASC (Haskin and others, 1968; Gromet and others, 1984). Triangles-mine waters, crosses-natural springs.

more sinusoidal pattern and three display a middle REE enriched pattern. The two samples with the sinusoidal pattern are from draining adits on the north side of the basin, which is predominantly underlain by propylitically altered volcanic rocks, and the three middle REE

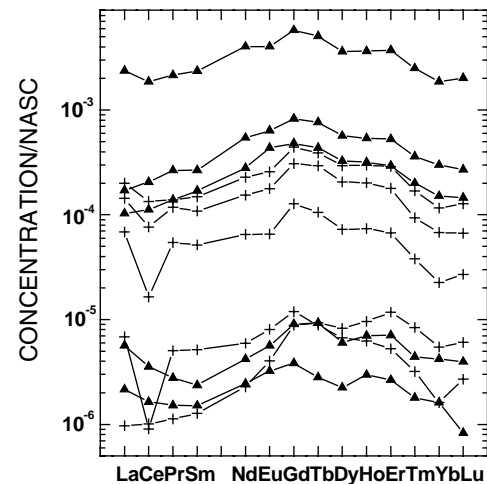


Figure 3. Rare earth element diagram of waters from Middle Fork Mineral Creek. Triangles-mine waters, crosses-natural springs.

enriched mine waters are from the south side of the basin, within or near the quartz monzonite porphyries. The REE patterns of the spring waters display middle REE enrichment with four of the five samples having negative Ce anomalies.

The presence of a negative Ce anomaly most likely reflects differing redox conditions in some of the spring environments as compared with the mine settings. Cerium anomalies have been observed in shallow groundwater samples from the Carnmenellis district, England and are believed to be a result of the oxidation of Ce (III) to insoluble Ce (IV), with subsequent removal (Smedley, 1991). The loss of Ce relative to its neighboring REEs, La and Pr, produces a negative Ce anomaly in the REE patterns. Because Ce anomalies were only observed in some of the spring samples, Ce anomalies may not prove to be a usable source signature. Determinations of whole rock REE compositions of the major geologic units within the subbasins are underway. Preliminary data indicate that the REE patterns of the waters, with the exception of the negative Ce anomaly, reflect the REE compositions of the lithologies along the flow paths.

In the Boulder watershed (Montana) acid mine waters from Crystal Mine and Bullion Mine were analyzed to compare the REE patterns of the Animas water samples with waters derived from different geologic terrains. The two mines occur along a mineralized structure within the Butte Quartz Monzonite of the Boulder batholith (Ruppel, 1963). The REE patterns (fig. 4) are nearly flat with negative Eu anomalies. The host monzonite is characterized by a relatively flat REE pattern with a negative Eu anomaly (Lambe, 1981).

Because the REE patterns of the acid waters seem to reflect the REE patterns of the host rocks, a contrast in the REE composition of the host rock is needed to enable use the REE patterns of acid waters as a source signature. In the Animas basin studies, the mineralization does not appear to significantly affect the REE concentration of the acid waters, such that comparing the REE concentrations to other metals enriched in the mineralized zones may distinguish mine waters from natural springs. In the suite of samples from MFMC and Prospect Gulch, for a given La

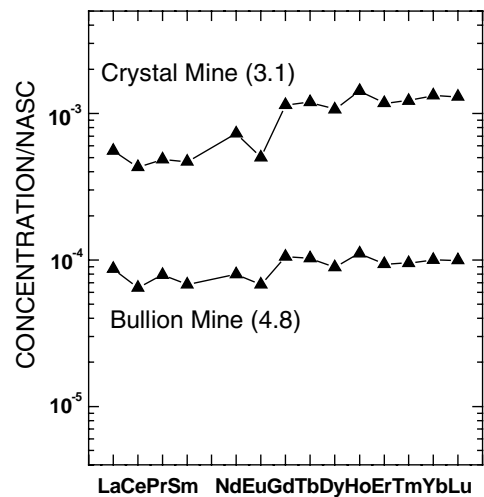


Figure 4. Rare earth element diagram of two mine waters, Boulder basin, Mont. Value of pH in parentheses. Crystal Mine sampled at adit, Bullion Mine sampled in creek below dump pile.

concentration, the mine waters have distinctly higher Zn concentrations compared to background spring samples (fig. 5). Other elements that are not enriched in the mineralized areas may act similarly to La. This observation may prove useful for differentiating between mining and natural sources in areas where the origin (natural or mining-influenced) of acid seeps is uncertain.

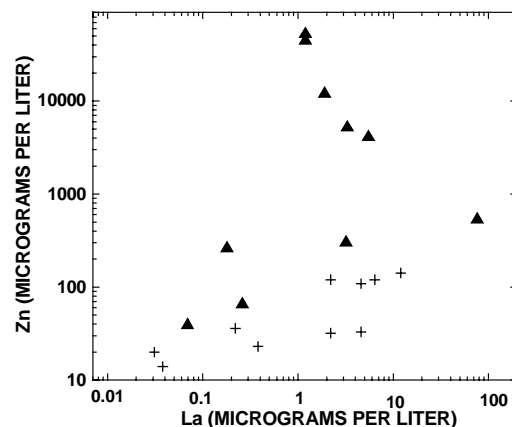


Figure 5. Relation of dissolved La to Zn for mine (triangles) and spring (crosses) waters in Prospect Gulch and Middle Fork Mineral Creek.

In-Stream Processes

The fate and transport of REEs entering the stream environment were investigated using field and laboratory studies. A 2-km stream reach of the South Fork Cement Creek (SFCC), Colo. was sampled during low flow in October 1996. Downstream the pH decreases from 7.1 to 5.1, and loading of REEs and major and trace elements increase due to the addition of acid mine drainage and acid springs. Comparing the measured load at the lowermost sampling site to the sum of the input loads accounts for 77 to 93 percent of the REEs. In contrast, measured loads of Ca, Sr, SO_4 , Zn, and Co averaged 117 ± 3 percent of the summed input loads. Values less than 100 percent suggest that REEs are probably being removed in this acidic, alpine stream. Loss of REEs may be related to iron and aluminum colloids that are actively precipitating in the stream channel.

To investigate fate and transport of REEs in a stream reach where pH increases, a suite of samples was collected from Uncle Sam Gulch in the Boulder watershed, Mont. during July 1997. In contrast to SFCC where a number of acid water sources contribute metals to the creek, Uncle Sam Gulch has only one dominant acid water source. Acid mine water from the Crystal Mine (pH=3.1) enters the stream, lowering the pH from 7.2 to 3.6. Within 2 km, the stream pH increases to 6.9, apparently due to dilution or neutralization by circumneutral waters. The streambed is coated with iron precipitates throughout this reach. Upstream of the lower most sampling site, the iron stained stream bed is a lighter color than below the mine site, suggesting that aluminum is precipitating as well.

The total REE concentrations of the stream water along this reach decrease from $31.2 \mu\text{g/L}$ to $0.5 \mu\text{g/L}$. To evaluate if the reduction in the REE concentrations is due to REE removal or due to dilution, we compare the REE variation with a conservative solute, SO_4 . Downstream from the mine, the $\Sigma\text{REE}/\text{SO}_4$ ratio remains relatively constant until the pH of the stream is above a value of 4.3 (fig. 6) indicating that the REEs behave conservatively through this pH range. Compared to SO_4 , the REEs are removed from

solution before the next sample site, which has a pH value of 6.9. A similar pattern is

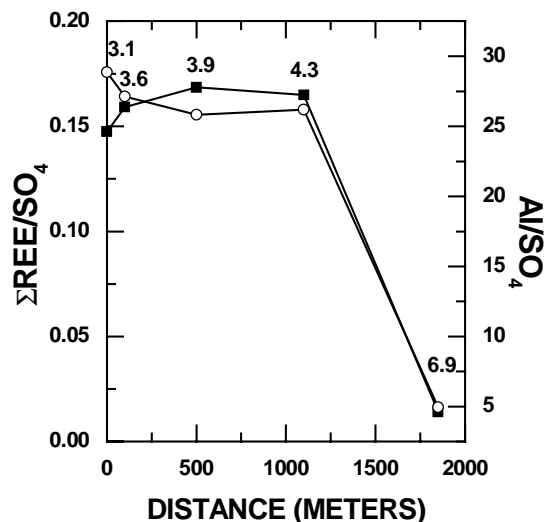


Figure 6. Dissolved $\Sigma\text{REE}/\text{SO}_4$ (squares) and Al/SO_4 (circles) for stream water samples, Uncle Sam Gulch, Mont. Distance downstream from Crystal Mine adit. Numbers above symbol = pH value of sample.

observed with Al, suggesting that the REEs may have coprecipitated or adsorbed onto aluminum colloids. With this limited data set, we are not able to differentiate between the relative importance of the increase in pH on the extent of adsorption and the role colloid composition plays on the removal of REEs and other metals.

During the August 1998, a tracer experiment was carried out in Uncle Sam Gulch. A subset of samples are being analyzed for REEs and trace metals to better determine the roles of colloid formation and pH variation on the attenuation of REEs and other metals and to quantify the mass transfer from solution to colloid during transport.

REE Partitioning during Laboratory Iron Oxidation Experiment

A laboratory experiment was undertaken to study the partitioning of the REEs between iron colloids and aqueous solutions. These laboratory results will provide a geochemical framework for interpreting field data on fate and transport of

REEs and other metals in acidic streams. Unfiltered, unacidified mine water samples were collected, and the Fe (III) allowed to oxidize at room temperature for six months. The set of waters had initial pH values ranging from 1.7 to 6.2, specific conductance from 775 to 17,000 microsiemens per centimeter, dissolved Fe concentrations from 50 to 675,000 $\mu\text{g/L}$, and La concentrations from 1 to 210 $\mu\text{g/L}$. The dissolved iron oxidized and precipitated during the 6-month interval, and at the conclusion, water and precipitates were separated and analyzed for major and trace elements.

The precipitates are enriched in REEs relative to their respective waters, with the enrichment strongly dependent on pH (fig. 7). The REE patterns of the filtrates and precipitates are convex-up with enrichment in the middle REEs relative to the light and heavy REEs. For a given sample, the filtrates and their original waters have similar REE patterns and concentrations because less than 5 percent of the REEs were removed from solution during the experiment. These results indicate that during iron colloid formation, the REEs may be removed from solution without altering the REE pattern of the solution and at pH values less than approximately 4.5, most of the REEs stay in solution.

REEs as Chemical Analogues for Actinides

Rare earth elements have been used as chemical analogues for actinides in a number of biological and geological studies because of their similarity to the actinides in ionic charge and ionic radius (Weimer and others, 1980). We have investigated the role of water composition and colloids in the attenuation of U, Th, and REEs in an acidic weathering environment, and the extent to which the natural analogue concept is appropriate. Within the upper Animas River basin, naturally-occurring acid springs (pH 2.7-6.8) and acid mine drainage (pH 2.3-6.4) dissolve minerals in the country rock, releasing U, Th, and REEs, which are predominantly derived from apatite, monazite, and epidote. Upon entering the stream system, concentrations of trace elements can be attenuated by adsorption to colloids or

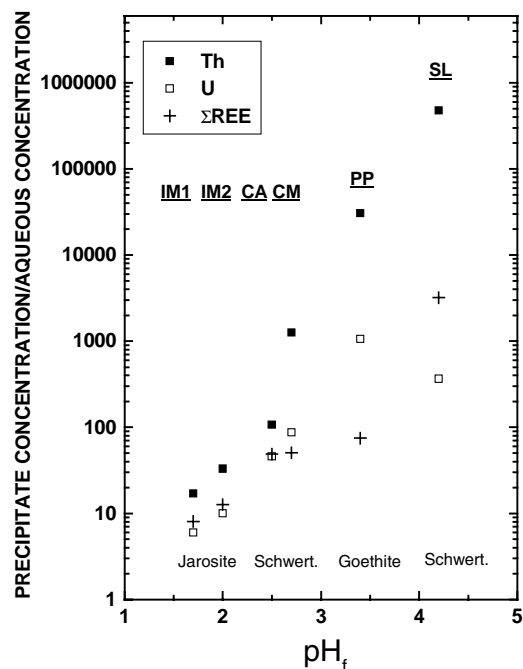


Figure 7. Relation of solid phase enrichment to pH. Concentration in precipitate ($\mu\text{g/g}$) relative to aqueous phase ($\mu\text{g/g}$) from iron oxidation experiments. Sample designation: IM1 - Iron Mountain site, Calif. ($\text{pH}_i = 1.6$, $\text{pH}_f = 1.7$), IM2 - Iron Mountain site, Calif. ($\text{pH}_i = \text{unknown}$, $\text{pH}_f = 2.0$), CA - Chandler adit, Colo. ($\text{pH}_i = 2.6$, $\text{pH}_f = 2.5$), CM - Crystal Mine, Mont. ($\text{pH}_i = 3.1$, $\text{pH}_f = 2.7$), PP - Paradise portal, Colo. ($\text{pH}_i = 5.3$, $\text{pH}_f = 3.4$), and SL - Silver Ledge Mine, Colo. ($\text{pH}_i = 6.1$, $\text{pH}_f = 4.2$). $\text{pH}_i = \text{pH initial}$, $\text{pH}_f = \text{pH final}$. Dominant mineral phase of precipitate shown below sample. Schwert. = schwertmannite.

coprecipitating. Laboratory iron oxidation experiments on mine waters, described above, were run to determine the partitioning of the U, Th, and REEs over a range of pH conditions.

In the Animas water samples U, Th, and the REE concentrations are inversely correlated with pH (fig. 8); however, the slopes are strikingly different. The ΣREE show a gradual decrease in concentrations with increasing pH, where as U and Th concentrations have large decreases between pH 3 and 4, then remain relatively low and constant above a pH of 4. Results from the laboratory experiments show that the precipitates become increasingly enriched in U, Th, and REEs compared to the aqueous phase with increasing

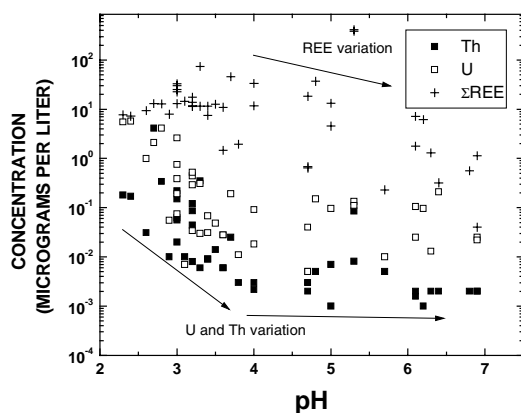


Figure 8. Relation of dissolved U, Th, and Σ REE vs. pH for upper Animas River basin samples, including natural springs, mine effluents, and stream waters.

pH (fig. 7). With the exception of the $\text{pH}_i = 5.3$ sample that was predominately goethite, compositions of the solid phases vary from dominantly jarosite in the low-pH samples to dominantly schwertmannite in the high-pH samples. Aluminum-rich phases were not observed in any of the precipitates.

The field and laboratory results suggest that U and Th are primarily adsorbed by hydrated ferric oxides at pH values of 3 to 4. In contrast, REEs tend to remain dissolved until higher pH values are reached, in a manner similar to Al. Aluminum remains in solution until the pH reaches about 5, then hydrolyzes and precipitates as a hydroxysulfate mineral (Nordstrom and Ball, 1986). REEs will likely coprecipitate or adsorb with aluminum-rich solids.

CONCLUSIONS

The AML pilot watersheds are well-suited for investigating the REE geochemistry of acid waters because of the numerous acid water sources and the interdisciplinary approach to watershed characterization. Using REE patterns as a tool to identify source signatures of acid waters is valuable when the REE patterns of the lithologies along the flow path have different REE patterns. To differentiate between natural springs and mine waters using only the REE patterns, either the mineral deposits must have a

REE signature distinct from the surrounding lithologies, or secondary processes in the mining or spring environment must lead to REE fractionations. Within the subbasins of the upper Animas watershed, using REE patterns to differentiate between acid springs and mine waters may not be conclusive. Although many acid springs have REE patterns with negative Ce anomalies and the mine waters do not, not all the springs sampled have such patterns.

Within the Animas River basin, the mine environment does not appear to enrich the acid drainage in REEs; thus, comparing the REE concentrations to other metals enriched in the mine waters, such as Zn, may provide a means to discriminate between mining and natural acid water sources. This differential enrichment should provide a useful tool, in conjunction with other geochemical indicators, for determining if seeps in areas impacted by mining are natural or mining-related.

Formation of Fe and Al colloids plays a role in the attenuation of REEs and other metals in streams that receive acid waters. Field and laboratory experiments demonstrate that REEs are removed from solution at pH values greater than 4.5 and that only minor fractionations occur.

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