

Review of Rare Earth Element Concentrations in Oil Shales of the Eocene Green River Formation

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U.S. Department of the Interior
U.S. Geological Survey

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By Justin E. Birdwell

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Conversion Factors

Multiply	By	To obtain
Length		
meter (m)	3.281	foot (ft)
Volume		
liter (L)	0.2642	gallon (gal)
cubic centimeter (cm ³)	0.06102	cubic inch (in ³)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$

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Abstract

Concentrations of the lanthanide series or rare earth elements and yttrium were determined for lacustrine oil shale samples from the Eocene Green River Formation in the Piceance Basin of Colorado and the Uinta Basin of Utah. Unprocessed oil shale, post-pyrolysis (spent) shale, and leached shale samples were examined to determine if oil-shale processing to generate oil or the remediation of retorted shale affects rare earth element concentrations. Results for unprocessed Green River oil shale samples were compared to data published in the literature on reference materials, such as chondritic meteorites, the North American shale composite, marine oil shale samples from two sites in northern Tibet, and mined rare earth element ores from the United States and China. The Green River oil shales had lower rare earth element concentrations (66.3 to 141.3 micrograms per gram, $\mu\text{g g}^{-1}$) than are typical of material in the upper crust (approximately $170 \mu\text{g g}^{-1}$) and were also lower in rare earth elements relative to the North American shale composite (approximately $165 \mu\text{g g}^{-1}$). Adjusting for dilution of rare earth elements by organic matter does not account for the total difference between the oil shales and other crustal rocks. Europium anomalies for Green River oil shales from the Piceance Basin were slightly lower than those reported for the North American shale composite and upper crust. When compared to ores currently mined for rare earth elements, the concentrations in Green River oil shales are several orders of magnitude lower. Retorting Green River oil shales led to a slight enrichment of rare earth elements due to removal of organic matter. When concentrations in spent and leached samples were normalized to an original rock basis, concentrations were comparable to those of the raw shale, indicating that rare earth elements are conserved in processed oil shales.

Introduction

Rare earth elements (REEs) are essential materials in a wide range of products, including chemical catalysts, advanced electronics, glass-polishing agents, rechargeable batteries, and high-tech magnets (Haxel and others, 2002). To be considered viable for commercial development, REE ore content generally must be greater than approximately 1 weight percent (wt %), and several reports on the most commonly exploited REE minerals (bastnäsite and monazite) are available from the U.S. Geological Survey (USGS) (Long and others, 2010; Cordier and Hedrick, 2010). During a meeting of the Congressional Subcommittee on Energy and Mineral Resources, held on August 24, 2011, in Grand Junction, Colo., a question was posed regarding the availability of REEs in oil shale of the Eocene Green River Formation (Tipton, 2011). As data on REE concentrations in Green River oil shales are rare in the peer-reviewed literature and other publicly available documents, the purpose of this report is to provide a cursory review of REE concentrations in Green River oil shales.

Oil-shale deposits in the Eocene Green River Formation of the Piceance Basin of Colorado, the Uinta Basin of Utah and Colorado, and the Greater Green River Basin of Wyoming, Colorado, and Utah

(fig. 1) are among the richest in the world, with in-place resources estimated at 1.525 trillion barrels of oil (TBO) in the Piceance Basin (Johnson and others, 2010a), 1.32 TBO in the Uinta Basin (Johnson and others, 2010b), and 1.44 TBO in the Greater Green River Basin (Johnson and others, 2011). The Green River Formation was deposited in two large paleolakes: Lake Uinta in the Uinta and Piceance Basins and Lake Gosiute in the Greater Green River Basin (fig. 1; Johnson, 1981). Oil shale, despite the name, does not actually contain oil, but rather a type of organic matter called kerogen. The kerogen in Green River oil shale is an immature, solid organic material that, like other kerogens, is essentially insoluble in nearly all organic solvents. In order to convert kerogen into hydrocarbon oil and gas, it must be heated, in the absence of oxygen (pyrolysis), to temperatures between 350 and 500°C or higher in a process referred to as “retorting.” Traditionally, oil shale has been utilized by mining the rock and processing it in separate above-ground retorting facilities. However, processes in which oil-shale deposits are heated in place to generate oil and gas, referred to as *in situ* retorting, have recently become the preferred approaches for many developers attempting to access these deeply buried resources in the Green River Formation (Burnham and others, 2010; Ryan and others, 2010). Processing oil shale at the surface generates retort oil and gas products along with spent shale that contains mostly mineral components and some organic char. Because the organic richness of oil shale varies widely, the amount of spent shale generated by surface retorts can represent a wide range of values, although it typically will be between 60 and 90 wt % of the original rock.

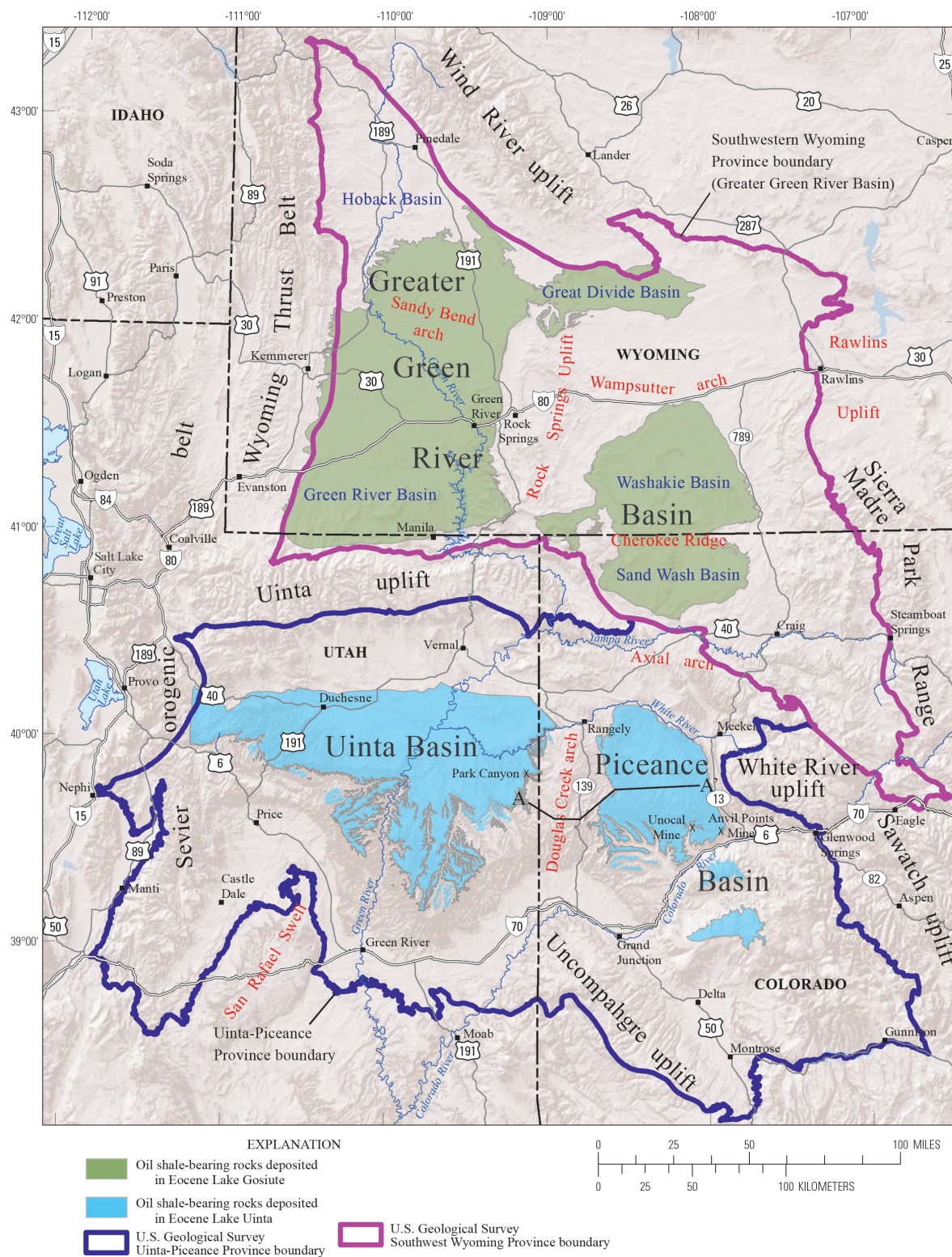


Figure 1. Map showing extent of Uinta, Piceance, and Greater Green River Basins, and approximate extent of oil shale in the Green River Formation. Sub-basins in the Greater Green River Basin labeled in blue. Major uplifts

are labeled in black, and minor structural arches are labeled in red. Extent of the Uinta and Piceance Basins (dark blue) is the same as the Uinta-Piceance Province boundary (U.S. Geological Survey Uinta-Piceance Assessment Team, 2003). Extent of the Greater Green River Basin is the same as the Southwest Wyoming Province boundary (U.S. Geological Survey Southwest Wyoming Province Assessment Team, 2005). For the extent of oil shale in the Piceance Basin, the base of the Parachute Creek Member of the Green River Formation as mapped by Tweto (1979) was used for all but the northwest part of the basin, where the base of the lower member of the Green River Formation is used. For the extent of oil shale in the eastern part of the Uinta Basin, the base of the Parachute Creek Member as mapped by Cashion (1973) and Rowley and others (1985) was used. In the western part of the basin, the top of the Mahogany bed as mapped by Witkind (1995) was used. In the northern part of the Uinta Basin, only the area where oil shale is at a depth of 6,000 feet or less is shown; this area was outlined by using a structure contour map of the top of the Mahogany oil shale bed compiled by Johnson and Roberts (2003). For the Sand Wash, Washakie, Great Divide Basins, and southeastern part of the Green River Basin, the base of the Tipton Shale Member as mapped by Tweto (1979) and Love and Christiansen (1985) was used to show extent of oil shale. For the western part of the Green River Basin, the base of the Wilkins Peak Member of the Green River Formation, and for the northern part of the Green River Basin, the base of the Laney Shale Member of the Green River Formation as mapped by Love and Christiansen (1985) were used. Location of cross section A-A' of figure 2 is shown. Locations of Unocal and Anvil Points mines and Park Canyon sample locations are also shown.

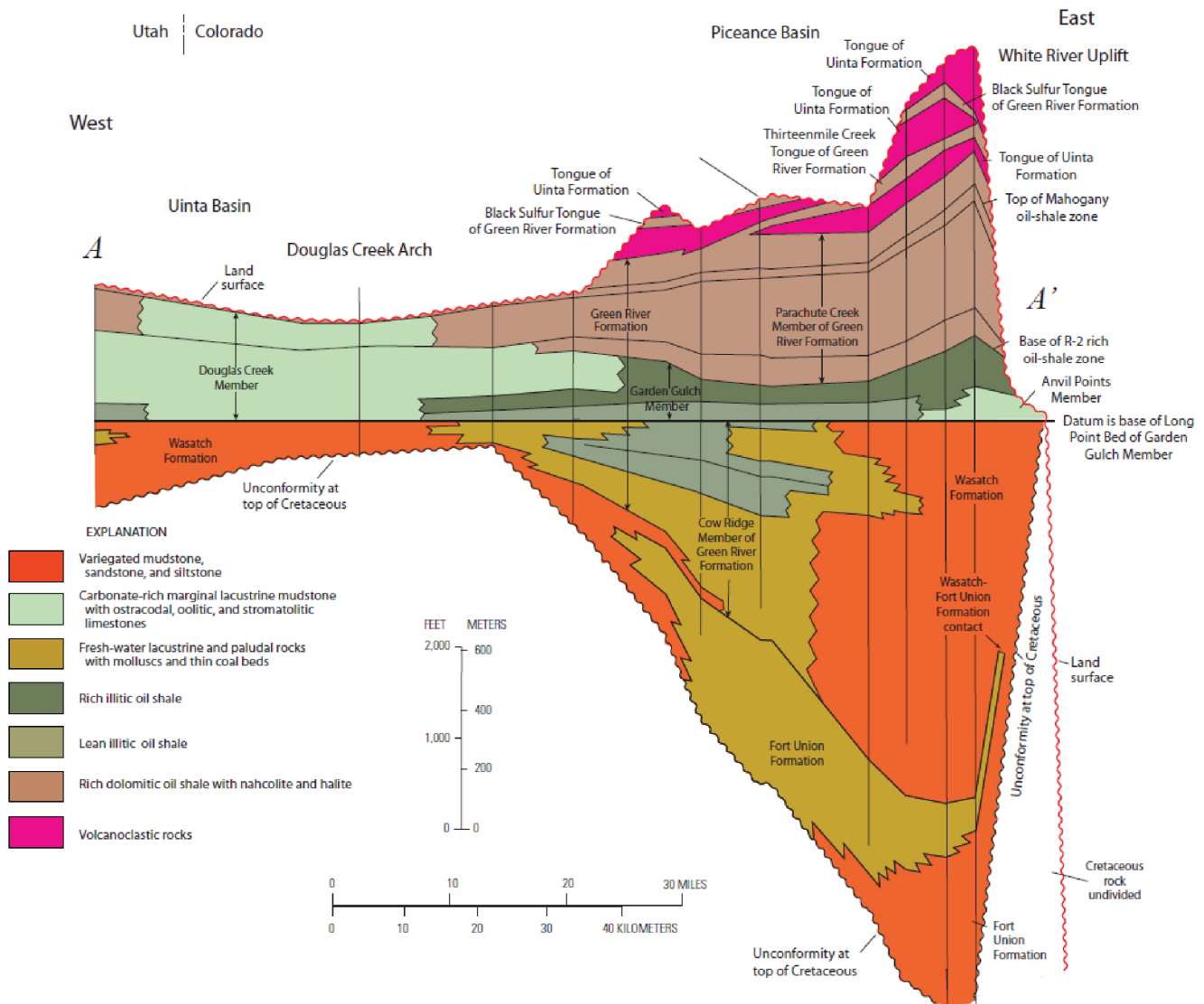


Figure 2. East-west cross section through the Piceance Basin, the Douglas Creek arch, and the eastern part of the Uinta Basin showing member subdivisions of the Green River Formation and lower Tertiary units that underlie and overlie that formation. Modified from Johnson and others (2011a).

Spent shale is a major disposal issue for above-ground oil shale processors and has led to many attempts to identify co-products that can be extracted from the spent shale for beneficial uses (Hanni, 1996). For example, Piceance Basin oil shales rich in the mineral dawsonite ($\text{NaAl}(\text{OH})_2\text{CO}_3$) are considered to be potential aluminum ores (Smith and Milton, 1966), as sodium aluminate can be leached from spent dawsonitic oil shales following high-temperature processing (Dyni, 1972). Spent oil shale is also used in countries like Estonia as a component of cement and other building materials (Hanni, 1996). Recently, it has been suggested that lanthanide series or REEs and yttrium could be exploited as co-extraction products from Chinese marine oil shales (Fu and others, 2010a, 2010b).

This report presents the results of analyses conducted on Green River Formation oil shale samples from the Piceance and Uinta Basins, focusing on REE concentrations in (1) the Mahogany

zone, which has been targeted for development by a number of companies; and (2) the Garden Gulch Member of the Piceance Basin, which is also being considered for use (fig. 2). In addition to raw oil shales, samples processed using different pyrolysis methods and leached samples that have been extracted with water under different conditions have also been analyzed to assess the effects that retorting and leaching have on REE concentrations.

Methods

Oil Shale Samples

Samples were collected from outcrops at the Anvil Points Mine (APM) near Rifle, Colo. (fig. 1); they are representative of lacustrine oil shales from the Green River Formation Mahogany zone (fig. 2) in the Piceance Basin of northwestern Colorado. A sample of Uinta Basin Mahogany zone oil shale (UMZ) was collected from outcrops near Park Canyon, Utah (fig. 1). A Unocal Mine (UNO; fig. 1) oil shale sample was provided by Phil Hansen of Shale Technologies, LLC, and a sample of the Garden Gulch Member oil shale from well cuttings was supplied by Alan Burnham of American Shale Oil, LLC. The USGS Green River shale reference material, SGR-1, was also included as a quality-control check for REE concentrations determined in this study. Additional samples used in this study include APM oil shales that have been subjected to (1) various pyrolysis methods meant to mimic retorting processes used to generate liquid oil and (2) leaching tests to assess the potential release of harmful pollutants from spent shale tailings piles or exhausted *in situ* retort materials. Table 1 contains additional information on the shale samples used in this study, including oil yields, total organic carbon (TOC) and organic matter (kerogen + bitumen) contents.

Table 1. Summary of information on Green River Formation oil shale samples. (m, meters; wt %, weight percent; APM, Anvil Points Mine)

Sample Description	Lab Abbreviation	Longitude	Latitude	Depth (m)	TOC (wt %) ¹	Fischer Assay Oil Yield (wt %) ²	Recovered Rock (wt %) ³	Organic Matter Content (wt %) ⁴
Anvil Points Mine (APM) Mahogany zone oil shale (Piceance Basin)	APM	-107.9529	39.5346	Outcrop	19.30	15.58	-	24.32
Unocal mine oil shale (Piceance Basin)	UNO	-108.0050	39.5667	Outcrop	14.10	12.98	-	18.80
Utah Mahogany zone oil shale (Uinta Basin)	UMZ	-109.1249	39.8454	Outcrop	29.70	28.22	-	43.82
Garden Gulch Member illitic oil shale (Piceance Basin)	GGM	-108.3833	39.8667	640	9.96	10.29	-	16.00
USGS Green River shale Mahogany zone reference material	SGR-1	NA ⁵	NA	NA	24.71	20.39	-	ND ⁶
In Situ Simulator (ISS) spent APM oil shale	APM ISS	-107.9529	39.5346	-	11.21	-	85.0	ND
High temperature leached spent APM oil shale (ISS-288h, leached 1h)	APM ISS HTL-1	-107.9529	39.5346	-	9.69	-	93.4	ND
High temperature leached spent APM oil shale (ISS-288h, leached 24h)	APM ISS HTL-24	-107.9529	39.5346	-	9.75	-	88.5	ND
High temperature leached spent APM oil shale (Fischer Assay spent, leached 1h)	APM FA HTL-1	-107.9529	39.5346	-	5.77	-	89.3	ND
High temperature leached spent APM oil shale (Fischer Assay spent, leached 24h)	APM FA HTL-24	-107.9529	39.5346	-	5.71	-	88.1	ND
Room temperature leached APM oil shale	APM RTL	-107.9529	39.5346	-	19.30	-	99.5	ND
Room temperature leached Fischer Assay spent APM oil shale	APM FA RTL	-107.9529	39.5346	-	5.66	-	79.7	ND
Room temperature leached ISS-288h spent APM oil shale	APM ISS RTL	-107.9529	39.5346	-	11.21	-	85.0	ND
Hydrous pyrolysis spent APM oil shale	APM HP	-107.9529	39.5346	-	7.00	-	76.8	ND

¹ Total organic carbon (TOC) content determined by Weatherford International (Shenandoah, Tex.) using the Leco method.

² Oil yields determined using modified Fischer Assay (American Society for Testing and Materials, 1980) by Shale Technologies, LLC (Rifle, Colo.).

³ Recovered rock, wt % of original rock recovered following retorting and(or) leaching.

⁴ Organic matter (kerogen + bitumen) content estimated by measuring the change in sample mass following muffling at 425°C for 24 hours.

⁵ Not available.

⁶ Not determined.

Pyrolysis Methods

Prior to pyrolysis, aliquots of APM oil shale were crushed and sieved to obtain a uniform material with a particle size range (-8 to +35 mesh or 0.500 to 2.380 millimeters) consistent with the American Society for Testing and Materials Fischer Assay procedure (American Society for Testing and Materials, 1980). Samples were processed using three different pyrolysis methods. The first, modified Fischer Assay (American Society for Testing and Materials, 1980), was used to generate spent shale similar to that of surface retorts. In brief, the Fischer Assay procedure involves heating a 100-gram (g) sample to 500°C at a rate of 12°C/minute (min) (approximately 40-min heat-up time) and holding at that temperature for 40 min or until oil generation is complete. The second pyrolysis method uses a batch system meant to mimic *in situ* retorting using an apparatus described by Birdwell and others (2011). The In Situ Simulator (ISS) consists of a reactor and gas/oil vapor collection vessel connected by a stainless steel flexhose. A 100-g oil shale sample is heated to 360°C at a rate of approximately 3°C/min. The sample is held at that temperature for a predetermined time, which can be as short as 6 hours (h) or as long as 12 days. The shale sample discussed in this study was held at temperature for 288 h. Before the end of the heating period, the collection vessel is prepared by evacuating it to less than 0.6 psia and cooling to an internal temperature of less than or equal to 5°C using a laboratory chiller. The reactor is then vented to the collection vessel for 1 min. The reactor and collector are then removed from the heater and chiller, respectively, and left until they reach room temperature, at which point the products and spent shale are collected for further analysis. The third pyrolysis method applied to the APM oil shale was hydrous pyrolysis (HP), which is an approach used to generate pyrolysates similar to natural petroleum (Lewan, 1997). A typical HP experiment involves heating a 200-g source rock sample with approximately 400 milliliters (mL) of deionized water in a 1-liter (L) batch reactor to 360°C at a rate of approximately 6°C/min and holding for 72 h, although other combinations of time and temperature can be used depending on the goals of the particular study (Lewan, 1997; Lewan and Roy, 2010).

Leaching Experiments

All aspects of the High-Temperature Leaching (HTL) experiments were conducted in the same way as the HP experiment, except that the spent shale samples were only held at 360°C for 1 or 24 h and a lower shale/water ratio (20 g to 475 mL) was used. Room-Temperature Extraction (RTE) experiments were conducted using between 7 and 10 g of pulverized rock added to between 240 and 290 mL of deionized water. The RTE samples were then placed on a rotary shaker operating in the dark at 150 RPM for 10 days. At the end of the extraction period, waters were decanted into appropriate sample containers and the solids were collected for analysis.

Analytical Methods

Lanthanide and yttrium concentrations in raw and processed oil shale samples were determined on ball-milled samples by SGS Laboratories (Toronto, Canada) using a method that provides concentrations for 55 major (excluding silicon and sodium) and trace elements with analysis by inductively coupled plasma–atomic emission spectrometry (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS) (U.S. Geological Survey, 2010). Samples (0.1 g) were decomposed using a sodium peroxide sinter method (450°C) and the resultant material was leached with water and acidified with nitric acid. Following extraction, tartaric acid was added and aliquots of each prepared sample were analyzed. Values reported for individual elements are based on results from either ICP–AES or ICP–MS, depending on which is optimal for each species. Reporting limits for REEs are shown in table 2.

Table 2. Detection limits of ICP–AES/MS for rare earth elements using USGS Method 22, 55 Element ICP-AES-MS sodium peroxide sinter (U.S. Geological Survey, 2010). ($\mu\text{g g}^{-1}$, micrograms per gram)

Element	Symbol	Atomic No.	Lower Limit ($\mu\text{g g}^{-1}$)	Upper Limit ($\mu\text{g g}^{-1}$)
Yttrium ¹	Y	39	0.5	10,000
Lanthanum	La	57	.1	10,000
Cerium	Ce	58	.1	10,000
Praesodymium	Pr	59	.05	1,000
Neodymium	Nd	60	.1	10,000
Samarium	Sm	62	.1	1,000
Europium	Eu	63	.05	1,000
Gadolinium	Gd	64	.05	1,000
Terbium	Tb	65	.05	1,000
Dysprosium	Dy	66	.05	1,000
Holmium	Ho	67	.05	1,000
Erbium	Er	68	.05	1,000
Thulium	Tm	69	.05	1,000
Ytterbium	Yb	70	.1	1,000
Lutetium	Lu	71	.05	1,000

¹ Though not a lanthanide series element, yttrium has many of the same properties as the rare earth elements and therefore is commonly included with them.

Data Analysis

The distributions of REEs and yttrium in geologic samples are generally assessed by first normalizing the measured concentrations to those present in chondritic meteorites. By plotting chondrite-normalized REE concentrations against atomic number, patterns can be assessed relative to the average REE distributions in the upper crust (Taylor and McLennan, 1981) or to standard geologic materials such as the North American shale composite (NASC; Gromet and others, 1984). For shale samples, normalization to the NASC values can also be informative (Fu and others, 2010a, 2010b).

In addition to examining the distribution patterns for REE concentrations, a set of parameters are available for assessing various aspects of REE geochemistry in geologic media. The light REEs (LREE), which include the elements lanthanum through europium, are present in higher concentrations in most rocks. Accumulations of the heavy REEs (HREE), including gadolinium through lutetium, are particularly rare and therefore are commercially very valuable. The ratio of LREEs to HREEs is between 7 and 10 in most of the upper crust and provides a rough descriptor for the REE distribution in a sample (Taylor and McLennan, 1995; Fu and others, 2010a, 2010b).

Another parameter used to describe REE data is the europium anomaly, Eu/Eu^* , which is based on an idealized, smooth REE distribution. Europium, like the other lanthanides, occurs in a trivalent (3+) oxidation state, but can also be reduced to (2+) under certain conditions. Europium anomalies are primarily due to the preferential incorporation of the divalent form into plagioclase as a substitute for strontium (2+) in reducing magmas (Taylor and McLennan, 1981, 1995). If the magma accumulates plagioclase crystals prior to solidifying, it will be enriched in europium, whereas if the plagioclase is separated from the magma prior to solidification, the rock formed will be depleted in europium. The europium anomaly is calculated as follows (Taylor and McLennan, 1995; Fu and others, 2010a, 2010b):

$$Eu/Eu^* = [Eu]_N / ([Sm]_N \times [Gd]_N)^{0.5} \quad (1)$$

Where,

Eu/Eu^* represents the ratio of the actual concentration of europium in the sample to the ideal concentration, assuming an REE distribution profile matching that of a reference material, in this case chondrites (dimensionless),

$[Eu]_N$ is the chondrite-normalized concentration of europium (dimensionless),

$[Sm]_N$ is the chondrite-normalized concentration of samarium (dimensionless), and

$[Gd]_N$ is the chondrite-normalized concentration of gadolinium (dimensionless).

Values of Eu/Eu^* less than one are called negative anomalies, whereas values greater than one are considered positive.

A similar parameter, the cerium anomaly (Ce/Ce^*), is used to assess cerium enrichment or depletion in a sample relative to a smooth, chondrite-normalized pattern (Taylor and McLennan, 1995; Fu and others, 2010a, 2010b). Like europium, cerium has an additional oxidation state and can be oxidized to (4+). Cerium (3+) is the more soluble form, whereas in oxic waters, cerium dioxide and stable cerium hydroxides precipitate (Elderfield, 1988; Taylor and McLennan, 1995). This leads to the enrichment of cerium in sedimentary rocks deposited in oxic environments and depletion in anoxic or more reducing environments (Wilde and others, 1996). The cerium anomaly is calculated as follows (Taylor and McLennan, 1995; Fu and others, 2010a, 2010b):

$$Ce/Ce^* = [Ce]_N / ([La]_N \times [Pr]_N)^{0.5} \quad (2)$$

Where,

Ce/Ce^* represents the ratio of the actual concentration of cerium in the sample to the ideal concentration, assuming an REE distribution profile matching that of a reference material, in this case chondrites (dimensionless),

$[Ce]_N$ is the chondrite-normalized concentration of cerium (dimensionless),

$[La]_N$ is the chondrite-normalized concentration of lanthanum (dimensionless), and

$[Pr]_N$ is the chondrite-normalized concentration of praeosodymium (dimensionless).

When discussing compositional data for processed samples, it is useful to employ a stoichiometric conversion factor before comparing the processed samples to the original. This is particularly important for samples like oil shale when they are subjected to pyrolysis, as this process can (1) remove a significant amount of solid organic mass during the conversion of kerogen to liquid and gaseous products and (2) lead to possible inorganic mass loss if carbonate minerals are present and the pyrolysis conditions are such that the carbonates decompose. In mass balance pyrolysis experiments, the total mass of solid residue that remains is determined, which can be divided by the initial mass of solid material to determine the fraction of recovered rock. The concentration of any species measured in the residue can be converted to an original rock basis by multiplying concentration by the fraction of recovered rock. This allows for a more meaningful comparison of concentration changes in samples before and after processing.

Results and Discussion

Unprocessed REE concentrations in oil shale samples along with values for REEs in reference materials are listed in table 3. Good agreement between SGR-1 REE concentrations determined in this study and those reported on the certificate of analysis for the material (Wilson, 2001) was taken as validation of our analytical results. Chondrite-normalized REE concentration-distribution patterns for Green River oil shales were generally similar to each other and to patterns for the upper crust and NASC (fig. 3). However, all Green River samples had lower REE concentrations relative to the reference materials. Among the Green River samples, the oil shale with the highest organic richness and oil yield (UMZ) had the lowest concentration of total REEs ($66.3 \mu\text{g g}^{-1}$ (micrograms per gram)), whereas the sample with the lowest TOC content and Fischer Assay oil yield had the highest REE content (GGM, $141.3 \mu\text{g g}^{-1}$). Samples from the Piceance Basin Mahogany zone (APM, UNO, and SGR-1) all had similar REE concentrations that were between those of the GGM and UMZ samples (approximately $95 \mu\text{g g}^{-1}$), consistent with their intermediate TOC values and oil yields. These results indicate that the organic matter present in oil shale has the effect of diluting REE concentrations in the bulk rock. Sample concentrations were recalculated on an organic-free basis using the organic matter content data reported in table 1. These recalculated REE concentrations were still approximately 25 percent lower than those of the upper crust or NASC for all samples with the exception of the GGM oil shale, which has a lower carbonate content than the Mahogany zone samples. This implies that carbonates may also be diluting the REE concentrations in Green River oil shales relative to other crustal rocks. None of the samples showed similarities to REE ores from the United States (Mountain Pass carbonitite) or China (laperitic clay ore) in terms of REE concentrations or chondrite-normalized distributions.

The Green River oil shales had LREE/HREE ratios that were all around 11, which is slightly higher than ratios for rocks from the upper crust or other shales (table 3). It is unclear if this difference is related to enrichment of LREEs in oil shale or depletion of HREEs. The europium anomaly values for the Green River Formation samples collected in the Piceance Basin were slightly more negative than anomalies for the NASC or the UMZ sample, which could be due to different sources of detrital and other sedimentary material deposited in the Piceance and Uinta Basins during oil shale formation (Taylor and McLennan, 1985). The cerium anomaly values in the UMZ were slightly less negative

(0.95) than those for the NASC and Piceance Basin samples (0.91-0.92, excluding the UNO sample that may have been affected by weathering), possibly indicating that conditions in the Uinta Basin during formation of the Mahogany zone oil shales were slightly more oxidizing than in the Piceance Basin (Elderfield, 1988; Taylor and McLennan, 1995; Wilde and others, 1996).

Table 3. Rare earth element (REE) concentrations in Green River Formation oil shale, reference materials, and currently or previously mined U.S. and Chinese REE ores. ($\mu\text{g g}^{-1}$, micrograms per gram)

REE ¹	Atomic No.	APM ²	UNO ²	UMZ ²	GGM ²	SGR-1 ²	Chondrite ³	Upper Crust ⁴	NASC ⁵	MPC ⁶	CLO ⁷	SGR-1 Ref. ⁸
Y	39	9.0	9.8	6.7	14.2	9.3	2.1	22	NR	146	180	13
La	57	20.1	18.5	13.3	29.8	20.3	.354	30	31.1	38000	20	20
Ce	58	37.7	36.1	25.8	54.2	37.5	.934	64	67.03	55700	40	36
Pr	59	4.34	4.14	2.90	6.21	4.29	.129	7.1	9.1	4630	8	NR ⁹
Nd	60	15.1	15.2	10.6	21.6	15.2	.676	26	30.4	12540	45	16
Sm	62	2.8	2.8	1.8	4.0	2.5	.213	4.5	5.98	1000	20	2.7
Eu	63	.52	.49	.37	.72	.44	.080	.88	1.25	120	2	.56
Gd	64	2.25	2.26	1.58	3.16	2.09	.283	3.8	5.5	240	30	2
Tb	65	.31	.30	.22	.44	.28	.053	.64	.85	18	11	NR
Dy	66	1.68	1.75	1.24	2.65	1.76	.341	3.5	5.54	40	50	1.9
Ho	67	.36	.36	.25	.58	.33	.082	.8	1.27	4.5	9	.4
Er	68	.98	1.17	.72	1.55	.94	.225	2.3	3.275	7	30	1.1
Tm	69	.13	.14	.10	.26	.17	.034	.33	.54	1	5	.17
Yb	70	1.1	1.0	.6	1.7	1.1	.234	2.2	3.11	4	30	.94
Lu	71	.1	.2	.1	.3	.2	.036	.32	.456	.7	5	NR
ΣREE^{10}		96.5	94.2	66.3	141.3	96.4	5.8	168.4	165.4	112,451	485.0	94.8
LREE/ HREE ¹¹		11.6	10.8	11.4	11.0	11.7	1.9	9.5	7.1	355.3	.8	11.6
δCe^{12}		.92	.94	.95	.91	.92	ND ¹⁴	1.00	.91	.96	.72	ND
δEu^{13}		.64	.60	.67	.62	.59	ND	.65	.67	.75	.25	.74

¹ All concentrations reported in $\mu\text{g g}^{-1}$.

² See table 1 for explanation of lab abbreviations.

³ Chondrite concentrations are the average of values reported by Wakita and others (1971) and Taylor and McLennan (1981).

⁴ Upper crust values reported by Taylor and McLennan (1981).

⁵ North American shale composite, reported by Gromet and others (1984).

⁶ Mountain Pass carbonatite, California, reported by Haxel and others (2002).

⁷ Chinese laterite ore, reported by Haxel and others (2002).

⁸ From the USGS Certificate of Analysis for SGR-1, reported by Wilson (2001).

⁹ NR, Not reported.

¹⁰ Sum of all REEs + Y in $\mu\text{g g}^{-1}$.

¹¹ Ratio of the sum of the concentrations of the light REEs (La through Eu) divided by the sum of the heavy REEs (Gd through Lu).

¹² Cerium concentration anomaly (calculated using equation 2).

¹³ Europium concentration anomaly (calculated using equation 1).

¹⁴ ND, Not determined.

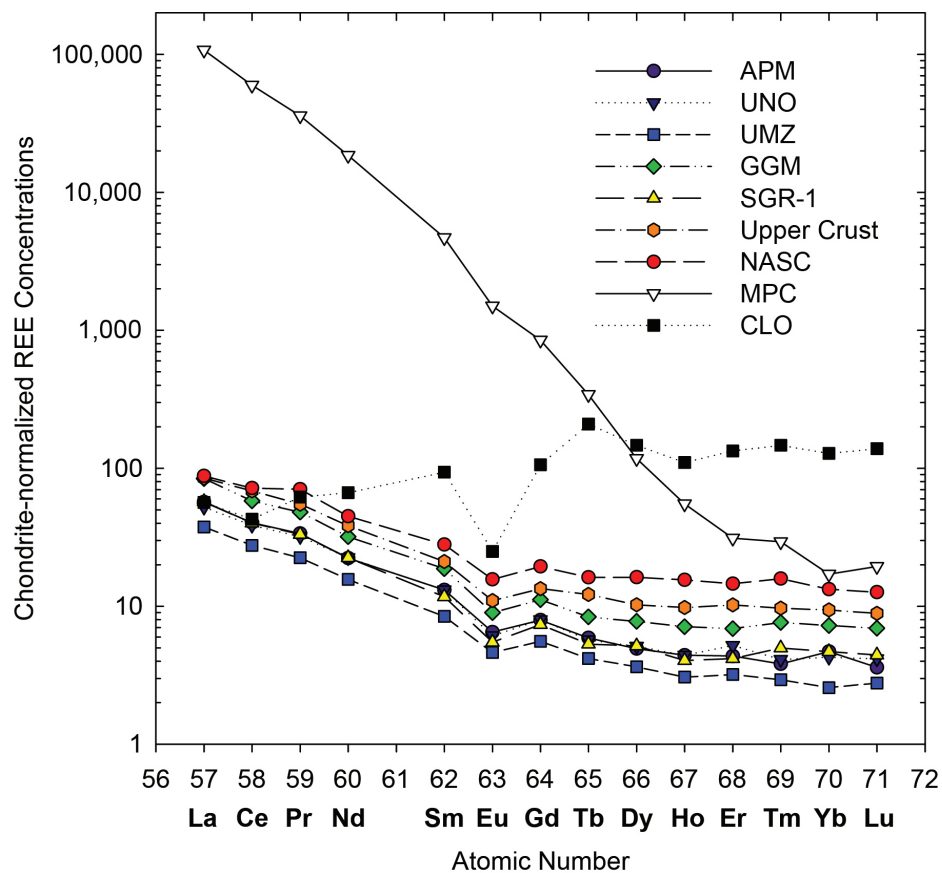


Figure 3. Chondrite-normalized rare earth element concentrations for Green River Formation oil shales, reference materials, and currently or previously mined U.S. and Chinese rare earth element ores (see tables 1 and 3 for explanations of abbreviations).

Distribution patterns for NASC-normalized REE concentrations in Green River oil shales (fig. 4) again show that the oil shale samples have lower REE content than typical shales, as all values plotted well below unity. Concentration data representative of two marine oil shale deposits in northern Tibet are plotted with the Green River shales (fig. 4). Similar concentrations of the LREEs are observed between the Piceance Basin Mahogany zone oil shales and the Tibetan samples; however, the pattern beyond samarium shows the Changshe Mountain Area (CMA) and Bilong Co. Area (BCA) shales to have somewhat higher concentrations of the HREEs, although they are lower than those in the GGM shale.

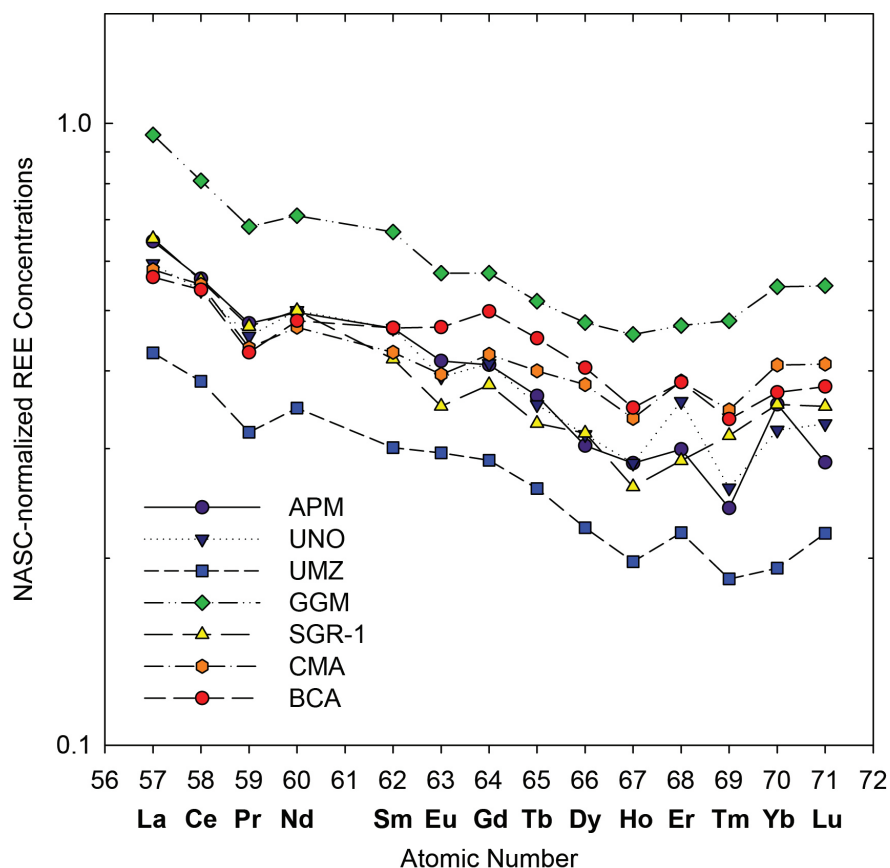


Figure 4. Rare earth element concentrations in Green River Formation (lacustrine) and marine oil shales from northern Tibet normalized to the North American shale composite (CMA, Changshe Mountain Area; Fu and others, 2010a; BCA, Bilong Co. Area; Fu and others, 2010b). CMA and BCA values shown are based on average concentrations for the data reported in Fu and others, 2010a and 2010b (see table 1 for explanation of abbreviations).

The REE concentrations measured on post-pyrolysis and leached APM shale samples are given in table 4, and recovered rock fractions are given in table 1. Comparison of the uncorrected concentrations in the spent and leached samples to that of the original APM shale showed that REE concentrations are approximately 25 percent higher on average, which is clearly shown on a parity plot (fig. 5a). However, when the spent and leached sample concentrations were adjusted to an original rock basis, the differences were significantly smaller and all data essentially fall on a 1:1 line (fig. 5b). This indicates that REEs are retained in the refractory fraction of spent oil shale and are not readily susceptible to leaching.

Table 4. Rare earth element (REE) concentrations in spent and leached Anvil Points Mine oil shale samples reported as measured¹.

REE ¹	Atomic No.	APM ²	APM FA	APM ISS	APM HP	APM RTL	APM FA RTL	APM ISS RTL	APM ISS HTL-1	APM ISS HTL-24	APM FA HTL-1	APM FA HTL-24
Y	39	9.3	11.7	10.8	11.4	9.1	10.9	10.8	11.5	11.7	11.8	11.6
La	57	20.8	25.6	24.6	26	20.2	24.3	25	24.7	26.1	26.6	25.8
Ce	58	39.1	47.1	45.9	49.5	38.1	47.2	46.7	46.4	49.9	50.4	49.2
Pr	59	4.50	5.28	5.24	5.38	4.39	5.24	5.31	5.24	5.56	5.59	5.54
Nd	60	15.6	18.6	18.3	19.6	15.7	19	18.4	18.2	20.8	19.5	20.1
Sm	62	2.9	3.0	2.9	3.3	2.7	3.3	3.3	3.3	3.5	3.3	3.7
Eu	63	.54	.63	.62	.67	.52	.64	.59	.69	.76	.62	.59
Gd	64	2.33	2.77	2.56	2.77	2.07	2.51	2.71	2.46	2.87	2.93	2.66
Tb	65	.32	.38	.35	.39	.35	.37	.36	.37	.4	.41	.35
Dy	66	1.74	2.2	2.26	2.12	1.91	2.35	2.26	2.22	2.31	2.37	2.3
Ho	67	.37	.44	.43	.45	.34	.43	.42	.44	.46	.41	.46
Er	68	1.02	1.19	1.1	1.21	1.03	1.32	1.08	1.19	1.39	1.34	1.2
Tm	69	.13	.18	.17	.18	.13	.19	.17	.18	.19	.18	.21
Yb	70	1.1	1.3	1.1	1.4	.9	1.1	1.3	1.1	1.2	1.3	1.1
Lu	71	.1	.18	.17	.17	.11	.18	.17	.17	.19	.18	.17

¹ All concentrations reported in $\mu\text{g g}^{-1}$ as measured in the recovered rock. To adjust from the measured concentration ($\mu\text{g-REE g}^{-1}\text{-recovered rock}$) to an original rock basis, multiply the concentration determined for the sample by the fraction of recovered rock following pyrolysis or leaching (see table 1 for values).

² See table 1 for explanation of lab abbreviations.

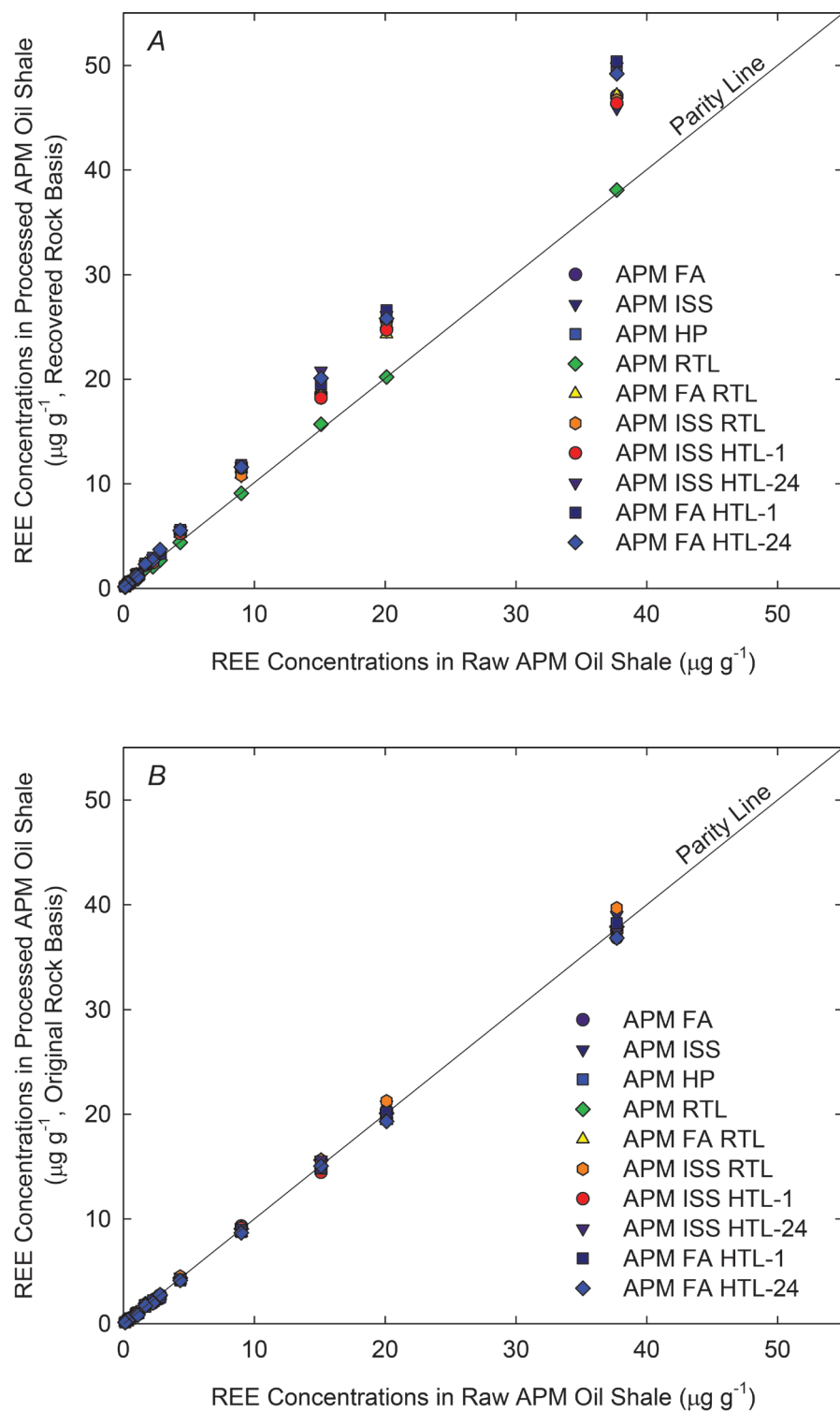


Figure 5. Comparison of rare earth element concentrations in raw and processed Anvil Points Mine oil shales; *A*, concentrations in processed samples are on an as-measured or recovered rock basis, and *B*, concentrations in processed samples on an original-rock basis (see table 1 for explanation of abbreviations), ($\mu\text{g g}^{-1}$, microgram per gram).

Conclusions

Lanthanide plus yttrium concentrations were determined for a limited set of Green River Formation oil shale samples collected primarily from surface mineable deposits in Colorado and Utah. The results show that Green River oil shales contain lower REE concentrations than is typical of the upper crust in general and other North American shales in particular. These lower concentrations are likely due to dilution by organic matter and carbonates, with REEs being concentrated in the aluminosilicate minerals. REE concentrations measured in shale samples following pyrolysis and(or) leaching showed that these processes do not have a significant effect on REE content. The lacustrine Green River oil shales are similar to marine oil shales collected from deposits in northern Tibet in terms of REE concentrations. Green River Formation oil shales do not resemble REE ores mined in the United States or China in terms of total REE content or their relative distributions.

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