Rare Earth Occurrences Proximal to the Cretaceous/Tertiary Boundary in the Raton Basin, South-central Colorado*

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Abstract

The Raton Coal Basin of Colorado and New Mexico is one of the premier coal basins where the Cretaceous/Tertiary boundary can be viewed and samples of coals, tonsteins, and shaly materials proximal to this boundary can be readily obtained. Near

Trinidad, CO, extensive coal deposits exist that straddle this boundary. Further, the presence of near-by igneous features such as the Sangre de Cristo Mountains and associated dikes and sills provide a possible source of anomalous geochemical features found in the coals. Reconnaissance geochemical investigations utilizing a hand-held X-Ray Fluorescence Spectrometer (XRF) indicate that appreciable amounts of Ti, Zr, Y, and light rare-earth elements (REE) are present within the coals and coal partings near the boundary of the Cretaceous Vermejo Formation and the overlying Tertiary Raton Formation. In some instances, semi-quantitative determinations indicate elevated quantities of Y and light REE (hundreds of parts per million) are present in select raw coal samples in the area. Earlier studies of the REE content of coal samples in the basin were conducted by the USGS and presented in their CoalQual database. The results of the XRF spectroscopy corroborates the findings reported in that database.

Altered kaolinitic pyroclastic ash is present in the basin that is interpreted to be in-part sourced from the Cretaceous/Tertiary (K-T) impact. This thin claystone or tonstein is present in at least 20 locations. This thin layer is generally overlain with a thin layer of coal reported to be 4 to 16 cm thick, (Izett, 1987). Interestingly, 2 samples of this material did show detectable and elevated concentrations of iridium, titanium, and other exotic heavy metals, the REE were not detected suggesting possible other sources of the REE in the coals. Further, aside from the purported impact ash fall materials from localized volcanic episodes within the basin, intrusive igneous activity is also reported in the general area. Geochemical studies of dikes, stocks, and other intrusive material in the Spanish Peaks and the Sangre de Cristo Mountains show similarly elevated REE content. There is an apparent proximal relationship between elevated Y and REE in coal samples to these tonstein features. Additional study of REE occurrences associated with tonstein deposits and kaolinized ash within the coal as well as in the coal material itself is warranted. If the REE occurrence is found to be widespread and stratigraphically predictable, then strategies for mining the coal and segregating coal ash and other coal waste products might be developed to exploit and extract REE resources when processing the coal.

Introduction

The Raton Basin is a Laramide structural basin (Baltz, 1985). It is an asymmetrical, elongated sedimentary basin formed covering approximately 4,000 mi^2 in southwestern Colorado and northeastern New Mexico. The oldest sedimentary units in the basin are marine beds of Devonian and Mississippian age. Units of interest in this paper are the late Cretaceous and early Tertiary sediments of terrestrial origin. Baltz, 1985 reports these units reached an aggregate thickness of 12,000 feet in the northern portion of the basin. Geographically the basin extends from Ute Park, New Mexico to Huerfano Park, Colorado and is bound on the western side by the Sange de Cristo Mountains, on the north by the Wet Mountains and the Apishipa Arch, and on the southeast by the Sierra Grande Uplift (Keighin, 1995). Figure 1 (from Flores and Bader, 1999) shows the generalized K-T geology and areal extent of the basin. Thick coal deposits are present in portions of the basin. Flores and Bader, 1999 report that lower coal units in the Raton Formation in the Raton Basin are interspersed over a 100 to 250 foot thick lower unit comprised of coal, carbonaceous shale, mudstone, siltstone, and sandstone. An upper tertiary coal-bearing unit is also present and is comprised of between 600 to 1100 ft. thick unit of sandstone, siltstone, mudstone, coal and carbonaceous shale. Coal units in these sequences can range up to 10 ft. or more in thickness with total coal thicknesses ranging between 10 and 140 feet (EPA, 2004). The underlying Vermejo Formation (upper Cretaceous) contains numerous coal bearing seams range between a few inches to up to 14 feet with total coal thicknesses ranging between 5 to 35 feet (EPA, 2004). Note also that the Spanish Peaks igneous complex lies within the northwestern portion of the Basin. This complex is composed of intermediate to silicic Cenozoic volcanics

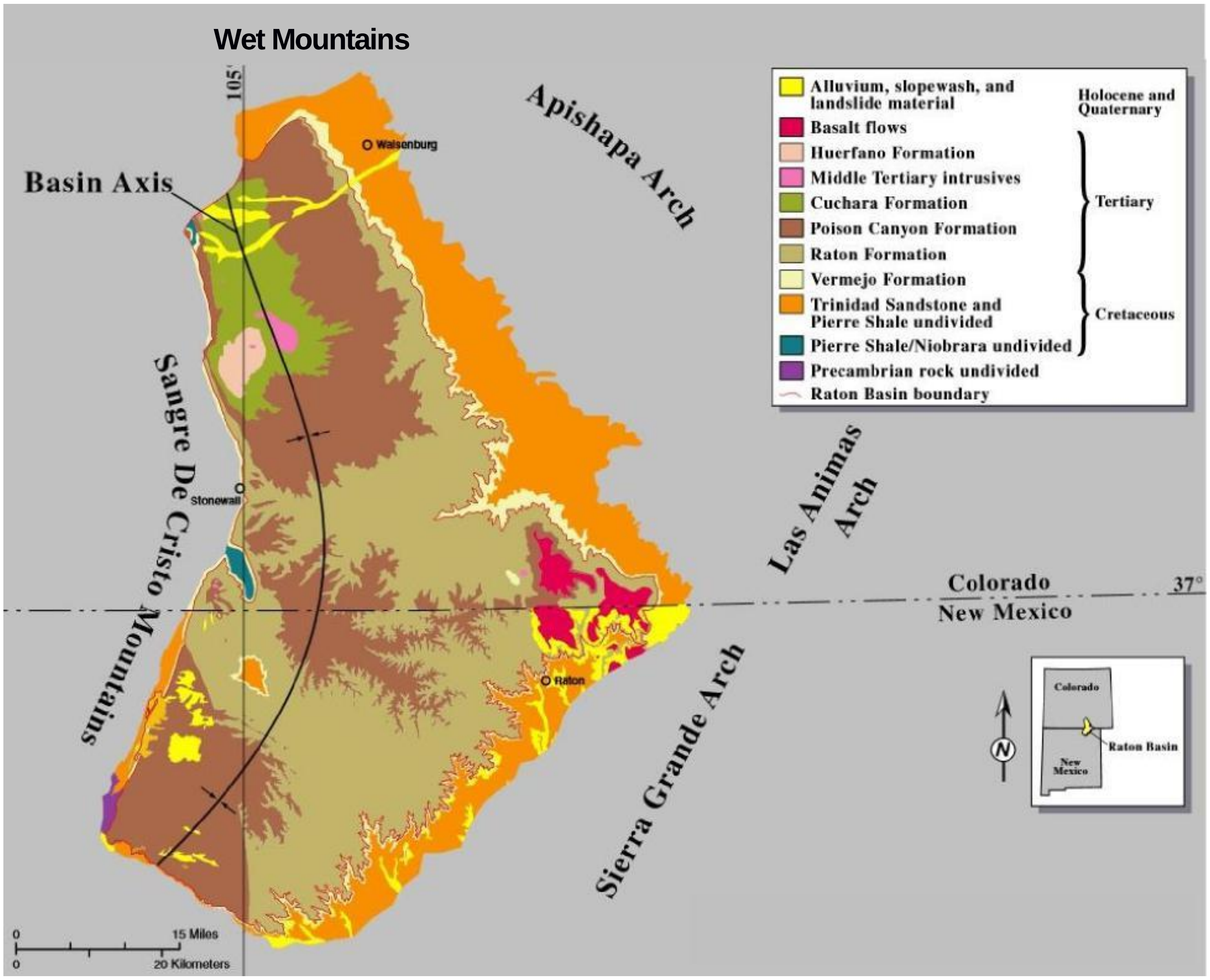

Figure 1 Generalized Geologic Map of the Raton Basin, Colorado and New Mexico (After Flores and Bader, 1999)

Rare Earth Associations in the Raton Basin

Rare earth elements (REE) are a group of 17 elements with similar chemical properties made up of the 15 lanthanides and the elements yttrium and scandium. Figure 2 from Rare Element Resources (2014) shows where they fall within the periodic chart of elements. Because of their particular fractionation behavior, most rare earth deposits appear to occur in rocks that are under-saturated with respect to silica and are believed to be products of differentiation of partial melts derived from undepleted metosomatically enriched mantle material (Sheard, 2010). As such nepheline syenite lamprophyre, and other alkaline rocks have been known to favor REE enrichment. Both the Spanish Peaks and Wet Mountains of Colorado exhibit elevated REE content. Petrographically, the Spanish Peak rocks are a continuous serial gradation from granite to gabbro, with syenodiorite being the most common rock type (Johnson, 1968) and alkaline rocks high in both Th and REE are present in the Wet Mountains (Armbrustmacher, 1984).

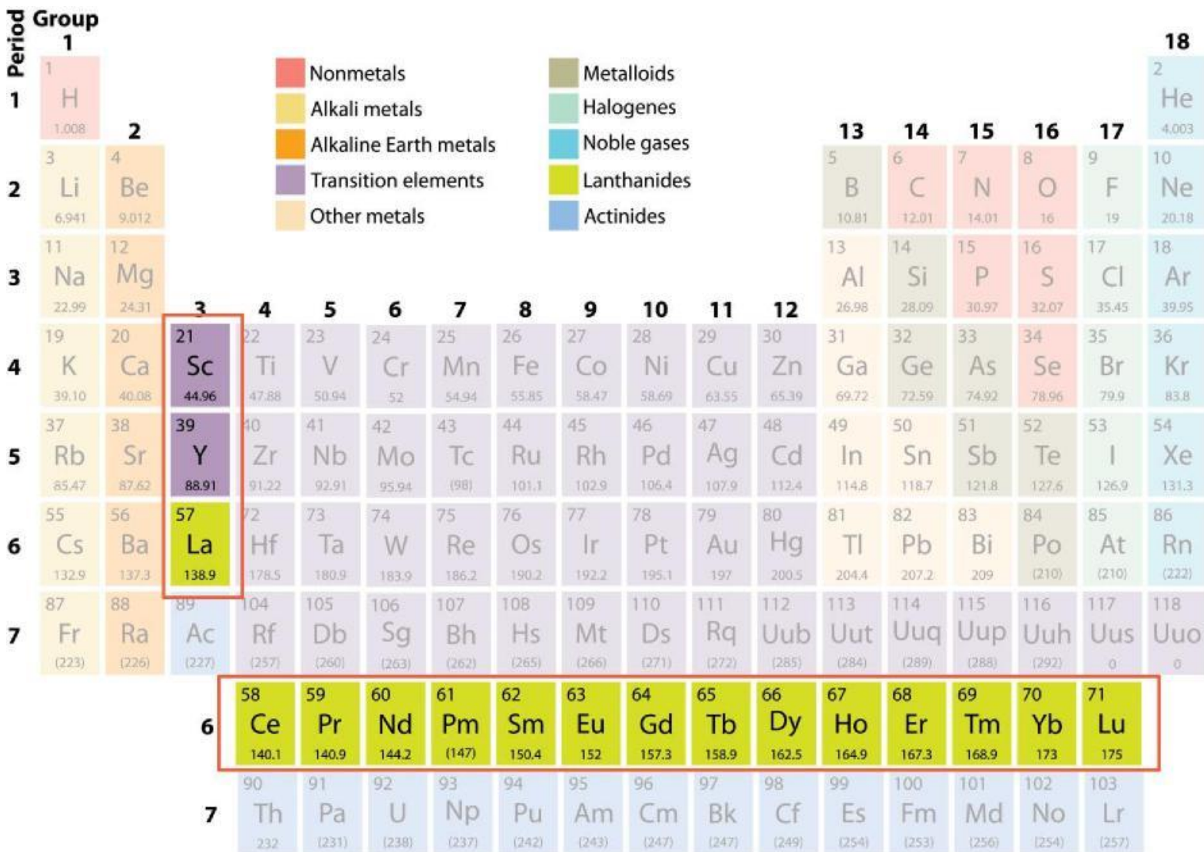

Figure 2 General Periodic Chart showing Rare Earth Elements (REE) (Rare Element Resources, 2014)

When considering possible mechanisms on how REE material can be introduced into coal and coal bearing basins, recent studies by Andersen et al., (2015) suggest three plausible means.

These include

1) introduction of REE via widespread volcanic ash falls (or tuff),
2) introduction of REE from igneous intrusions (diapirs, dikes, sill, and pipes), and
3) introduction of REE with the fluvial-detrital transport of resistate heavy black sands.

Figure 3 schematically shows the expected influence and distribution of REE in a basin using these three mechanisms (Andersen, et al, 2015). Based on the known geology history and character of the Raton basin, the influence of kaolinitic-rich volcanic ash/tuff deposits or tonsteins layers (for example the K-T layer tonstein) plus local igneous activity during the middle Tertiary resulted in the formation of igneous dikes and sills associated with the development of the Spanish Peaks are likely sources for the observed REE content in both the coals and coaly shales. Many of these igneous features “coked” coal in place in portions of the basin. If they contained REE then their influence on the observed REE in sediments may be substantial.

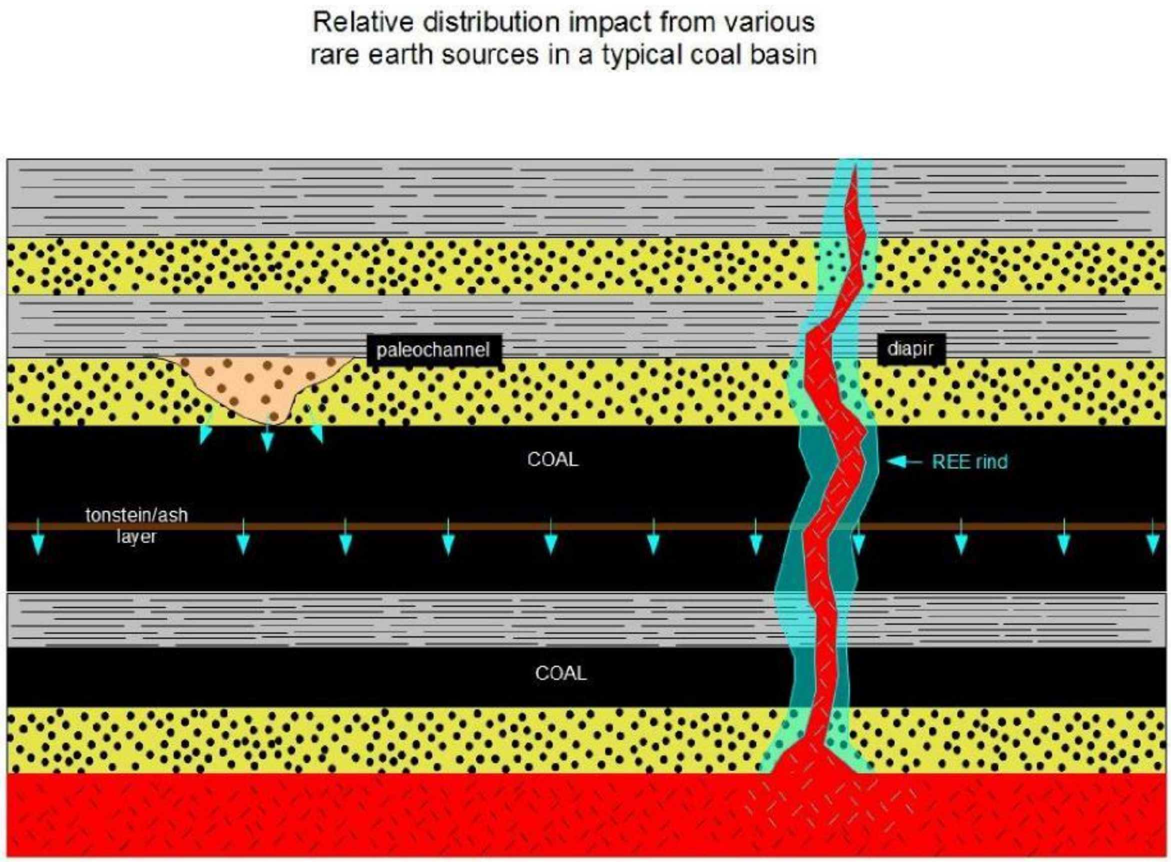

Figure 3 Mechanisms for introducing REE into Coal Basins (Andersen, et al, 2015)

When considering the Raton Basin, certainly ash falls associated with either the K-T impact, as well as earlier and later volcanic activity could be involved as could direct involvement of intruding dikes and sills. While not discounting fluvial influence as a possibility, this mechanism was not investigated in this report. In the Colorado portion of the Raton Basin, elevated occurrences of light REE in coals and coaly shales are found close to K-T boundary. This boundary is defined by a thin claystone (tonstein) layer, (Izett, 1990). In a recent field trip (Taylor, 2015) by the authors to this area, 2 samples of the actual K/T boundary clay were sampled by XRF. Figure 4 shows one site visited located in the Trinidad Lake State Park. The boundary is depicted by the thin white clay layer just beneath the massive sandstone in this figure. Interestingly enough, while samples from both sites exhibited extremely elevated levels of iridium and tungsten, as well as traces of other heavy metals, no rare earth elements were seen in the analysis. This area however, the basin is punctuated by extensive igneous activity associated with the formation of the Spanish Peaks and the associated radial lamprophyre dikes. In fact, coal

Figure 4 Cretaceous-Tertiary Boundary Clay at Trinidad Lake State Park

has actually been coked naturally in some areas of the basin suggesting that both volcanic ash as well as igneous intrusion could be responsible for the elevated REE content in the basin coals and coaly shales. Published REE data (Knight, 2011) on the rocks of the Spanish Peaks as well as new data obtained by the authors utilizing a portable X-Ray Fluorescence Spectrometer (XRF) on dike material and coal/coaly shale along the K/T boundary of the area. Knight's data appears in Table 1. These data were obtained utilizing instrumental neutron activation analysis (INAA) along with literature derived values.

Table 1. Rare Earth Elemental Data of Select Spanish Peak Igneous Samples

Sample	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
bj15	74.31	138.2	62.4	10.43	2.82	8.2	5.25	2.46	1.99	0.288			
bj19	36.5	69.4	32.9	6.4	2.04	5.75	4.62	2.26	1.89	0.277			
bj2	64.55	127.6	64.2	11.23	2.93	8.25	5.42	2.51	1.98				
bj23	33.61	56.32	19.47	3.09	0.737	2.45	1.7	0.9	0.79	0.117			
bj25	58.08	110.6	44.4	7.41	1.985	5.56	3.99	1.933	1.692	0.258			
bj29	36.4	70.82	34.5	6.43	1.86	5.61	4.28	2.4	2.16	0.271			
bj37	55.2	101.8	44.7	7.77	2.08	6.47	4.65	2.3	1.84	0.272			
bj5	97.3	195.1	92	14.18	3.6	9.5	4.85	1.94	1.41	0.192			
bj64	34.03	59.28	19.15	3.3	0.56	2.76	3.2	2.17	2.72	0.475			
bj65	68.7	122	46.9	7.61	2.14	5.73	4.23	1.97	1.7	0.26			
bj8	95.46	199.2	96.3	14.69	3.72	8.86	4.61	1.844	1.48	0.196			
bj8-18	91.2	154.5	50.1	6.95	1.98	4.32	3.33	1.74	1.65	0.254			
bj8-40	68.1	132.4	60.9	10	2.82	7.4	4.88	2.16	1.77	0.226			
bj8-w	22.17	42.59	19.64	4.1	0.8	3.66	3.97	2.63	2.89	0.467			
rj108	61.6	108	6.27	1.93	6.1	0.91	1	1.96	0.36				
rj113	71.4	113	6.01	1.64	7.4	0.804	1.1	2.22	0.44				
rj137	55.7	108	8.48	2.97	9.4	1.26	1.4	2.54	0.45				
rj16	0.59	3.33	0.9	0.348	2.1	0.358	0.48	1.03	0.18				
rj168	85	185	13.5	3.54	12	1.5	2.3	2.16	0.31				
rj173	84.6	159	11.3	3.21	11	1.36	2.3	2.36	0.33				
rj178	29.7	74.4	7.13	2.28	8.4	1.05	0.92	2.2	0.36				
rj5	1.39	4.45	0.78	0.299	1.5	0.204	0.23	0.43	0.08				
rj78	58	68	3.24	0.754	4	0.435	0	1.35	0.35				
rj86	80.3	130	6.77	1.88	8.3	0.957	1.3	3.21	0.58				
rj97	200	403	23.5	6.5	19	1.94	3.6	2.66	0.38				
rjESP	64.6	76.6	5.04	0.707	6.3	0.821	0	4.72	1.02				
rjMtMest	4.06	6.23	0.96	0.349	0	0.212	0	0.91	0.21				
rjSWPeak	18.8	40.5	3.08	0.911	2.4	0.361	0.35	0.94	0.15				
sp101	55.9	111	47	8.44	2.16	6.82	0.927	1.2	0.408	2.59	0.363		
sp118	17.8	34.4	15	2.6	0.653	1.82	0.245	0.312	0.118	0.688	0.096		
sp121	39.9	89.2	42.1	8.21	1.91	6.23	0.857	0.886	0.292	1.74	0.252		
sp123	33.5	69.9	31.8	5.61	1.48	3.72	0.548	0	0.269	1.54	0.236		
sp124	3.7	8.19	4.31	1.31	0.424	1.57	0.223	0.27	0.079	0.455	0.053		
sp131	94.6	206	98	14.2	3.56	8.95	0.969	0.779	0	1.4	0.185		
sp134	57.7	110	40.5	6.46	1.46	5.68	0.76	1.08	0.469	2.91	0.431		
sp18	30.4	65.6	32.3	6.26	1.74	5.05	0.658	0.777	0.293	1.73	0.252		
sp20	42.2	88.1	41.6	7.87	2.06	6.3	0.847	1.02	0.42	2.65	0.393		
sp21a	39.7	92.7	46.8	9.61	2.36	8.22	1	1.03	0.313	1.67	0.226		
sp21b	70.3	142	63.9	10.7	2.77	7.21	0.926	0.921	0	1.69	0.263		
sp23	40.8	81	34.6	5.82	1.58	4.37	0.574	0.753	0.299	1.81	0.264		
sp33	51.2	97.9	39.1	7.18	2.03	5.64	0.755	0.881	0.324	1.8	0.253		
sp34b	70	150	71.5	11.3	3.07	9.11	1.1	1.29	0	2.61	0.382		
sp34ts	48.9	107	51.2	9.48	2.4	6.62	0.884	0.988	0.344	2.01	0.297		
sp37	52.5	116	60	11.2	2.88	7.66	0.958	0.976	0.302	1.77	0.246		
sp41	44.5	94.9	43.6	8.47	2.22	6.86	0.878	0.924	0	1.86	0.269		
sp42	62.1	132	57.1	9.67	2.23	6.6	0.803	0.892	0.292	1.66	0.242		
sp46	49.3	101	42.9	8.01	2.11	6.33	0.776	0.731	0	1.44	0.206		
sp5	69.8	160	76.5	12	3.09	7.7	0.857	0.788	0	1.44	0.183		
sp51	59.1	119	53.6	9.4	2.5	7.91	0.965	1.08	0	1.9	0.259		
sp52	66.2	142	65.3	11.1	2.83	8.13	0.939	0.91	0.303	1.8	0.262		
sp57	41.9	87.9	38.3	6.82	1.8	5.41	0.721	0.93	0	2.57	0.383		
sp58	53.1	113	51.7	8.7	2.28	6.09	0.752	0.691	0	1.26	0.181		
sp58b	53.1	111	52.1	8.86	2.3	6.42	0.748	0.688	0	1.25	0.169		
sp65	52.5	114	52.4	9.25	2.54	7.21	0.867	0.866	0.303	1.72	0.244		
sp70	107	262	129	18.9	4.39	11.3	1.05	0.786	0	1.15	0.154		
sp70b	109	271	132	19.5	4.51	11.2	1.06	0.807	0	1.21	0.151		
sp95	60.2	119	51.2	8.69	2.29	7.3	0.932	1.13	0	2.5	0.357		

In the above table, samples beginning with "bj" are from Jahn (1973), and samples beginning with "rj" are from Johnson (1968).

Surface outcrop samples of coal and shaly-coal material from the Colorado portion of the Raton basin were analyzed for their light REE content using a Niton XL3T Gold++ portable X-ray fluorescence (XRF) spectrometer. Table 2 shows the results of several of these samples as well as some from the Florence, Colorado, area. What is interesting about the Raton samples is they were collected near the Cretaceous/Tertiary boundary and are situated next to the Spanish Peaks volcanics and associated lamprophyre dikes. The Florence samples, collected northwest of the Raton Basin are adjacent to the Wet Mountains, which are reported to contain appreciable thorium and REE (Long et al., 2010) in syenitic and carbonatite dikes.

Coal samples were collected by USGS in the Raton Basin as part of their CoalQual Database effort (USGS, 2014). That study sent coal samples for laboratory analysis using inductively coupled plasma/mass spectrometry (ICP/MS) to determine their REE contents. Comparison of XRF results for samples collected by Tetra Tech in the Raton Basin with the reported USGS values shows that the Raton Basin consistently has elevated REE contents. Figure 5 shows the Colorado portion of the Raton Basin with both light REE values from the USGS CoalQual database coal samples (colored squares) and the XRF spectrometer-derived values of surface coal, coaly shale, and igneous dike samples (colored diamonds). As reported, four USGS coal samples had light REE contents greater than 100 ppm, and two samples had light REE contents greater than 200 ppm. The results for several other samples of coal and coaly shale obtained using the field-portable XRF unit found light REE contents in excess of 1,000 ppm. Samples obtained from a Tertiary lamprophyre dike just southwest of the Town of La Veta showed similarly high light REE contents as the coal samples. This implies that, in addition to introducing REE in the basin via tonstein deposits within the coal, igneous injection of dikes and sills could also be a possible sourcing mechanism for introducing REE. In some portions of the basin, coal has actually been converted to coke due to igneous activity. Further study should include obtaining samples of this naturally occurring coke to ascertain its REE content. Pertinent REE data and other elements derived from XRF analysis within the Raton basin in south-central Colorado appears in Table 2.

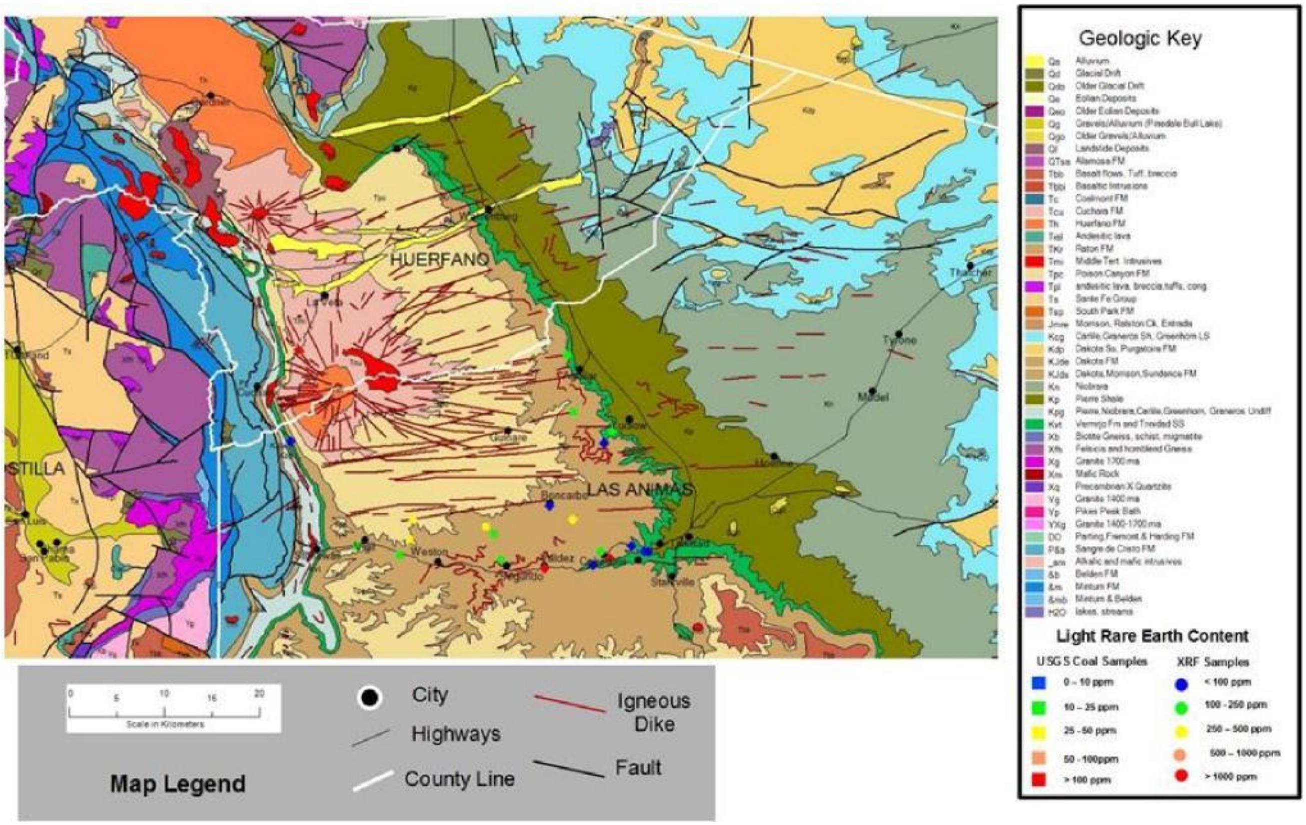

Figure 4 Rare Earth Element Outcrop Samples in Raton Basin

Table 2. Rare Earth Elemental analysis of Raton Basin samples by XRF Spectroscopy

SAMPLE	Ti	V	Th	U	Y	Sc	La	Ce	Pr	Nd
cosotr002	762.42	64.17		15.35	317.17					
tr001	541.23	60.44			218.14					
tr001a	196.44				185.81					
tr001ta	400.11	21.27	10.78		137.67					
tr001zn			8.9		117.16					
tr001b	332.34				116.32					
cosotr002					67.15					
cosogj001	1118.37	123.35		13.75	47.21	103.68				
cosofp0001	917.41	67.08	21.79		25.16	13.03				321.42
kr007	3131.35		18.81		24.86		237.69	242.94	404.73	599.37
kt003	1738.04				24.04					
kt004	5632.97	198.96	9.92		22.98		119.04	135	176.96	304.69
nmsofw0001	1745.39	113.88	13.63		22.28	86.22	74.24	102.28	119.33	286.9
fl011	670.36			7.58	20.25					
cosofr0001	1793.21	89.22	9.62		18.59	125.77				
kt001	4269.5	39.87			16.88					
cosofr0002	1055.23	75.71		79.75	15.75		98.68	126.25	180.57	325.9
fl011	1729.24	95.93	4.93		15.03	51.23				
cosogj0001	493.88	25.24			14.85	21.45				
kt006	1654.15				14.71					
tr003	480.38			16.05	13.92	243.96				
nmsofr0003	1525.3	76.5	13.7		13.76	173.32				
fl011	3905.29	171.28	10.39	8.07	13.47	126.87				117.67
kt005	4295.69	129.15	6.85		11.06		182.35	197.7	300.84	513.28
fl011	80.83	22.36			10.21	6.9				
lu008			10.57		9.98					
lu006	2366.67	148.12			9.13		227.93	252.71	434.37	702.07
lu008	1543.5	66.6	10.01		8.52					
tr004a	290.25	14.22			7.78	5.85				
cocdfr0001	2189.01	99.36		5.82	7.26	167.27				
kt002	3818.34	86.46			7.17					
kt008	2449.95		10.87	5.12	5.93					
l dike	1573.09		21.03	9.81	5.13		159.79	158.63	348.55	549.88
l dike2	988.02	21.22	16.79	10.68	5.08		192	199.65	351.15	535.1
tr005	3226.66	121.95		11.04	4.8	40.6				

Conclusions

Coal, shaly coals and tonstein samples collected in the greater Raton basin of Colorado exhibited elevated rare earth content. Several of these samples were collected proximal to the K-T layer inferring that ash derived from this impact which resulted in the formation of a thin tonstein layer could be a plausible source. Volcanic and other igneous activity in the basin could also be responsible and post-dates the K-T boundary, suggesting that hydrothermal fluids and/or direct contact with igneous dikes and sills could introduce REE into the samples. Certainly, samples of Cenozoic lamprophyre dike material collected at the northern edge of the basin exhibited REE contents that were as high as or higher than those observed in the coal and coaly shale samples.

If a systematic survey over the entire basin can be conducted, then the association of REE-rich layers with coal might provide a means to formulate a strategy to exploit these elements as a by-product of coal production. Future work should include careful scrutiny of exploration cores in the basin if available to identify samples of tonstein, the K/T clay, and fresh coal above and below these layers to determine if the source of REE in the coals are from volcanic ash, intrusives, or the K/T impact.

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