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MCKELVEYITE, A NEW HYDROUS SODIUM BARIUM RARE-EARTH URANIUM CARBONATE MINERAL FROM THE GREEN RIVER FORMATION, WYOMING[1]

CHARLES MILTON, BLANCHE INGRAM, JOAN R. CLARK AND
EDWARD J. DWORNIK *U. S. Geological Survey, Washington, D. C.*

ABSTRACT

A new mineral of composition

$$\mathrm{Na}^{1+}_{1.9}\mathrm{Ba}^{2+}_{4.0}\mathrm{Ca}^{2+}_{1.1}\mathrm{Sr}^{2+}_{0.2}\mathrm{RE}^{3+}_{1.5}\mathrm{U}^{4+}_{0.3}(\mathrm{CO}_3)^{2-}_9\cdot 5\mathrm{H}_2\mathrm{O}$$

occurs in 4 subsurface localities some 20 miles apart in Sweetwater County, Wyoming. It is the first known mineral with considerable uranium (4.6% as UO_2) from the Green River Formation. Two types are known, one (very rare) in apple green crystals and simple morphology, which has not been analyzed, and a more abundant type, dark green or black, massive and in crystal aggregates, both of which have been analyzed. The massive material contained 20.7% insoluble (organic 8.7%, acmite 3.5%, biotite 7.5%, quartz 1.0%); and the crystal aggregates contained 18% insoluble (organic 3.0%, acmite 2.45%, biotite 9.4%, quartz 3.0%). This is the first authigenic biotite recognized in the Green River Formation. All these insoluble constituents are presumably syngenetic with mckelveyite. The analysis of mckelveyite (crystal aggregates) recalculated for these impurities, is BaO 40.6, CaO 4.0, SrO 1.7, Y_2O_3 7.7, La_2O_3 0.09, Ce_2O_3 0.16, Pr_2O_3 0.05, Nd_2O_3 0.26, Sm_2O_3 0.34, Eu_2O_3 0.19, Gd_2O_3 1.18, Tb_2O_3 0.38, Dy_2O_3 1.00, Ho_2O_3 0.28, Er_2O_3 0.95, Tm_2O_3 0.12, Yb_2O_3 0.61, Lu_2O_3 0.08, UO_2 4.6, ThO_2 0.1, Na_2O 3.9, K_2O 0.1, CO_2 25.7, H_2O 6.1, sum 100.2.

The crystals are trigonal, space group $P\bar{3}$, a 9.174±0.002 Å, c 19.154±0.007 Å, cell volume 1396.1±0.7 Å^3; the three strongest observed x-ray powder lines are 2.942 (100), 4.47 (85), 6.40 Å (35). The density calculated for two formula units per cell is 3.62 g cm^{-3}; the measured density of the massive aggregate is 2.87, of the crystals 3.14; corrected for impurities, the density of mckelveyite in the massive aggregate computes to 3.58, in the crystals 3.47 g cm^{-3}. There is no good cleavage, but fractures are approximately paralled to (0001) and $(11\bar{2}1)$. Piezoelectric tests are negative. Forms observed: c {0001}, r $\{10\bar{1}1\}$, e $\{01\bar{1}2\}$, m $\{10\bar{1}1\}$, $-m$ $\{01\bar{1}0\}$. Mckelveyite is uniaxial, negative, $\epsilon=1.57$, $\omega=1.66$, pleochroic, green, $\omega>\epsilon$.

Mckelveyite with essentially yttria rare earths occurs together with burbankite, a cerium rare-earth mineral.

The mineral is named in honor of Vincent E. McKelvey, geologist of the U. S. Geological Survey.

INTRODUCTION AND OCCURRENCE

In studying waste residues from soda ash production of the trona mine of the Food Machinery Corporation at Westvaco near Green River, Wyoming, tiny green crystals have occasionally been found (Fig. 1). Although there were not enough of these crystals for chemical analysis, optical, spectrographic, and x-ray diffraction powder studies indicate that the crystals represent a new mineral species. More crystals of the new mineral were found in a core from the Intermountain Chemical

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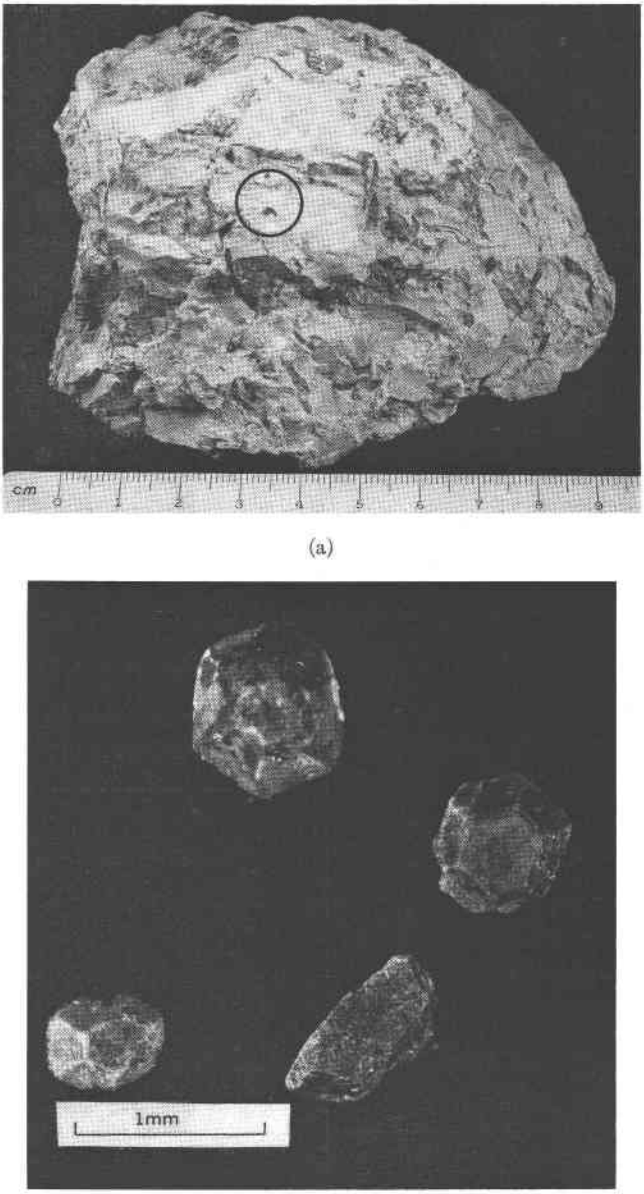
[1] Publication authorized by the Director, U. S. Geological Survey.



(a)

(b)

FIG. 1. (*a*) Green mckelveyite crystal (circled) in matrix of dolomitic marlstone with coarse shortite crystals. Drillcore, Westvaco, Wyoming. (*b*) Green mckelveyite crystals removed from matrix, in trona milling operations at Westvaco.

Company John Hay No. 1, Wyoming (Fahey, 1962) at a depth of 1557 feet near the main trona bed, associated with labuntsovite, leucosphenite, searlesite, and other typical minerals of the Green River Formation (Milton and Eugster, 1959; Milton and Fahey, 1960; Milton *et al.*, 1960). Enough material for chemical analysis finally became available in 1959 when the new mineral was found in relative abundance in a few inches of core taken at a depth of 1576 feet from the Diamond Alkali Daco No. 3, Sweetwater County, Wyoming. The core was obtained by J. D. Love, U. S. Geological Survey, in the course of a study of the newly discovered uranium-phosphate dolomite zones in the Wyoming Green River Formation (Love and Milton, 1959). The several hundred milligrams of crystals (Figs. 2, 3) in this core were used in the present study. Although these crystals were usually black rather than green in color, and varied somewhat in habit from the crystals found earlier, the evidence indicates that the color differences are due merely to the presence of contaminants. The new mineral is shown in typical thin section in Fig. 4. According to J. D. Love (writt. comm., 1961), the mineral is known to occur at four localities, all in the Wilkins Peak Member of the Green River Formation (Fig. 5).

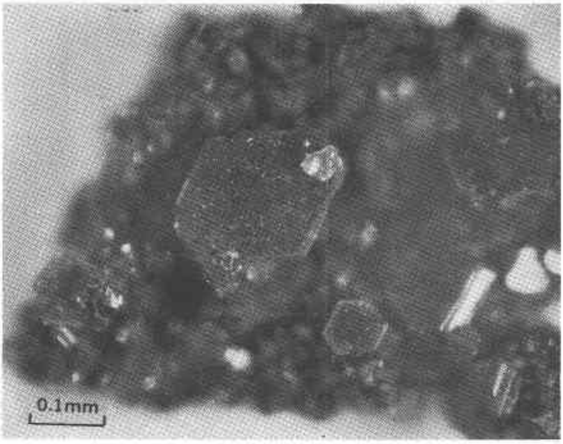


FIG. 2. Aggregate of mckelveyite crystals as used in chemical analysis. Magnification: 100×. Crystals from Diamond Alkali Daco No. 3 core, depth 1576′, Sweetwater County, Wyoming.

Several years of intermittent labor in handpicking the samples for analysis were required. The analyses were made on microquantities and their interpretation presented special problems because of the presence of contaminants. Nevertheless, the results of the present study ade-

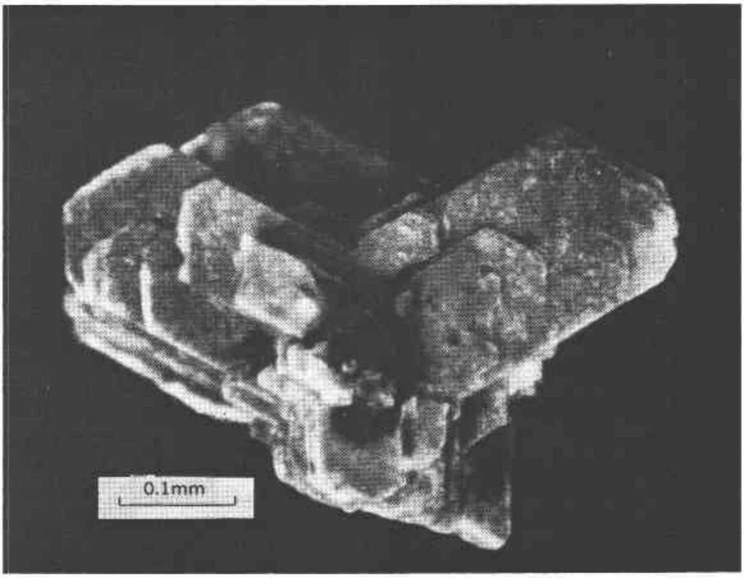


FIG. 3. Mckelveyite crystals from the core taken at 1576 feet, Diamond Alkali Daco No. 3, Sweetwater County, Wyoming. Magnification: 150×. Characteristic habit of the analyzed crystals is shown. The hexagonal base of the crystals is usually dark green or black; the trigonal array of lighter colored (to pale green) platelets superposed on the base reveals the three-fold symmetry.

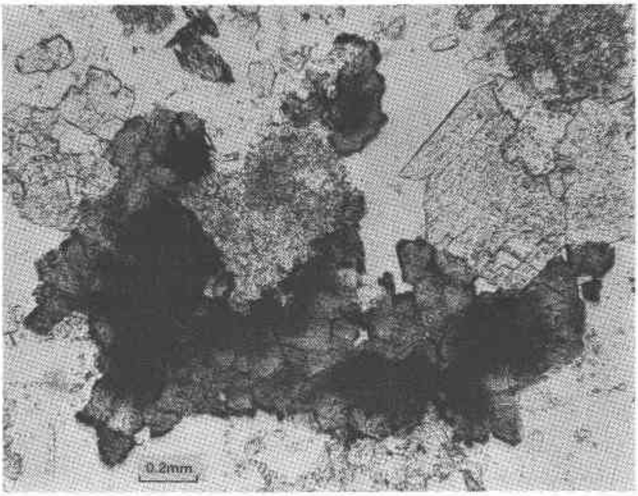


FIG. 4. Thin section in ordinary light showing dark hexagonal mckelveyite crystals in dolomitic marlstone, associated with semi-opaque limonite (?) and clear dolomite. Specimen from John Hay No. 1, Sweetwater County, Wyoming, depth 1797.5 ft. Magnification: 38×.

quately characterize the new mineral, even though some minor details may require revision in the future.

The new mineral is named mckelveyite in recognition of the studies of the Phosphoria Formation of Wyoming and Idaho by Vincent E. McKelvey, geologist of the U. S. Geological Survey. The specimens described have been placed in the collections of the U. S. National Museum.

Chemical Studies of Mckelveyite

Description of samples and methods of analysis. Two chemical analyses were made of mckelveyite. The first analysis was carried out on 500 mg of massive, formless black aggregate material, and the second, on 180 mg of selected crystals. The samples were from the core taken at 1576 feet in Diamond Alkali Daco No. 3, Sweetwater County, Wyoming. Particular care was taken in assembling both samples to insure freedom from the dolomite matrix. Data from both analyses (Tables 1–6) show the nature of the problems involved and the observed differences between the two samples.

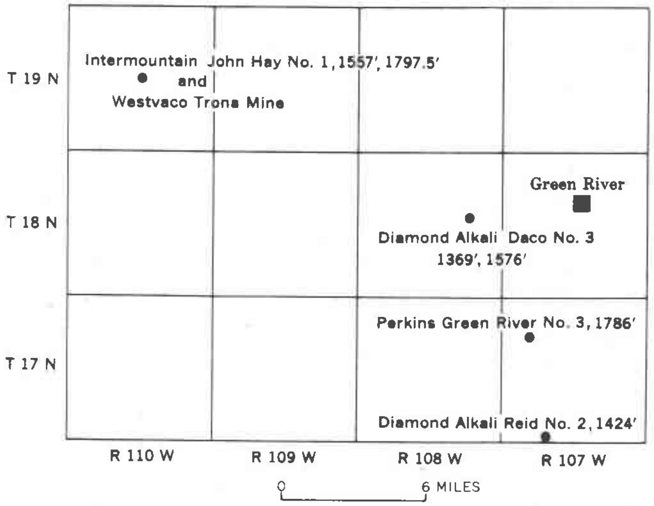


FIG. 5. Map showing the location in Sweetwater County, Wyoming, of the four known occurrences of mckelveyite. Footage indicates depth of occurrence in drill holes.

The selection of procedures for analysis was based on initial microspectrochemical analyses of the samples by Claude L. Waring, U. S. Geological Survey. The spectrochemical analyses confirmed the essential similarity of the massive material and the selected crystals. Only those elements shown present in amounts greater than 0.1% were determined chemically. Each sample was divided into acid soluble and insoluble fractions by treatment with 1+3 HCl. Spectrographic analyses were made on both fractions of the black aggregate sample to decide which elements were to be determined in each fraction. A similar division of elements was assumed to occur in the selected crystals. The insoluble fractions were decomposed for analysis either by fusion with Na_2CO_3 or by HF-$HClO_4$ treatment. A description of the methods used follows, and the basic data from the two analyses are given in Table 1.

1) *CO_2, H_2O.* Determined gravimetrically. The sample for determination of total CO_2 and H_2O was mixed with V_2O_5 and heated in a combustion train at 900° C. in a stream of oxygen. The sample of massive material was first treated with 1+3 HCl in a beaker and the insoluble residue collected in a perforated platinum boat on an ignited asbestos filter. The insoluble residue in the boat was dried at 110° C. and then ignited in the combustion furnace. Complete transfer was impossible due to the tendency of the residue to creep and to adhere to the beaker. Consequently, the procedure was modified for the sample of crystals, which was treated with 1+3 HCl in a small Munroe crucible. The soluble portion was separated by filtration and the residue dried and then ignited in the combustion furnace without transfer from the crucible. H_2O in the soluble fraction is obtained by subtracting H_2O^- and H_2O in the insoluble from total H_2O.

2) *F.* Determined spectrophotometrically with thoron after distillation from H_3PO_4-$HClO_4$ medium. The sample for determination of total F was first decomposed by Na_2CO_3-ZnO fusion; the fusion mixture was leached with H_2O, and the leachings distilled. For determination of acid soluble F, the sample was placed directly in the distillation flask and the F soluble in H_3PO_4-$HClO_4$ was distilled.

3) *BaO.* Determined gravimetrically as $BaSO_4$.

4) *CaO, SrO, Na_2O, K_2O.* Determined by flame photometer.

5) *RE_2O_3, U_3O_8, ThO_2.* The oxides were weighed as a group after separation by NH_4OH precipitations to the phenolphthalein end point. Using a separate sample, uranium was determined fluorimetrically and thorium was determined spectrophotometrically with thoron. The ignited weight was also corrected for the small amount of Fe_2O_3 present. Total RE_2O_3 was determined by difference. A concentrate of 3.1 mg. rare-earth oxides, with uranium and thorium oxides, obtained from the analysis of the crystals was analyzed spectrographically, after treatment with HF to remove Fe_2O_3 (and part of the U_3O_8), for determination of the relative proportions of the various rare-earths.

6) *Fe_2O_3* (total iron). Determined spectrophotometrically with *o*-phenanthroline. (No determination of ferrous iron was undertaken.)

7) *Al_2O_3.* Determined spectrophotometrically with alizarin red S.

8) *MgO.* Determined spectrophotometrically with thiazole yellow.

9) *SiO_2.* Determined gravimetrically after double dehydration.

Included organic matter in mckelveyite. The black coloration that varies from one mckelveyite crystal to another, and the excess of total CO_2 over acid-evolved CO_2 (Table 1) are attributed to the presence of varying amounts of organic material included in mckelveyite crystals. The organic matter is presumably amorphous since its presence does not affect the *x*-ray diffraction powder patterns of mckelveyite samples. Smith (1963) has shown that the oil shale of the Mahogany zone, Green River

TABLE 1. CHEMICAL ANALYSES OF MCKELVEYITE FROM SWEETWATER COUNTY, WYOMING
Blanche Ingram, analyst (except as noted)

	Weight Per Cent	
	Massive	Crystals
Determined on total sample		
Total H_2O	10.6	7.7
Total CO_2	45.5	30.0
CO_2, acid evolution	20.0	21.2
Total F	0.05	—
Loss at 110° C.	0.7	—
Insoluble (1+3 HCl)	19.7	18.2
Determined on fraction soluble in 1+3 HCl		
BaO	33.4	33.5
CaO	3.0	3.3
SrO	1.7	1.4
UO_2[1]	3.8	3.8
ThO_2[2]	0.11	—
RE_2O_3	9.0	11.0
Fe_2O_3	0.69	0.75
Na_2O	3.6	3.2
K_2O	0.16	0.10
SiO_2	0.33	0.20
F	0.02	—
H_2O (by difference)	4.8	5.0
Determined on fraction insoluble in 1+3 HCl		
SiO_2	5.2	7.8
Fe_2O_3	3.3	3.7
Al_2O_3	0.69	0.14
MgO	—	0.68
Na_2O	0.47	0.33
K_2O	0.60	0.94
C as CO_2[3]	22.1 (25.5)	9.3 (8.8)
H_2O	5.1	2.7

[1] Analyst, Joseph Budinsky, U. S. Geological Survey.

[2] Analyst, Lillie Jenkins, U. S. Geological Survey.

[3] The values in parentheses are those obtained by difference of total CO_2 and acid-evolved CO_2 and are considered more accurate than the values from direct determination because of the transfer difficulties.

Formation, contains a hydrocarbon of nearly constant composition with $C=80.5\%$. The reasonable assumption can be made that the organic contaminant in mckelveyite is similar to that of the hydrocarbon described by Smith. Thus 8.7 weight per cent of the massive sample and 3.0

weight per cent of the crystal sample may be attributed to the organic contaminant (Table 2).

Biotite, acmite and quartz in mckelveyite. X-ray diffraction powder photographs reveal acmite, biotite and quartz intimately associated with mckelveyite. Acmite and quartz are common authigenic minerals in the Green River Formation, but biotite has not been recognized previously.

TABLE 2. COMPOSITION ASSUMED FOR ORGANIC MATTER IN MCKELVEYITE

Analytical data (Table 1):	Weight Per Cent	
	Massive	Crystals
Total CO_2	45.5	30.0
CO_2, acid evolution	20.0	21.2
Difference (organic CO_2)	25.5	8.8
Equivalent C	7.0	2.4
Organic matter[1]	8.7	3.0

[1] Assuming organic matter with C=80.5% (Smith, 1963).

X-ray diffraction powder patterns were prepared both from selected mckelveyite crystals and from the residue remaining after mckelveyite crystals had been treated with dilute HCl. The observed data for the pattern obtained from the acid-treated residue are compared in Table 3 with representative data for quartz, acmite and biotite. Selection of biotite data for comparison is necessarily arbitrary, since such data vary,

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[1] Camera diameter, 114.59 mm.; radiation Ni-filtered Cu, CuKα, $\lambda=1.5418$ Å; b=broad, d=diffuse. Lower limit of 2θ measurable, approximately 7° (13 Å). Film no. 16184, powder spindle no. 12397, prepared by Mary E. Mrose, U. S. Geological Survey, from residue after treatment of mckelveyite crystals with dilute HCl.

[2] *X*-ray diffractometer measurements; radiation, Mn-filtered Fe, Fe Kα, $\lambda=1.9373$ Å; internal standard, silicon. Annite synthesized at 600° C., 2,070 bars.

[3] Zr-filtered Mo radiation; camera diameter 16 inches. Reference given on A.S.T.M. card is "Sample from boiler scale."

[4] Ni-filtered Cu radiation; G. C. diffractometer. Reference given on A.S.T.M. card is Swanson and Fuyat, NBS Circular 539, Vol. III (1953).

[5] Line attributed to biotite.

TABLE 3. *X*-RAY POWDER DIFFRACTION DATA COMPARED FOR ACID-TREATED RESIDUE OF MCKELVEYITE AND BIOTITE, ACMITE AND QUARTZ

Acid-Treated Residue, Mckelveyite		Synthetic Annite		Acmite		Quartz	
Present Study[1]		Eugster and Wones (1962)[2]		ASTM 3-0621[3]		ASTM 5-0490[4]	
I	d_{obs} (Å)	d_{obs} (Å)	I	d_{obs} (Å)	I	d_{obs} (Å)	I
70	10.2	10.264	100				
<2	6.51			6.5	40		
<2	5.00	5.070	3				
10	4.53	4.644	5				
d	to			4.43	40		
20	4.26					4.26	35
		3.975	3				
5	3.64	3.711	5	3.64	7		
5	3.49[5]						
100	3.35	3.380	80			3.343	100
5	3.24	3.179	15				
5	3.12	3.106	10				
5	3.01			2.99	100		
10	2.92			2.91	40		
5, d	2.70	2.734	5				
15, b	2.60	2.654	70	2.54	60		
		2.532	15				
2	2.46	2.465	40	2.48	27	2.458	12
5	2.41[5]						
5	2.28					2.282	12
5, b	2.23			2.20	20	2.237	6
5	2.16	2.199	20				
5	2.13			2.12	20	2.128	9
5	2.005	2.018	10	2.03	20		
2	1.982			1.98	7	1.980	6
		1.932	5	1.93	7		
10	1.820					1.817	17
						1.801	<1
				1.73	13		
	1.673	1.692	20	1.68	7	1.672	7
5, b	to						
	1.659			1.66	7	1.659	3
2	1.635	1.635	1	1.63	7		
				1.61	7	1.608	<1
5	1.542	1.556	40	1.54	7	1.541	15
5	1.514	1.538	10	1.51	13		
		←plus additional lines→					

depending on the composition of the biotite. *X*-ray fluorescence analysis by H. J. Rose, Jr., U. S. Geological Survey, of the acid-treated residue from mckelveyite showed only major Fe. Crushed crystals of mckelveyite were then examined optically by D. R. Wones, U. S. Geological Survey, who identified minute biotite fragments among the crushed crystals and obtained a maximum index of refraction 1.633±0.004. This value, together with the *x*-ray measurement of 1.542 Å for d_{060} indicates that the biotite is a variety containing 35 to 45% Fe end-member annite (D. R. Wones, writt. comm., 1961). Comparison with the *x*-ray powder data for synthetic annite (Table 3) therefore seems reasonable. All the observed lines in the residue pattern can be satisfactorily accounted for as due to biotite, acmite, or quartz. Thus the evidence given in Table 3 establishes identification of these impurities intimately associated with mckelveyite.

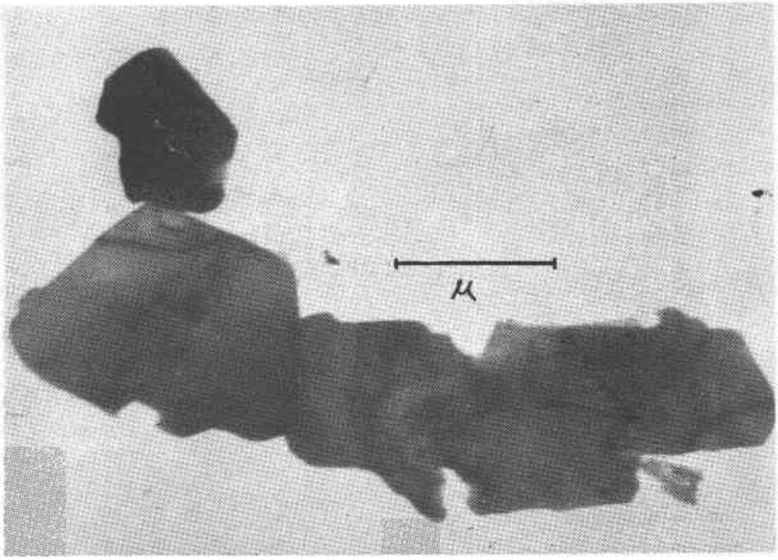

FIG. 6. Electron micrograph of micaceous particles in mckelveyite crystals. 22000×.

In an attempt to examine the micaceous inclusions in closer detail than was possible with optical microscopy, a carefully handpicked grain of mckelveyite was prepared for electron microscope study. The sample was disaggregated by gentle crushing and further by ultrasonic treatment in a water suspension. Droplets of the finely dispersed material were placed on collodion-covered support screens and the water allowed to evaporate.

Platy particles assumed an orientation parallel to the substrate which on insertion in the microscope would be normal to the electron beam.

Several different mounts were scanned in an effort to locate micaceous flakes suggestive of biotite. Micaceous minerals transparent to electrons characteristically exhibit a "wavy extinction" such as shown in Fig. 6. The hexagonal outlines of the platelets are readily apparent. During the course of observation, micaceous flakes and aggregates were isolated from the other material in the field of view with the selected area diffraction device. A typical electron diffraction spot pattern obtained and the sample yielding that pattern are illustrated in Fig. 7. This type of pattern is characteristic of micas and structurally related clay minerals. No electron diffraction patterns could be obtained for the mckelveyite itself because of the inability of the electron beam to penetrate the thicker and more dense particles.

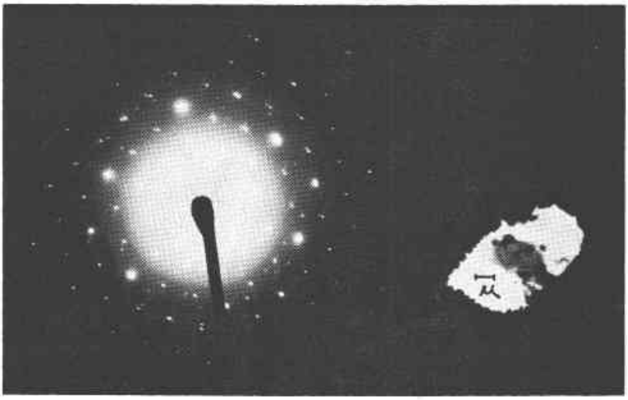

FIG. 7. Electron diffraction spot pattern of micaceous flakes from mckelveyite and sample from which pattern was obtained. 3000×.

With the knowledge provided by the x-ray diffraction and electron microscope studies, the chemical analyses of the acid-insoluble fractions (Table 1) can be interpreted. The calculations are presented in Table 4 and show the approximate weight percentages that can be assigned to each impurity.

Iron in the insoluble fraction was calculated as Fe_2O_3 which is acceptable for acmite but questionable for the biotite, which undoubtedly contains some ferrous iron. Since the ratio of $FeO:Fe_2O_3$ in the biotite is unknown, however, the figures for iron (Table 4) are given simply as total iron, all Fe_2O_3. Biotite analyses cited by Foster (1960) and by Deer, Howie, and Zussman (1962) show the wide range of variability in reported biotite compositions. The approximate formula, $K_2O \cdot 6(Fe,Mg)O \cdot (Fe,Al)_2O_3 \cdot 6SiO_2 \cdot 2H_2O$, may be assigned to the biotite in mckelveyite. Considering the difficulties associated with the analysis of such small samples, the chemical analyses, *x*-ray diffraction data and electron-microscope patterns are all in reasonable agreement and, considered together, confirm the nature and approximate quantities of the silicate contaminants in mckelveyite.

TABLE 4. CHEMICAL CALCULATIONS FOR ACMITE, BIOTITE AND QUARTZ IN MCKELVEYITE

	Analysis[1]		Acmite[2] $Na_2O \cdot Fe_2O_3 \cdot 4SiO_2$		Biotite[3]			Quartz SiO_2	
	Weight Per Cent	Molecular Ratio $\times 10^4$	Assumed Molecular Ratio $\times 10^4$	Weight Per Cent	Assumed Molecular Ratio $\times 10^4$	Weight Per Cent	Weight Per Cent Recal. to 100%	Assumed Molecular Ratio $\times 10^4$	Weight Per Cent
A. Massive aggregate sample, acid-insoluble fraction									
SiO_2	5.53	920	304	1.83	456	2.74	36.5	160	0.96
Fe_2O_3 (total Fe)	3.99	250	76	1.21	174	2.78	37.1		
Al_2O_3	0.69	68			68	0.69	9.2		
MgO	(0.43)[4]	107			107	0.43	5.7		
Na_2O	0.47	76	76	0.47					
K_2O	0.60	64			64	0.60	8.0		
H_2O	(0.23)	128			128	0.23	3.1		
F	0.03	16			16	0.03	0.4		
Σ	11.97						100.0		
Σ	11.97			3.51		7.50			0.96
B. Crystals, acid-insoluble fraction									
SiO_2	8.00	1331	212	1.27	617	3.71	39.5	502	3.02
Fe_2O_3 (total Fe)	4.45	279	53	0.85	226	3.60	38.3		
Al_2O_3	0.14	14			14	0.14	1.5		
MgO	0.68	170			170	0.68	7.2		
Na_2O	0.33	53	53	0.33					
K_2O	0.94	100			100	0.94	10.0		
H_2O	(0.28)	155			155	0.28	3.0		
F	0.05	26			26	0.05	0.5		
Σ	14.87						100.0		
Σ	14.87			2.45		9.40			3.02

[1] Analysis (Table 1) of fraction insoluble in 1+3 HCl of mckelveyite samples; figures for SiO_2 and Fe_2O_3 also include the value found in the soluble portion of the sample. Value for H_2O derived by assuming 3% by weight of biotite. Value for F in crystals assumed equal to total F in massive aggregate.

[2] Assumed by assigning all Na_2O to acmite and stoichiometric proportions to Fe_2O_3 and SiO_2.

[3] Biotite analysis derived from subtraction of acmite from total insoluble plus assumption of 8.0% K_2O in massive aggregate analysis, 10.0% in crystals. [The formula given calls for more Fe (about 1% Fe_2O_3) than was determined.

[4] MgO value not determined for massive aggregate sample; value assumed in proportion to the ratio of K_2O determinations in massive aggregate and crystal samples.

Composition of mckelveyite. The results of the spectrographic analysis for rare earths in a 3.1 mg sample of oxides from the crystal sample are shown in Table 5, together with the calculations in terms of per cent RE_2O_3 that are used in arriving at the formula of mckelveyite.

TABLE 5. RARE EARTHS IN MCKELVEYITE

Rare earth element	Analysis[1]	Calculated as RE_2O_3	Weight Per Cent				Molecular Weight, RE_2O_3	Average Weighted Molecular Weight, RE_2O_3
			Recalculated[2] RE_2O_3 for		Recalculated[3] RE_2O_3 for			
			Massive	Crystals	Massive	Crystals		
Y	34							
Yttria		43.2	5.17	6.32	6.51	7.69	226	226
La	0.43	0.5	0.06	0.07	0.07	0.09	326	
Ce	0.75	0.9	0.11	0.13	0.14	0.16	328	
Pr	0.23	0.3	0.04	0.04	0.05	0.05	330	
Nd	1.2	1.4	0.17	0.21	0.21	0.26	337	
Sm	1.6	1.9	0.23	0.28	0.29	0.34	348	
Eu	1.0	1.1	0.13	0.16	0.16	0.19	352	
Cerium Earths		6.1	0.74	0.89	0.92	1.09		341
Gd	5.8	6.69	0.80	0.98	1.01	1.18	362	
Tb	1.8	2.07	0.25	0.31	0.32	0.38	366	
Dy	5.0	5.74	0.68	0.83	0.86	1.00	373	
Ho	1.4	1.60	0.19	0.23	0.24	0.28	378	
Er	4.6	5.26	0.64	0.78	0.81	0.95	382	
Tm	0.59	0.67	0.08	0.10	0.10	0.12	386	
Yb	3.0	3.42	0.41	0.50	0.52	0.61	394	
Lu	0.40	0.45	0.06	0.07	0.08	0.08	398	
Yttrium earths (other than Y_2O_3)		25.9	3.11	3.80	3.94	4.60		375
Σ	61.80	75.2	9.02	11.01	11.37	13.38		

[1] Spectrographic analysis made on 3.1 mg of precipitated rare earths, uranium and thorium oxides from crystals, by Sol Berman, U. S. Geological Survey.

[2] The massive mckelveyite is assumed to have rare earth ratios similar to that of the crystals. Obtained by multiplying RE_2O_3 by 1/75.2, then (for massive) by 0.09, (for crystals) by 0.11.

[3] Obtained by further multiplying by 1/80 and 1/82 (mckelveyite respectively 79.3% in massive and 82.2% in crystal samples, Tables 2 and 4. From Table 6 slightly different, but practically equivalent factors are obtained, 1/79.6 and 1/82.5).

The calculations from which the proposed formula of mckelveyite is obtained are presented in Table 6. The analyses are those of the fractions soluble in (1+3) HCl (Table 1) plus the CO_2 evolved on acid treatment (Table 1) plus values of H_2O obtained by difference, but not including the soluble Fe_2O_3 and SiO_2 which have been assigned to the silicates (Table

4). Despite the analytical difficulties, the results from both analyses agree reasonably well. If the cation content is calculated from the analysis of crystals on the assumption on that there are 32 oxygen atoms in one formula unit, the following carbonate formula results:

$$Na^{1+}_{1.9}Ba^{2+}_{4.0}Ca^{2+}_{1.1}Sr^{2+}_{0.2}RE^{3+}_{1.5}U^{4+}_{0.3}(CO_3)^{2-}_{9}\cdot 5H_2O$$

CRYSTALLOGRAPHY AND OPTICS OF MCKELVEYITE

Mckelveyite crystals have trigonal symmetry and the true space group is $P\bar{3}$. However, only a few reflections violate the symmetry of space group $P\bar{3}m1$, and the morphologyis consistent with presence of the mirror plane. The unit-cell constants were obtained from measurements of

TABLE 6. CALCULATIONS FOR THE CHEMICAL FORMULA OF MCKELVEYITE

Oxide	Molecular Weight, Oxide	Analysis[1] Weight Per Cent		Recalculated Analysis[2] Weight Per Cent		Molecular Ratios		Oxide Formula Units	
		Massive	Crystals	Massive	Crystals	Massive	Crystals	Massive	Crystals
BaO	153.3	33.4	33.5	42.0	40.6	.274	.265		
CaO	56.1	3.0	3.3	3.8	4.0	.068	.071		
SrO	103.6	1.7	1.4	2.1	1.7	.020	.016		
Σ alkaline earths						*.362*	*.352*	6.0	5.4
Y_2O_3	226	5.2	6.3	6.5	7.7	.029	.034		
Ce earths	341	0.7	0.9	0.9	1.1	.003	.003		
Y earths (other than Y_2O_3)	375	3.1	3.8	3.9	4.6	.010	.012		
UO_2	270.0	3.8	3.8	4.8	4.6	.018	.017		
ThO^2	264.0	0.11		0.1	0.1				
$\Sigma RE_2O_3 + UO_2$						*.060*	*.066*	1.0	1.0
Na_2O	62.0	3.6	3.2	4.5	3.9	.073	.063		
K_2O	94.2	0.16	0.10	0.2	0.1	.002	.001		
Σ Alkalis						*.075*	*.064*	1.2	1.0
CO_2	44.0	20.0	21.2	25.1	25.7	*.570*	*.584*	9.5	9.0
H_2O	18.0	4.8	5.0	6.0	6.1	*.333*	*.339*	5.5	5.2
Σ mckelveyite		79.6	82.5	99.9	100.2				
Organic (Table 2)		8.7	3.0						
Acmite (Table 4)		3.51	2.45						
Biotite (Table 4)		7.50	9.40						
Quartz (Table 4)		0.96 12.0	3.02 14.9						
Total Σ		100.3	100.4						

[1] See Table 1.

[2] Recalculated to 100% mckelveyite.

TABLE 7. *X*-RAY DIFFRACTION POWDER DATA FOR MCKELVEYITE
Trigonal, $P\bar{3}$: $a=9.174\pm0.002$, $c=19.154\pm0.007$ Å

Calculated[1]		Measured[2]		Calculated[1]		Measured[2]	
hkl	d_{hkl}	d_{hkl}	I	hkl	d_{hkl}	d_{hkl}	I
001	19.154			117	2.350	2.349	5
002	9.577			304	2.318		
100	7.945	7.98	5	220	2.294		
101	7.339			108	2.292		
003	6.385	6.40	35	221	2.277	2.276	20
102	6.115			207	2.253		
103	4.977	5.03	2 d	222	2.230	2.229	5
004	4.788	4.64	<2	310	2.204		
110	4.587			311	2.189		
111	4.461	4.47	85	216	2.187		
112	4.137	4.15	20	305	2.178		
104	4.101			223	2.158		
200	3.973			312	2.147		
201	3.890	3.88	<2	009	2.128	2.127	15
005	3.831			118	2.122		
113	3.725	3.73	<2	313	2.083		
202	3.669			224	2.069	2.069	15
105	3.450			109	2.056		
203	3.373			208	2.051		
114	3.312	3.32	30	306	2.038	2.040	30
006	3.192	3.19	10	217	2.023		
204	3.057			314	2.002	2.001	<2
210	3.003			400	1.986		
211	2.967			401	1.976		
106	2.962			225	1.968	1.967	15
115	2.940	2.942	100	402	1.945		
212	2.865			119	1.931		
205	2.758			0, 0, 10	1.915		
007	2.736			315	1.910		
213	2.717			307	1.903		
300	2.648	2.648	40			1.767	10
301	2.623					1.728	10
116	2.620					1.659	10
107	2.587					1.629	10
302	2.553					1.578	5
214	2.544					1.527	5
206	2.488					1.466	5
303	2.446	2.445	15				
008	2.394					plus additional lines, all with I≤5	
215	2.363						

[1] All possible calculated d_{hkl} listed for $d\geq1.900$ Å. The hkl are Miller-Bravais indices; i is omitted.

[2] Camera diameter, 114.59 mm; radiation, Ni-filtered Cu, $\lambda(\text{Cu}K\alpha)=1.5418$ Å. Lower limit measurable for 2θ, approximately 7° (13 Å); d=diffuse. Film no. 16183, powder spindle no. 12392, prepared by Mary E. Mrose, U. S. Geological Survey, from hand-picked green mckelveyite crystals, Sweetwater County, Wyoming.

single-crystal precession photographs and were refined by a least-squares analysis (Evans *et al.*, 1963), using the preliminary single-crystal information in conjunction with the measured *x*-ray diffraction powder data. The final values obtained for the hexagonal cell are: $a=9.174\pm0.002$, $c=19.154\pm0.007$ Å, cell volume $=1396.1\pm0.7$ Å^3. Final indexing of the powder diffraction lines, and the observed powder diffraction data are given in Table 7.

Mckelveyite crystals of several different habits were observed (Figs. 1*b*, 2, 3). All crystals tend to be platy on *c* $\{0001\}$; a hexagonal outline is formed by rhombohedra *r* $\{10\bar{1}1\}$ or *e* $\{01\bar{1}2\}$. Small hexagonal prism forms *m* $\{10\bar{1}0\}$ and $-m$ $\{01\bar{1}0\}$ may also be present. Other crystals are bounded by the hexagonal prisms *m* $\{10\bar{1}0\}$ and $-m$ $\{01\bar{1}0\}$ with small *e* $\{01\bar{1}2\}$ terminal forms. The trigonal symmetry is strikingly demonstrated by frequent occurrence of a threefold radiating array superposed on a hexagonal base (Fig. 3). No easy perfect cleavage was noted, but imperfect fractures can be produced approximately parallel to (0001) and $(11\bar{2}1)$. Piezoelectric tests were negative. The crystals are optically uniaxial negative, $\epsilon = 1.57$ and $\omega = 1.66$. Basal sections are pale green and nonpleochroic; prismatic, strongly pleochroic in green, with $\omega > \epsilon$. The brown color of the organic matter persists in the nonpleochroic position, so the crystals appear brown rather than colorless when much organic matter is present.

The measured specific gravities of the mckelveyite samples are 2.87 (massive, by pycnometer) and 3.14 (crystals, flotation in iodomethane plus acetone). The density calculated for two formula units,

$$\mathrm{Na}^{1+}_{1.9}\mathrm{Ba}^{2+}_{4.0}\mathrm{Ca}^{2+}_{1.1}\mathrm{Sr}^{2+}_{0.2}\mathrm{RE}^{3+}_{1.5}\mathrm{U}^{4+}_{0.3}(\mathrm{CO}_3)^{2-}_{9}\cdot 5\mathrm{H}_2\mathrm{O}$$

in the cell volume 1396.1 Å^3 is 3.62 g cm^{-3}. If the measured specific gravities are corrected for the presence of the impurities (Table 4), assuming specific gravities as follows: acmite 3.5, biotite 2.9, quartz 2.65, organic matter 1.0, the values become 3.58 for the massive material and 3.46 for the crystals. If the same assumptions for the silicates and organic are used, plus the calculated value of 3.62 for mckelveyite, a value of 2.89 is found for the massive sample (compared with 2.87 measured) and 3.25 for the crystals (compared with 3.14 measured).

RARE-EARTH CONTENT COMPARED IN MCKELVEYITE AND BURBANKITE, AND EXEMPLIFICATION OF ODDO AND HARKINS' RULE IN MCKELVEYITE

Mckelveyite and burbankite (Pecora and Kerr, 1953) are both probably fairly widespread minerals in the Wyoming Green River Formation; burbankite is also known from many Green River localities in Utah (Milton and Eugster, 1959). Compositions of these two rare-earth carbonates are compared in Table 8, which includes analyses for burbankite from Montana (Pecora and Kerr, 1953), Wyoming, and Russia (Borodin and Kapustin, 1962). These analyses show that the rare-earth content of burbankite remains relatively constant despite the mineral's occurrence in diverse geological environments (*e.g.*, alkalic pegmatite and lacustrine Green River). Even though mckelveyite and burbankite (Fig. 8) are presumably formed under virtually identical geochemical conditions, in the same place at the same time, the two minerals are altogether distinct

TABLE 8. COMPOSITIONS COMPARED FOR MCKELVEYITE FROM WYOMING AND BURBANKITE FROM WYOMING, MONTANA, AND RUSSIA

	Mckelveyite		Burbankite							
	Wyoming[1]		Wyoming[2]		Montana[3]		Russia[4]		Russia[5]	
BaO	40.6		Major		14.02		14.60		11.62	
CaO	4.0		1.4		13.68		9.81		10.86	
SrO	1.7		3.6		19.70		9.96		12.86	
		46.3				47.40		34.37		35.34
Y_2O_3		7.7		0.05		0.10		0.26		0.00
La_2O_3	0.09		1.2		2.34		4.24		4.73	
Ce_2O_3	0.16		1.2		4.65		8.34		8.18	
Pr_2O_3	0.05				0.37		0.64		0.53	
Nd_2O_3	0.26		1.2		1.40		2.45		1.61	
Sm_2O_3	0.34		1.4		0.10		0.17		0.06	
Eu_2O_3	0.19		0.42		—		—		—	
		1.1		5.4		8.86		15.84		15.11
Gd_2O_3	1.18			—		0.08		0.12		0.01
Tb_2O_3	0.38									
Dy_2O_3	1.00									
Ho_2O_3	0.28									
Er_2O_3	0.95									
Tm_2O_3	0.12									
Yb_2O_3	0.61									
Lu_2O_3	0.08									
		4.6								
UO_2		4.6		—		—		—		—
ThO_2		0.1		—		—		—		—
Na_2O	3.9		4.0		10.17		12.19		11.44	
K_2O	0.1		0.1		—		0.74		0.99	
Σ alkalies		4.0		4.1		10.17		12.93		12.43
CO_2		25.7				33.39		32.14		34.30
H_2O		6.1						2.60		0.97
Al_2O_3		0.0						0.00		1.05
Fe_2O_3		—						0.10		0.48
MgO		—						0.00		0.35
SiO_2		—						0.06		0.19
		100.2				100.00		98.42		100.23

[1] Mckelveyite, Wyoming, this report.

[2] Burbankite, Wyoming—preliminary spectrographic data—unpublished.

[3] Burbankite, Montana—Pecora and Kerr, 1953.

[4] Burbankite, Karelia, Russia, Borodin and Kapustin, 1962; greenish-yellow or pink in dolomite-ankerite.

[5] Burbankite, Karelia, Russia, Borodin and Kapustin, 1962; yellow in calcite.

from one another in rare-earth content. A virtually complete segregation of yttrium earths has occurred in mckelveyite, whereas cerium earths have segregated in burbankite. The controlling factor in such rare-earth segregation cannot therefore be the geochemical environment but must instead be attributed to the crystal chemical character of the minerals. In monazite and xenotime, often associated, a similar segregation is observed.

Fig. 9 shows that the cerium earths in mckelveyite conform to Oddo and Harkins' rule, the quantity of the various elements with even atomic numbers always exceeding that of their neighbors with odd atomic number (Rankama and Sahama, 1950).

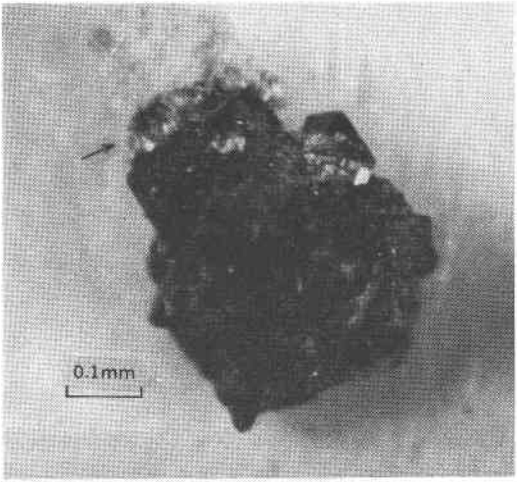

FIG. 8. Black mckelveyite crystal aggregate with burbankite seam (arrow) separating it from light gray dolomitic limestone at top. Magnification, 100×.

RADIOACTIVITY OF MCKELVEYITE

Attention was first drawn to the core containing mckelveyite because of its strong radioactivity. J. D. Love, U. S. Geological Survey, in a written communication (January 29, 1963), noted that the cores which later were found to contain mckelveyite were among the most radioactive of all tested by γ-ray scintillator in his examination of several thousand Green River cores and outcrop samples. Nevertheless, after separation of the mckelveyite, the radioactivity (and also the phosphate content) of the remaining material were found to be quite low, a result which shows that these cores did not owe their radioactivity to the presence of uraniferous apatite. It may also be noted that the zone in which mckelveyite occurs in the basal Wilkins Peak appears to contain more Ce, La, Y, Sc, Ga, Yb, Nd, Ti, Zr, Cu and Nb than any uraniferous phosphatic zone in the Wilkins Peak Member of the Green River Formation. This zone is also the only one in Wyoming known to contain Sm and Sn (Love, in press.) Sm^{147} with a half-life of 6.7×10^{11} years is radioactive, being the only known natural emitter of alpha particles aside from the heavy radioactive elements (Hand. Chem. and Phys. 1961–2, p. 483). However, the strong radioactivity of the core is largely attributed to the uranium content of mckelveyite, the first mineral with considerable uranium content to be found in the Green River Formation.

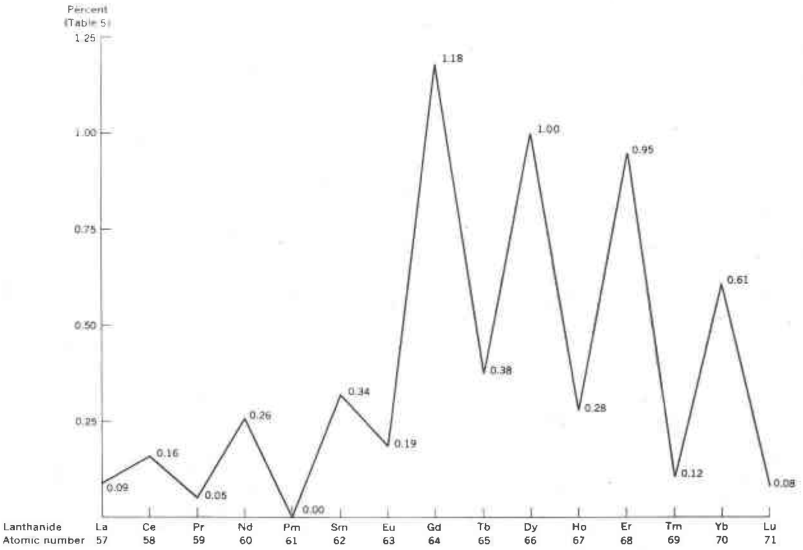

FIG. 9. Oddo and Harkins' Rule, exemplified in mckelveyite.

Irving A. Breger, U. S. Geological Survey, has suggested that during or following deposition of the Green River sediments, the rare earths in solution were entrapped or chelated by organic complexes, and this local enrichment of nucleation eventually resulted in formation of rare-earth mineral complexes, such as mckelveyite. Meanwhile the originally light-colored organic matter underwent bombardment by the radioactive elements present, thus causing the black coloration of the organic material associated with mckelveyite.

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