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THE CHEMISTRY OF FIVE ACCESSORY ROCK-FORMING APATITES

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Abstract.—Chemical and physical data are given for five samples of rock-forming apatite from diverse geologic environments in Nevada and Colorado. Four of these apatites contain rare-earth assemblages in which the cerium group is well represented but the yttrium group predominates. The fifth apatite contains a highly fractionated assemblage of the lighter (cerium group) rare earths similar to the assemblage typical of alkalic rocks.

Before the advent of modern techniques of mineral purification many minerals being considered for analysis were selected on the basis of their easy availablity, and thus many of the early analyses were performed on minerals from pegmatites, tactites, or drusy cavities, from which large crystals could be handpicked with minimal effort. Fewer analyses were performed on minerals from some of the more common igneous and metamorphic rocks, especially rather fine-grained rocks. During the past 20 years or so, many analyses of the more common rock-forming minerals have been published. However, for some of the accessory (as opposed to essential) minerals—including apatite—there still is a dearth of chemical data on samples recovered from some of the more common rock types. This paper presents chemical data for four samples of accessory apatite and one sample of placer apatite.

The apatites described here were purified by the same methods used on accessory apatites from the southern Snake Range, Nev. (Lee and others, 1973). Indices of refraction were determined by the immersion method, using a spindle stage (Wilcox, 1959) and focal masking technique (Wilcox, 1962). Cell parameters were obtained by least-squares refinement of powder diffractometer data, using an internal standard of CaF_2 and a self-indexing computer program developed by Evans, Appleman, and Handwerker (1963).

Semiquantitative spectrographic results are based on their identity with geometric brackets whose boundaries are 1.2, 0.83, 0.56, 0.38, 0.26, 0.18, 0.12, and so forth, and are reported arbitrarily as midpoints of these brackets, 1., 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, respectively. The precision of a reported value is approximately one bracket at 68-percent confidence, or two brackets at 95-percent confidence.

FIELD SETTING OF APATITES

Apatite 244-MW-60 was recovered from a muscovite-rich granitoid rock collected at lat 39°35′55″ N.; long 114°7′55″ W., in the Kern Mountains of White Pine County, Nev. This granitoid rock is almost identical with the (southern Snake Range) Pole Canyon—Can Young Canyon intrusive type described in detail by Lee and Van Loenen (1971, p. 5, 38, 39), who ascribed its distinctive nature to assimilation of argillite. According to R. K. Hose and M. C. Blake, Jr. (oral commun., 1971), who prepared the geologic map of White Pine County, the distinctive nature of the granitoid rock from which apatite 244-MW-60 was recovered might also result from assimilation of argillite. Whatever the origin, the great similarity of these two granitoid rocks extends to the peculiar apatite-zircon relation described by Lee and Van Loenen (1971, p. 5, 39) and illustrated by Lee and others (1973, fig. 2). In each rock almost all the zircon is present as tiny, acicular inclusions in large, equant, rather poorly formed, and sparsely distributed apatite crystals.

Apatite 300-DL-64 was recovered from a placer concentrate collected at the mouth of Hampton Creek at lat 39°14′45″ N.; long 114°3′50″ W., in White Pine County, Nev. Except for some Middle Cambrian limestones resting above a thrust surface, all the Hampton Creek drainage is underlain by Lower Cambrian metaquartzites and metashales, as shown on the geologic map of White Pine County, Nev. (Hose and Blake, 1970). The ultimate environment(s) in which the crystals of apatite 300-DL-64 may have formed is problematical. However, the sample analyzed appeared to be homogeneous, for it gave an X-ray diffraction pattern with sharp peaks which in turn gave a good refinement of the unit cell parameters (table 1). Moreover, the Lower Cambrian metasedimentary rocks were the source of most or perhaps almost all of this placer apatite. In connection with potassium-argon age studies in the area (Lee and others, 1970; and unpub. data), we have done mineral separation work on several samples of these metasedimentary rocks. Minor amounts of apatite were commonly recovered, and petrographic study shows the apatite to be present as well-formed crystals that appear to be part of the metamorphic assemblage.

Table 1.—*Analytical data for five apatites*

[Descriptions of sample localities, methods of determination of physical properties, and general limitations of the semiquantitative method are given in text. Chemical analyses by E. L. Munson Brandt; semiquantitative analyses by L. D. Forshey]

Area of collection	White Pine County, Nev.			Elko County Nev.	Gilpin County, Colo.
Sample No.	244-MW-60	300-DL-64	301-DL-65	363-DL-66	1-CC
Physical properties					
Indices of refraction:					
ϵ (±0.001)	1.630	.....	1.630	1.634	1.630
ω (±0.001)	1.632	.....	1.632	1.640	1.632
$\omega-\epsilon$	.002	.....	.002	.006	.002
Specific gravity:					
Observed	3.20±.01	3.20±.01	3.20±.01	[1]3.226±.005	3.20±.01
Calculated	3.21	3.22	3.22	3.227	.....
Unit cell parameters:					
a (±0.001 A)	9.367	9.373	9.366	9.407	9.376
c (±0.001 A)	6.880	6.875	6.880	6.876	6.877
c/a	.734	.733	.734	.731	.733
Cell volume:					
Measured (±0.2 A^3)	522.9	523.1	522.6	527.0	523.6
Calculated	523.7	525.6	525.6	527.2	....
Chemical analyses (weight percent)					
SiO_2	0.06	0.04	0.24	0.55	0.11
Al_2O_3	.07	.06	.09	.04	.....
Fe_2O_3	.06	.02	.05	.14	.05
FeO	.03	.12	.04	.24	.04
MgO	.....	.05	......	.....	.....
CaO	54.54	54.97	54.21	53.91	55.09
Na_2O	.07	.05	......	.10	.....
K_2O	.01	.01	......	.01	.....
H_2O+	.....	.00	......	.....	.....
H_2O-	.....	.00	.....	.....	.....
P_2O_5	42.22	42.21	41.78	41.13	......
MnO	.11	.08	.15	.08	.....
Cl	.....	.02	.....	.71	.....
F	3.64	2.98	3.49	2.93	2.92
[2]R_2O_3	.41	.29	.88	1.69	.39
Insoluble residues[3]	.59	.22	.36	.13	.07
Subtotal	101.81	101.06	101.29	101.66	.....
Less O≡Cl,F	1.53	1.25	1.47	1.23	.....
Total	100.28	99.81	99.82	100.43	.....

Ions on basis of 26(O,OH,F,Cl)

	244-MW-60		300-DL-64		301-DL-65		363-DL-66		1-CC
P	6.024	6.034	6.048	6.055	5.996	6.037	5.930	6.024	.....
Si	.010		.007		.041		.094		.....
Al	.014	9.940	.012	10.061	.018	9.954	.008	10.048	.....
Fe^{3+}	.008		.003		.006		.018		.....
Fe^{2+}	.004		.017		.006		.034		.....
Mg	.....		.013		.....		.....		.....
Mn	.016		.012		.022		.012		.....
Ca	9.848		9.968		9.847		9.836		.....
Na	.023		.016		.....		.033		.....
K	.002		.002		.....		.002		.....
[4]Ce^{3+}	.025		.018		.055		.105		.....
F	1.940	1.940	1.595	1.601	1.871	1.871	1.578	1.783	.....
Cl	.....		.006		....		.205		.....

Table 1.—*Analytical data for five apatites*—Continued

[Descriptions of sample localities, methods of determination of physical properties, and general limitations of the semiquantitative method are given in text. Chemical analyses by E. L. Munson Brandt; semiquantitative analyses by L. D. Forshey]

Area of collection	White Pine County, Nev.			Elko County Nev.	Gilpin County, Colo.
Sample No.	244-MW-60	300-DL-64	301-DL-65	363-DL-66	1-CC
Semiquantitative spectrographic analyses (weight percent)					
Ba	0.0002	0.0002	0.0003	0.0005	0.0002
Cu	.0005	.0003	.0005	.005	.0007
Pb	.001	.0015	.0015	.0015	.001
Sr	.05	.05	.03	.15	.03
Ti	.005	.007	.01	.0002	.002
V	0	0	.0015	.007	.0007
Zr	.15	.01	.005	0	.003

[1] Specific gravity of sample 363-DL-66 was determined with greater precision than others.

[2] Rare-earth oxide precipitates. See table 2 for analyses.

[3] Insoluble in 1:1 HCl at 100°C. Results of X-ray diffraction work on these insoluble residues are given in text.

[4] Each rare-earth oxide precipitate calculated as Ce_2O_3 for sake of simplicity.

Apatite 301-DL-65 was recovered from a xenolith (of shaly quartzite?) collected at lat 38°56′49″ N.; long 114°16′26″ W., within the area of a detailed field and laboratory study by Lee and Van Loenen (1971).

Apatite 363-DL-66 was recovered from a granitoid rock collected at lat 40°20′55″ N.; long 114°34′ W., in the upper drainage of Cougar Canyon of the Dolly Varden Mountains, Elko County, Nev. This rock is the "augite monzonite" of Snow (1964, p. 69, 78), who described the various igneous rock types exposed in the area. On the basis of our mineral separation work we estimate that this apatite makes up more than 1 percent of the rock from which it was recovered.

Apatite 1-CC was recovered from a Precambrian metamorphic rock collected at lat 39°47′49″ N.; long 105°30′25″ W., about 1 mile south-southeast of Central City in Gilpin County, Colo. The rock is a fine-grained biotite-rich schist that occurs as a layer about 3 inches thick within a migmatitic biotite gneiss.

APATITE ANALYSES

Chemical analyses of the apatites (table 1) are calculated on the basis of 26(O,OH,F,Cl) to the apatite formula $Ca_5(PO_4)_3(F,Cl,OH)$, using the computer program described by Jackson, Stevens, and Bowen (1967).

Each analysis includes the weight percent of material insoluble in 1:1 HCl at 100°C., giving a good indication of the degree of purity of the apatites analyzed. Amount of impurity (insoluble material) ranges from 0.07 weight percent of apatite 1-CC to 0.54 weight percent in apatite 244-MW-60, and in each apatite probably all the insoluble material was present as inclusions in the apatite grains.

Each analysis also includes weight percent of the rare-earth oxide precipitate recovered. X-ray spectrographic analyses of these precipitates are calculated to atomic percent of total rare earths in each of the apatites (table 2) and discussed in some detail later in this paper.

The compositions (table 1) range from about 79 to 92 mole percent end-member fluorapatite. Sample 363-DL-66 is about 10 mole percent chlorapatite; the other four minerals are for the most part hydroxyfluorapatites, as indicated by the indices of refraction and unit cell parameters listed in table 1 (See Deer, Howie, and Zussman, 1962, p. 324, 331). There was enough material for determination of $H_2O(+)$ in only sample 300-DL-64. Each apatite in table 1 completely lacked effervescence when immersed in 1:1 HCl at 100°C., indicating absence of the carbonate ion.

Aside from rare earths, only minor amounts of other cations proxy for Ca^{2+} in the structural formulas (table 1). There is very nearly a straight-line relation between amounts of Si and rare earths present in the structural formulas, owing probably to the coupled $Si^{4+}RE^{3+,4+} \rightleftharpoons P^{5+}Ca^{2+}$ substitution.

The insoluble residues (table 1) were identified by means of X-ray diffraction study as follows: 244-MW-60, predominantly zircon; 300-DL-64, subequal amounts of quartz and zircon; and the other three, predominantly quartz. We attribute the zirconium values (table 1) to zircon inclusions in the apatite (0.02 weight percent zircon about equivalent to 100 ppm zirconium). The tiny amounts of the other minor elements listed most probably are present in the crystal structures of the apatites.

There are several methods of assessing the degree of fractionation of rare earths included in the structures of minerals from various geologic environments, a subject of considerable interest. Murata, Rose, and Carron (1953) pro-

Table 2.—*Analyses of rare-earth precipitates and calculation of* Σ(La+Ce+Pr) *for apatites in table 1*

Sample No.	244-MW-60	300-DL-64	301-DL-65	363-DL-66	1-CC
Weight percent of rare-earth precipitate[1]					
Y_2O_3	36.7	28.9	40.5	2.95	34.7
La_2O_3	3.11	1.85	2.53	21.3	1.76
CeO_2	11.0	6.71	9.16	41.6	7.06
Pr_2O_3	1.98	1.34	1.93	5.11	1.71
Nd_2O_3	10.5	7.73	10.4	14.3	9.47
Sm_2O_3	5.65	4.40	5.54	3.80	5.00
Eu_2O_3	1.13	1.85	1.20	1.69	1.47
Gd_2O_3	5.31	4.86	5.04	1.52	4.53
Tb_2O_3	1.69	1.62	1.45	.42	1.47
Dy_2O_3	6.79	7.27	6.39	.51	7.47
Ho_2O_3	2.26	2.18	2.17	.0	1.88
Er_2O_3	2.88	2.31	2.84	.21	3.00
Tm_2O_3	.62	.60	.77	.08	.71
Yb_2O_3	1.75	1.53	2.34	.0	2.76
Lu_2O_3	.90	.83	1.01	.0	.94
Total	92.27	73.98	93.27	93.40	83.88
Atomic percent of total rare earths in apatite					
Y	50.81	50.25	54.43	4.65	52.63
La	2.98	2.23	2.36	23.31	1.85
Ce	10.00	7.65	8.40	43.11	7.03
Pr	1.88	1.60	1.77	5.53	1.78
Nd	9.75	9.02	9.38	15.16	9.64
Sm	5.06	4.95	4.85	3.89	4.91
Eu	1.01	2.06	1.04	1.71	1.43
Gd	4.57	5.27	4.22	1.50	4.28
Tb	1.44	1.74	1.20	.40	1.38
Dy	5.68	7.64	5.20	.48	6.86
Ho	1.87	2.27	1.73	.0	1.70
Er	2.36	2.37	2.25	.19	2.68
Tm	.50	.61	.60	.07	.63
Yb	1.39	1.52	1.80	.0	2.39
Lu	.70	.82	.77	.0	.81
Total	100.00	100.00	100.00	100.00	100.00
Σ(La+Ce+Pr)	14.86	11.48	12.53	69.95	10.66

[1] X-ray spectrographic analysis by Frank Cuttitta, Ralph Christian, and Harry J. Rose, Jr. Sc_2O_3 not detected. Low totals probably due to presence of filter-paper ash in precipitate.

posed the quantity Σ(La+Ce+Pr) in atomic percent of total rare-earth elements as a numerical index of the composition and stage of fractionation attained by the rare-earth elements. Thus higher values of Σ(La+Ce+Pr) represent greater enrichment of the lighter, more basic rare-earth elements. Apatite 363-DL-66 has a sigma value of about 70, representing a much lighter assemblage of rare earths than any of the other four (with sigmas of 10.7–14.9, table 2).

Fleischer and Altschuler (1969, p. 729) based their discussion of the fractionation of lanthanides (excluding yttrium) on a triangular diagram with corners featuring (in atomic percent) the groups La–Nd, Sm–Ho, and Er–Lu. If the results in table

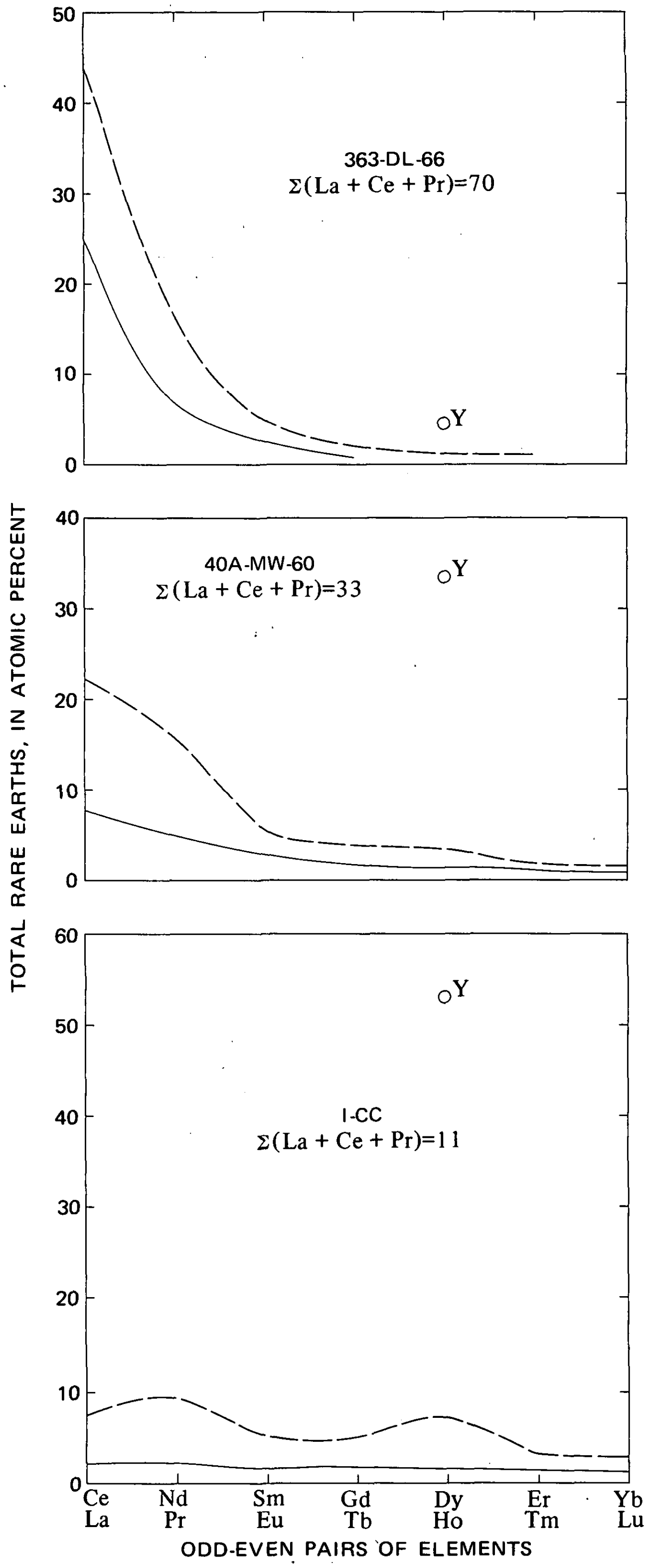

Figure 1.—Range of distribution of rare earths shown by three apatites, with Σ(La+Ce+Pr) value for each. Data for apatite 40A-MW-60 from Lee, Van Loenen, and Mays (1973); data for other two from table 2, this report. The relationship of yttritum (Y) to the other rare earths is indicated. Odd-even pairs of elements are arranged, left to right, in order of increasing atomic number.

2 are plotted on such a diagram, they include nearly the whole range of lanthanide compositions published for apatites from various environments, excluding a few apatites from pegmatites that show an extreme concentration of the heavier rare earths.

Adams (1969) summarized the several mechanisms (ionic radii differences, basicity, and accommodation in crystal lattices) that may contribute to fractionation of the lanthanide group of elements in rare-earth-bearing minerals. He illustrated lanthanide assemblages found in various minerals by means of graphs plotted in the form suggested by Semenov and Barinskii (1958), in which odd-even pairs of elements are arranged in order of increasing atomic number along the abscissa, and abundance in atomic percent along the ordinate.

The rare-earth assemblages of apatites 363-DL-66 and 1-CC are plotted in this way (fig. 1). Graphs for the other three apatites (table 2) are very similar to the one for 1-CC. A plot of the rare-earth assemblage present in apatite 40A-MW-60, from a hybrid granitoid rock (Lee and others, 1973), is included in figure 1. Fractionation of lanthanides in apatite 363-DL-66 is similar to that found in allanite, or even in bastnaesite (Adams, 1969, figs. 4*C* and 1*C*, respectively), while the assemblage in apatite 1-CC is similar to that found in gadolinite (Adams, 1969, fig. 1*E*). The plot for 40A-MW-60 does not resemble very closely any of the plots for various minerals featured by Adams (1969). As Fleischer and Altschuler (1969, p. 729) stated, "* * * the lanthanides in apatite * * * vary greatly in composition." Adams (1969, p. C43) also mentioned apatite as a mineral with a tolerance for all the rare earths, and a mineral which may therefore be a valuable guide "to changes in rare-earth composition that have taken place during the development of the rocks in which they are found."

The changes in rare-earth composition that took place during the development of the rock from which apatite 363-DL-66 was recovered may be similar to processes that lead to the formation of alkalic rocks and carbonatites. Goldschmidt, Hauptmann, and Peters (1933) and Goldschmidt (1937) first recognized the unusual abundance of rare-earth elements and the predominance of the most basic (lightest) of these elements in alkalic rocks, and Murata, Ross, Carron, and Glass (1957) emphasized the fact that cerium-earth minerals from alkalic rocks and carbonatites are rich in the most basic rare earths. Moreover, apatite is commonly well developed in alkalic rocks and carbonatites (see for example Deer, Howie, and Zussman, 1962, p. 333), and apatite 363-DL-66 makes up more than 1 percent of the host rock, as well as being unusually rich in total rare earths (table 1). Finally, the highest barium and strontium values were found in apatite 363-DL-66 (table 1), and these two elements are commonly enriched in alkalic rocks and carbonatites (Pecora, 1956).

Although it would be unwise to overinterpret data for a single mineral, we note finally that the granitoid rock containing apatite 363-DL-66 is exposed in contact with thinly interbedded limestones and sandstones (the Permian Pequop Formation of Steele, 1959; Snow, 1964, pl. 1). In a study of hybrid granitoid rocks from the southern Snake Range, Nev., Lee and Bastron (1967) found accessory allanite to contain a more basic assemblage of rare earths where the granitoid rock is in contact with limestone; and the rare-earth assemblages in accessory apatites from the same rocks show the same trend (Lee and others, 1973).

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