# COLORADO CERITE

Ross A. Hanson* and D. W. Pearce, *Dept. of Chemistry,*
*Purdue University, W. Lafayette, Indiana.*

### Abstract

Chemical analyses of samples of cerite from near Boulder, Colorado, give evidence for the formula $2CaO \cdot Al_2O_3 \cdot R.E._2O_3 \cdot 2SiO_2$ with a considerably higher $Al_2O_3$ content than heretofore observed in other samples. Some discussion is given concerning the peculiar structural relations existing between the purple fluorite (enclosed in the cerite and concentrated centrally), the cerite itself and its surrounding narrow border of black allanite. Combined spectrographic and chemical determination of the individual rare earths in the cerite and allanite shows that these minerals fit into their prescribed type in the Goldschmidt-Thomassen classification.

### Introduction

The recent article by E. N. Goddard and J. J. Glass[1] has thoroughly described the interesting radioactive cerite which occurs near Jamestown, Colorado. This cerite had been called to the attention of the present
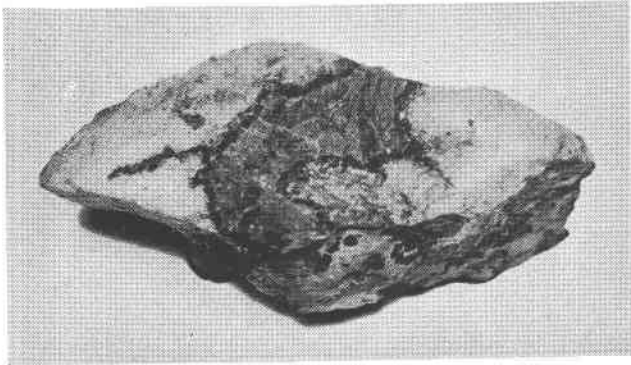


Fig. 1. Gray cerite with black border of allanite enclosed in sugary quartz. $\times \frac{3}{4}$.

writers by Mr. Jack Ingram of Boulder, Colorado, and was considered first as a possible source of rare earth group material for chemical work.

Aside from the fact that this was the first discovered occurrence of cerite in the United States, two observations on the sample first acquired

[1] *Am. Mineral.*, **25**, 381–404 (1940).

(Fig. 1) suggested some further study of the mineral. The first and most outstanding point observed was the thin, sharp shell of black material completely encircling the gray cerite lens and, in one place, running in a narrow stringer out into the surrounding sugary quartz. Qualitative examination showed that this "black border" was also a rare earth mineral. As it appeared probable that the two minerals had crystallized practically simultaneously from the same pegmatite liquor their close association seemed to offer an unusual opportunity to study the distribution of the individual rare earths between two such phases.
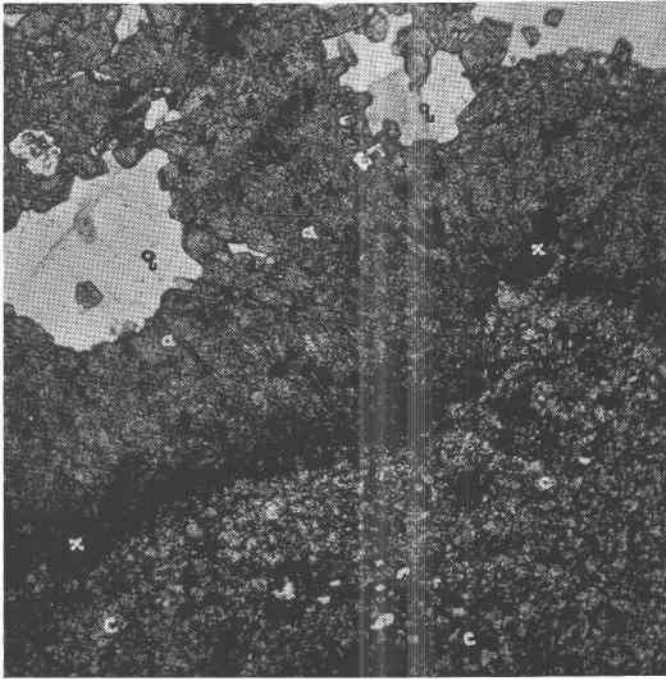


Fig. 2. Cerite (*c*)—allanite (*a*) contact, showing unidentified mineral (*x*) and quartz (*q*) inclusions in the allanite. ×32.

In the second place, close examination of the cerite itself, even with the naked eye, revealed the presence of minute specks of an unknown purple material concentrated in the central part of the mass. This material possessed the characteristic color of neodymium salts and further heightened the interest in this unusual mineral assemblage.

With the hope that some further discussion of these rare minerals might be of interest, our microscopic observations, chemical and spectrographic analyses and deductions therefrom are here presented.

THIN-SECTION EXAMINATION

Examination of several thin sections prepared from various specimens revealed interesting features. The "black border mineral" is yellow-brown in thin section (Fig. 2) and short crystals of it project at the contact into the surrounding (rarely enclosed) quartz and feldspar. The sharp terminal faces against the gangue minerals give good evidence of its earlier crystallization. Goddard and Glass have identified this mineral as allanite by its optical properties as well as by its chemical composition. The
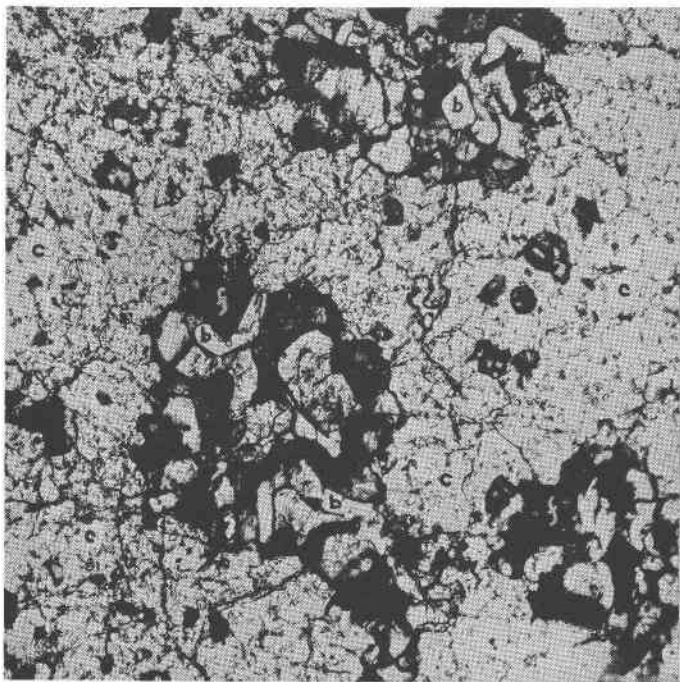


FIG. 3. Purple fluorite ($f$) in gray cerite ($c$). In places the fluorite has broken away leaving balsam ($b$). ×125.

allanite is not homogeneous throughout but contains a considerable amount of an unidentified black material which is highly concentrated in the form of specks and masses at the allanite-cerite border (Fig. 2). It appears to be entirely within the former as it presents a fairly sharp contact with the cerite, but becomes scattered and spread out away from this contact and toward the central part of the allanite band.

The cerite itself is gray and is made up of variously oriented grains showing no crystal faces but interlocked to present a texture approaching a mosaic. The enclosed purple material has been identified by Goddard

and Glass as fluorite. It occurs in the form of irregularly shaped masses which, in the central part of any particular cerite lens, become gathered into rosette-like groups roughly circular in shape (Fig. 3). Toward the boundaries of the cerite the rosettes become fewer and smaller and the purple segregations themselves very much more scattered until, close to the border, they are absent altogether.

The complete interpretation of the textural features of this intergrowth of minerals is not immediately clear. The allanite may have been rejected by the cerite as the latter crystallized and hence forced to the periphery where it crystallized with regular contact against the cerite while its crystals grew out into the remaining unsolidified pegmatite liquor. This hypothesis, however, is difficult to rationalize with the concentration of the purple material in the central parts of the cerite lenses. The irregularity in outline of this purple material would seem to require that it was segregated from the cerite melt and remained liquid after the solidification of its host material. Such segregation and concentration centrally would suggest, however, that the cerite masses cooled more rapidly at the borders than in the interior and therefore would seem to contradict the above suggested mechanism for the rejection of the allanite to the borders.

The opinion of Goddard and Glass that the allanite forms "replacement borders" (p. 386) would require the influx of younger pegmatite liquors after, or during, the solidification of the first and might be expected not to result in the fairly sharp contacts with the cerite, such as are to be observed in all our samples. Furthermore, spectrographic investigation has shown that the content of individual rare earths is much the same in the two minerals. Such similarity in the original and the replacing solution would seem unlikely.

## Chemical Analysis

In Table 1 is given the data resulting from the chemical analysis of the cerite and of its black border, allanite. The results are here compared with those of Goddard and Glass.

TABLE 1. ANALYSES OF CERITE AND ASSOCIATED ALLANITE

| | 'Cerite Rock" | | Pure Cerite Calc. | | Allanite | |
|---|---|---|---|---|---|---|
| | G. & G. | H. & P. | G. & G. | H. & P. | G. & G. | H. & P. |
| $SiO_2$ | 18.78 | 16.71[a] | 18.10 | 17.42 | 30.40 | 37.73 |
| $Al_2O_3(TiO_2)$ | 0.24 | 14.00 | 0.32 | 14.59 | 10.25 | 17.07 |
| FeO | 1.17 | 1.34 | 1.54 | 1.40 | 10.29 | 5.69 |
| $Fe_2O_3$ | — | — | — | — | 10.33 | 0.80[b] |
| $U_3O_8$ | 0.51 | spect. tr. | — | — | — | spect. tr. |
| $Ce_2O_3$ | 28.85 | 20.77[c] | 32.97 | 21.65 | 14.61 | 7.39[d] |
| $(La, Tb)_2O_3$ etc. | 27.20 | 26.43 | 35.72 | 27.55 | 10.32 | 17.54 |
| $Y_2O_3$ etc. | 2.94 | | 3.86 | | | |
| $ThO_2$ | 0.28 | none | — | — | — | none |
| MnO | 0.17 | 0.38 | 0.22 | 0.40 | 0.66 | 0.78 |
| ZnO | none | none | — | — | — | spect. tr. |
| CaO | 12.55 | 16.55 | 5.80 | 15.24 | 7.47 | 7.56 |
| MgO | 0.16 | 1.61 | 0.21 | 1.68 | 1.44 | 3.44 |
| PbO | 0.07 | spect. tr. | — | — | — | spect. tr.? |
| $Na_2O$ | — | — | — | — | 0.02 | s[e] |
| $K_2O$ | — | — | — | — | 0.16 | tr. |
| $TiO_2$ | — | none | — | — | 1.46 | s[e] |
| $H_2O$ | 0.96 | 0.067 | 1.26 | 0.07 | 1.95 | 0.145 |
| $CO_2$ | 1.00 | none | — | — | — | none |
| $P_2O_5$ | none | — | — | — | — | — |
| F | 5.94 | 1.30[f] | — | — | — | 0.01 |
| Cl | none | — | — | — | — | — |
| $B_2O_3$, BeO | none | none | — | — | none | — |
| | 100.82 | 99.16 | 100.00 | 100.00 | 99.36 | 98.16 |
| Less O for F | 2.52 | 0.55 | | | | 0.00 |
| | 98.30 | 98.61 | | | 99.36 | 98.16 |

[a] Includes 1.02% $SiO_2$ calcd. lost as $SiF_4$ during dissolution of the sample.

[b] Sample was finely chipped in removing from cerite and all $Fe^{+3}$ may have come from $Fe^{+2}$.

[c] By spectrographic method av. 23.16% (see Table 3).

[d] By spectrographic method av. 8.88% (see Table 3).

[e] Detected by spectrograph.

[f] Used as correction for $SiO_2$ see (a).

## Cerite

The recalculated analysis of the cerite gives the following molecular ratios:

|  | G. & G.[a] | H. & P. |
|---|---|---|
| $SiO_2$ | 301 | 290 |
| $TiO_2$ | — | — |
| $Al_2O_3$ | 3 | 143 |
| $Fe_2O_3$ | — | — |
| $Ce_2O_3$ | 100 | }148[c] |
| $RE_2O_3$ | 125[b] |  |
| FeO | 21 | 19 |
| MnO | 3 | 6 |
| CaO | 103 | 272 |
| MgO | 5 | 42 |
| $Na_2O$ | — | — |
| $K_2O$ | — | — |
| $H_2O$ | 70 | 4 |

[a] Calculated from the data presented by Goddard and Glass.

[b] Molecular weight of R.E.$_2O_3$ taken as 331.

[c] Molecular weight calculated from combined chemical and spectrographic data 331.37.

When compared with the cerite analysis as announced by Goddard and Glass and the corresponding molecular ratios, the new results reported above present several points of interest. Notable first is the great contrast in the amount of $Al_2O_3$ present; as pointed out by the previous investigators, the per cent of this constituent has not previously been found higher than 2.64 in all the published analyses of this rare mineral. Outstanding also is the very low, almost insignificant, $H_2O$ content; this, however, is in very good accord with the fresh appearance and apparently unaltered nature of all the material which we have obtained from this source. The molecular ratios calculated from these results are coherent: the formula appears quite definitely to be $2\ CaO \cdot Al_2O_3 \cdot R.E._2O_3 \cdot 2SiO_2$. It is felt that Al and Rare Earths should not here be regarded as vicarious constituents; in the first place it would require a fortuitous circumstance that the ratio of $Al_2O_3 : R.E._2O_3$ be 1:1 as it is here, and in the second place the ionic sizes of $Al^{+3}$ and R.E.$^{+3}$ are greatly different.[2] It would seem more probable, as indeed it is assumed by some for many other minerals, that R.E.$^{+3}$ and $Ca^{+2}$ are replaceable the one by the other within limits.[3] It must also be pointed out that the significance of the monoxides is not clear; in neither the results of Goddard and Glass nor in those here reported may the molecules of other divalent elements be added to the CaO without rather badly disrupting an apparently excellent fit. It may later be found to be of significance that in both analyses the sum (2H,

[2] Goldschmidt, V. M., *Geochemie, Handworterbuch d. Naturwiss., Zweite Aufl., Bd.* **2,** 886–904 (1933); *Kristallchemie, ibid., B.* **5,** 1–27 (1934); Principles of distribution of chemical elements in minerals and rocks: *Jour. Chem. Soc.,* 655–673 (1937).

[3] Goddard and Glass (*ibid.,* p. 596) have briefly considered this possibility.

Fe, Mn, Mg)O is in a simple ratio to the chosen unit; thus in the earlier work this ratio is 99:ca 100 (or 1:1), whereas in the present work it is 71:ca 142 (or 1:2).

The cerite analysis reported by Goddard and Glass yielded the formula $CaO \cdot 2R_2O_3 \cdot 3SiO_2 \cdot H_2O$; in their ratios $H_2O$ is low and $R_2O_3$ is somewhat high. The present work would, indeed, suggest that even *one* $H_2O$ is not an essential constituent of the mineral. It does not appear, however, that the present formula could be fitted into the series tentatively suggested by Goddard and Glass even if the $H_2O$ is regarded as unessential:

| | |
|---|---|
| CaO-free cerite | $2 R_2O_3 \cdot 3 SiO_2$ |
| Colorado cerite (G. & G.) | $CaO \cdot 2 R_2O_3 \cdot 3 SiO_2$ |
| Lessingite | $2 CaO \cdot 2 R_2O_3 \cdot 3 SiO_2$ |
| Colorado cerite (H. & P.) | $3 CaO \cdot 1 1/2 R.E._2O_3 \cdot 1 1/2 Al_2O_3 \cdot 3 SiO_2$ |

## *Allanite*

The molecular and atomic ratios calculated from our allanite analysis and those obtained by Goddard and Glass are as follows:

| | Molecular Ratios | | | Atomic Ratios | | | |
|---|---|---|---|---|---|---|---|
| | G. & G. | H. & P. | | G. & G. | | H. & P. | |
| $SiO_2$ | 506 | 628 | Si | 506 | | 628 | $Z = 628 = 3 \times 209$ |
| $Al_2O_3$ | 100 | 167 | Al | 201 | | 335 ⎫ | |
| $Fe_2O_3$ | 65 | 5 | Fe''' | 129 | | 10 ⎪ | |
| FeO | 143 | 79 | Fe'' | 143 | | 79 ⎬ | $Y = 509 = 3 \times 170$ |
| MgO | 36 | 85 | Mg | 36 | | 85 ⎪ | |
| $TiO_2$ | 18 | — | Ti | 18 | | — ⎭ | |
| $K_2O$ | 2 | — | K ⎫ | | | | |
| $Na_2O$ | 0 | — | Na ⎭ | 4 | | — ⎫ | |
| CaO | 133 | 135 | Ca | 133 | | ⎪ | |
| MnO | 9 | 11 | Mn | 9 | 135 | ⎬ | $X = 296 = 2 \times 148$ |
| $Ce_2O_3$ | 45[a] ⎫ | 75[b] | Ce | 89 ⎫ | 11 | ⎪ | |
| $R.E._2O_3$ | 31 ⎭ | | R.E. | 63 ⎭ | 150 | ⎭ | |
| $H_2O$ | 108 | 8 | (OH) | 216 | 16 ⎫ | | $2325 = 13 \times 179$ |
| | | | O | 2095 | 2309 ⎭ | | |

[a] Molecular weight of $R.E._2O_3$ taken as 330.

[b] Molecular weight calculated from combined chemical and spectrographic data 331.34.

Machatschki's formula $= X_2Y_3Z_3(O, OH, F)_{13}$.

Determined by Goddard and Glass $= X_{1.79}Y_{3.17}Z_{3.04}(O, OH)_{13.88}$.

Determined by Hanson and Pearce $= X_{1.65}Y_{2.84}Z_{3.50}(O, OH)_{12.98}$.

The data require little discussion. The ratios fit the formula of Machat-schki[4] probably not quite as well as do those of Goddard and Glass. The per cent of $SiO_2$ in the analysis is undoubtedly high. This may be due to the fact that quartz is occasionally to be found enclosed in the allanite border and also that it is difficult to manually separate the latter from the quartz in contact with it—preliminary to the analysis.

## RADIOACTIVITY

Five days exposure of a polished surface to a photographic plate gave only a slight indication of radioactivity and this appeared not to be concentrated in any particular areas of the sample, but to be generally distributed throughout it, in the cerite as well as in the allanite border. There was obtained no indication that the minute particles of black mineral in the allanite were more radioactive than any other part of our samples; it cannot be assumed that they are uraninite.

## SPECTRUM EXAMINATION

The intense purple-violet color of the fluorite would suggest that it carried a high content of either neodymium or trivalent manganese. Ex-

TABLE 2. SPECTROGRAPHIC ANALYSIS OF COLORADO CERITE AND ALLANITE FOR THE RARE EARTH ELEMENTS

|  | % R.E. metal in $R.E._2O_3 + CeO_2$ | |
| --- | --- | --- |
|  | Cerite | Allanite |
| Sc | abs. 100'' exp. | abs. 100'' exp. |
| Yt | tr. | abs. 100'' exp. |
| La | $21 \pm 3$ | $29 \pm 3$ |
| Ce | $41 \pm 5$[a] | $30 \pm 3$[b] |
| Pr | 1 | tr.-s |
| Nd | $26 \pm 3$ | $30 \pm 3$ |
| Sm | $6.5 \pm 2$ | $5 \pm 2$ |
| Eu | tr. | abs. 50'' exp. |
| Gd | tr. | abs. 100'' exp. |
| Tb | tr.? | abs. 100'' exp. |
| Dy | abs. 100'' exp. | abs. 100'' exp. |
| Ho | tr. | abs. 100'' exp. |
| Er | abs. 100'' exp. | abs. 100'' exp. |
| Tm | abs. 100'' exp. | abs. 100'' exp. |
| Yb | abs. 100'' exp. | abs. 100'' exp. |
| Lu | tr. | abs. 100'' exp. |

[a] 45.2% by chemical determination and calculation.

[b] 30.64% by chemical determination and calculation.

[4] Machatschki, F., *Centralbl. Mineral., Geol., u. Pal.*, Abt. A, 89–96; 154–158 (**1930**).

amination of the mineral in thin section by means of a Leitz microspec-troscope, however, revealed none of the characteristic rare earth absorption bands. On the other hand, neither were such bands detectable in the cerite or in the allanite in spite of the high content of neodymium later found to be present in both of these. The coloring matter of the fluorite is as yet undetermined.

The individual rare earths in the oxide mixture from each mineral were determined spectrographically by the use of the line density method. A Baird Associates grating spectrograph and Eastman No. 40 $8'' \times 10''$ spectrographic plates were used in this work. Exposures of thirty seconds were ordinarily employed; elements were recorded as absent if no lines were to be found on greatly over-exposed plates. The data are shown in Table 2.

TABLE 3. RARE EARTH OXIDE RATIOS IN CERITE AND ALLANITE

| Oxide | A Ave. % in Mineral | | B % in Mineral Calc. from A to chem. $RE_2O_3$ total | | C Calc. from B to 100% $RE_2O_3$ + $Ce_2O_3$ | | Ratio to $Sm_2O_3$ | |
|---|---|---|---|---|---|---|---|---|
| | Cerite | Allanite | Cerite | Allanite | Cerite | Allan-ite | Cerite | Allan-ite |
| $La_2O_3$ | 11.86 spect. | 8.60 | 10.41 | 7.98 | 22.06 | 32.01 | 3.26 | 5.86 |
| $Pr_2O_3$ | pres. spect. | tr. | — | — | — | — | — | — |
| $Nd_2O_3$ | 14.61 spect. | 8.84 | 12.83 | 8.20 | 27.18 | 32.89 | 4.02 | 6.02 |
| $Sm_2O_3$ | 3.63 spect. | 1.46 | 3.19 | 1.36 | 6.76 | 5.46 | 1.0 | 1.0 |
| Total $RE_2O_3$ | 30.10 spect. | 18.90 | 26.43 | 17.54 | | | | |
| $Ce_2O_3$ | (23.61 spect. | 8.88) | 20.77 chem. | 7.39 | 44.00 | 29.64 | 6.50 | 5.43 |
| $CeO_2$ | 21.78 chem. | 7.75 | (21.78 chem. | 7.75) | | | | |
| $RE_2O_3+CeO_2$ | 48.21 chem. | 25.29 | | | | | | |
| $RE_2O_3$ | 26.43 | 17.54 | | | | | | |
| $RE_2O_3+Ce_2O_3$ | | | 47.20 | 24.93 | 100.00 | 100.00 | | |

It was felt that the chemical data for the determination of cerium was of much greater reliability than that obtained by the spectrographic method, and furthermore that the total rare earth oxide content determined chemically was more reliable than the sum of the averages of the individual oxides obtained by calculation from the spectrographic data. Consequently the total: (spectrographic) sesquioxide content plus (chem-

ical) $CeO_2$ content was corrected to the chemically-determined total
(La, Pr, Nd, Sm etc.)$_2O_3 + CeO_2$; the individual sesquioxide amounts,
percentages and ratios were then calculated from this. The data are
shown in Table 3.

Cerium is probably present in the cerous state in both the cerite and
the allanite.[5] Account is to be taken of the fact, however, that cerous
oxalate is oxidized to ceric oxide upon ignition in air and is weighed as
such in quantitative determinations even when in admixture with typi-
cally trivalent rare earths.

## INDIVIDUAL RARE EARTH RATIOS

Goldschmidt and Thomassen[6] in their classical study have subdivided
rare earth minerals according to their average content of the individual
rare earths as determined by *x*-ray spectrography. Both cerite and allan-
ite (as well as bastnäsite, toernebohmite, eudialyte, eucolite, freyalite,
melanocerite, mosandrite and tritomite) fall into their Class B, Subclass
I, Type b. This class is that of minerals containing a selective group,
rather than a complete representation, of the earths; in this subclass
there is an outstanding content of cerium-group elements. The type is
that of minerals with a high content of the elements La through Nd, and
with only weak representation of Sm and Gd. Orthite (allanite) has lent
its name to the type. This stands in contrast to the Monazite Type (a)
which is similar but has high representation of La through Sm with still
important amounts of Gd. There follows a comparison of our values with
the Goldschmidt-Thomassen averages, representing the relative num-
bers of atoms, for this subclass. Shown also are ratios calculated from
averaged arc spectrum data of McCarty[7] for 10 monazites as well as
those calculated from other similar analyses reported by B. S. Hopkins
et al.[8]

[5] Goldschmidt, V. M., Elemente und Minerale pegmatitischer Gestein: *Nachr. Ges.
Wiss. Göttingen*, **1930**, *Math.-physik. Klasse, Fachgruppen IV Nr.* **4**, 370–378, has indicated
that cerium is present in the ceric state in certain minerals of the alkaline nepheline-
syenite pegmatites.

[6] Goldschmidt, V. M., and Thomassen, L., Röntgenspektrographische Untersuchungen
über die Verteilung der seltenen Erdmetalle in Mineralen: *Videnskapsselskapets-Skrifter*,
*I, Matemat. natur. Klasse, Kristiania*, No. 5 (**1924**).

[7] McCarty, C. N., Quantitative estimation of some of the rare earth ores by means
of their arc spectra. *Doctorate Thesis, Univ. Illinois* (**1935**).

[8] McCarty, C. N., Scribner, L. R., and Lorenz, Margaret with Hopkins, B. S., Quanti-
tative estimation of the rare earths by means of their arc spectra: *Ind. Eng. Chem., Anal.
Edn.*, **10**, 184–187 (1938).

| | 57 La | 58 Ce | 59 Pr | 60 Nd | 61 | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | 71 Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Colorado Cerite | 24 | 47 | ca.1 | 29 | — | 7 | tr. | tr. | tr? | abs | tr. | abs | abs | abs | tr. |
| Colorado Allanite | 35 | 32 | ≪1 | 35 | — | 6 | abs | abs | abs | abs | abs | abs | abs | abs | abs |
| G. & T. Class B, Subclass I | 12 | 50 | 8 | 24 | 0 | 7 | 0 | 4 | 0 | ca. 2 | — | — | — | — | — |
| 10 Monazites[7] | 19 | 45 | 9 | 25 | — | 3 | — | 6 | — | — | — | — | — | — | — |
| 1 Cerite[8] | 15 | not det. | not det. | 30 | — | 6 | — | 2 | — | 1 | — | — | — | 1 | — |
| 1 Allanite, 1 Orthite[8] | not det. | not det. | not det. | 24 | — | 7 | — | 4 | — | 3 | — | — | — | 2 | — |

In general the ratios reported at this time fit well into the average of the monazite and orthite types of Goldschmidt and Thomassen. While the latter did not report separate averages for the two types, and while the Illinois workers did not in some cases determine certain of the elements, some hypotheses may be put forward upon the above data. Thus it may be supposed that the Pr content of the subclass average is mainly due to a higher content of this element in monazite (and its associate, fluocerite or tysonite) than in cerite and orthite and their associates in the other type. Similarly, but on less conclusive evidence, one could assume the La content to be due to a greater extent to the allanite than to the monazite.