

MINERAL DETERMINATION BY ABSORPTION SPECTRA. I.

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With the perfecting of the immersion method for measuring the refractive indices of crystals, other means of mineral identification have been more or less relegated to the background, but their existence should not be forgotten entirely, for problems occasionally arise which they may aid in solving. Several years ago I published¹ a comprehensive study of the absorption spectra of minerals, as seen with the microspectroscope. That paper has long been out of print, but every now and then requests for certain information along this line are received, so the republication of part of the data included in it, together with some obtained from other sources, seems worth while. The method of presentation adopted is directed toward the identification of transparent or translucent, more or less distinctly colored, minerals,

The apparatus used in identifying minerals by their absorption spectra consists of a microscope eyepiece containing a direct-vision spectroscope. Of these there are two main types, one with relatively small dispersion, which yields the more intense effects, but does not permit of wave-length measurement, the other with greater dispersion, yielding fainter bands but providing for accurate measurement of their wave-lengths. As pointed out by Keeley,² the former type is well adapted to preliminary examination, and in many cases will produce such characteristic absorption phenomena that no further observations are needed; for final decision, however, the determination of the exact positions of the bands by means of the more elaborate instrument is desirable.

In the majority of cases, far more striking absorption spectra are obtained when the mineral is viewed by scattered instead of directly transmitted light. The stage of the microscope is accordingly best covered completely by a dull black card, and the most brilliant source of white light available adjusted so that a beam is concentrated on the side of the object under observation, by means of a condensing lens system or a parabolic reflector attached to the microscope objective. When minute grains are to

¹ The microspectroscope in mineralogy. *Smiths. Misc. Coll.*, 65, no. 5, 16 pp., 1915.

² Microspectroscopic observations. *Proc. Acad. Nat. Sci. Phila.*, 1911, 106-116.

be studied, they are first centered and brought into focus while the prism is out, and the latter is then inserted; if irregularities in the grain produce distortions in the spectrum, the microscope tube can be raised slightly, so that sharpness of focus is lessened. The field of the spectroscope should be narrowed, transversely to the spectrum, so that only the area of the grain itself is covered; and the slit should be reduced to the minimum opening through which light can be seen, to make the absorption bands as sharp a possible. If a wave-length scale is attached, this should be adjusted by bringing $589m\mu$ into coincidence with the yellow line seen when a sodium flame is viewed.

Minerals containing no constituents capable of producing well-marked absorption bands yield a continuous spectrum, which is visible from wave-length 700, at the red end, to 400, at the violet. When a chemical element which absorbs certain wave-lengths much more strongly than adjacent ones is present, however, one or more dark bands will be seen in the midst of this spectrum, and the positions of these are in many cases so characteristic that they can be used for identification both of the element and of the mineral. Absorption in narrow bands or lines is shown by certain of the rare-earth metals and by uranium, in broader bands by chromium, cobalt, copper, iron, manganese, vanadium, and occasionally other.

PART 1. ABSORPTION SPECTRA CONSISTING OF NARROW BANDS

Strongest band or group of bands in the yellow, a fairly strong one in the green, and many weaker ones at intervals throughout. . . . Cerium earths, group 1.
 Strongest band in the green-yellow, a fairly strong one in the green, and a few weaker ones elsewhere. . . . Yttrium earths, group 2.
 Strongest band in the red, a fairly strong one in the orange-yellow, and many weaker ones at intervals throughout. . . . Uranous uranium, group 3.
 Strongest band in the green-blue or the blue-green, and a few others, chiefly toward the violet end. . . . Uranyl uranium, group 4.

GROUP 1. THE CERIUM EARTHS, NEODYMIUM AND PRASEODYMIUM

The average wave-lengths of the principal absorption bands shown under the microspectroscope by minerals containing these elements will be listed first; the bands actually vary distinctly in wave-length and intensity from one compound to another. The minerals will then be discussed, class by class.

Spectrum-zone	red	orange	yellow	green	blue	b-v.
Wave-length.	675	620 595	580 570	530 520 510	485 470	445
Element. . . .	Nd	Nd Pr	Nd Nd	Nd Nd Nd	Pr Pr	Pr

Fluocerite, (tysonite of Dana), $(\text{Ce}, \text{X})\text{F}_3$

675	(623)	595	580-570	(532)	522	(513)	(485)	W.
...	...	590		587-586		584-575		573-568	...	K.

The most characteristic features of the spectrum of the specimen of this mineral I examined, as tabulated in the line marked W are the intensity of the bands centering at 675 and 595, and the relative weakness of the group of coalesced bands extending from 580 to 570. The one studied by Keeley³ as to the details of the bands in the yellow spectrum-zone, gave the data tabulated on the line marked K, and was evidently dissimilar in composition; its striking features consist of intense absorption at 584-575, and brilliant transmission at 586-584 and 575-573 (indicated by ||).

Bastnaesite, $(\text{Ce}, \text{X})\text{F}(\text{CO}_3)$

675	(623)	(590)	579		569	(532)	522	(511)	(485)	W.
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This mineral is characterized by the weakness of the lines due to praseodymium, and the intensity of the bands at 579 and 569 with transmission between them at 576-572.

Parisite, $\text{Ca}(\text{Ce}, \text{X})_2\text{F}_2(\text{CO}_3)_3$

675	623	590-570	533	...	522	512	485	(470)	(445)	W.			
...	...	584-576		575-568	K.			
ω 677	630	583	579	575	...	533	529	523	511	483	471	445	B.
ϵ 677	650	583	580	575	571	533	529	521	(512)	483	471	445	B.

Like many others in this group, parisite evidently varies in composition and correspondingly in absorption spectrum, from one specimen to another. Notable features of the one I studied are the intensity of the bands at 623 and 512, and the practical coalescence of the three bands in the yellow spectrum-zone, which in most rare earth minerals are rather distinctly separated. Keeley³ found this coalescence to be not quite complete, although the transmission at 576-575 is dim. Becquerel⁴ had previously studied the absorption spectrum of this species, from the viewpoint of the differences in the directions of the ordinary and extraordinary indices; but he used a large spectroscope, and was able to detect many more lines than could be found by the present method, so only the more significant of his wave-lengths are here given.

³ Notes on absorption spectra of certain minerals. *Festschrift Victor Goldschmidt*, 1928, 170-171 and pl. 7.

⁴ Researches on the variations of absorption spectra in crystals. *Ann. chim. phys.*, [6] 14, 170-257, 1888; especially page 193.

Ankylite, $\text{Sr}(\text{Ce}, \text{X})_2(\text{OH})_2(\text{CO}_3)_3$

(675) 590 580-575 (570) 521 (512) W.
 582-576 K.

In my previous paper, ankylite was reported to show no absorption spectrum, but the specimen was evidently wrongly labelled for one was found subsequently which yielded that here recorded. The most striking feature is the presence of a single strong band in the yellow, and the weakness of the one at 570 which is usually very intense in cerium-earth minerals.

Cordylite, $\text{Ba}(\text{Ce}, \text{X})_2\text{F}_2(\text{CO}_3)_3$

(675) (590) 583-579 (575) (533) 521 512 (485) 470 W.
 582-576 K.

Keeley found no difference between the absorption in the yellow of ankylite and cordylite, but they differ in the intensities of the lines in other spectrum zones.

Lanthanite, $(\text{Ce}, \text{X})_2(\text{CO}_3)_3 \cdot 9\text{H}_2\text{O}$

(675) (620) (590) ... 580-578||572-568 (532) 520 510 (485) (470) (445) W.
 (586-578) 578-574||572-568 K.

This mineral is often assigned the formula of a pure lanthanum carbonate, but the analyses on which this is based give no evidence of trustworthiness, and it seems more likely to be analogous in rare-earth constituents to the other minerals under discussion. Characteristic features are the weakness of the band centering at 590, and the brilliant transmission in the yellow, at about 573.

Calcite, neodymian, $(\text{Ca}, \text{X})(\text{CO}_3)$

582 (525) W.

That the violet calcite from Joplin, Missouri, owes its color to the presence of neodymium has been pointed out elsewhere.⁵ In this case side-illumination does not produce very good results, but on transmitting white light through a cleavage piece 3 or 4 cm. thick two distinct absorption lines are visible.

Strontianite, neodymian, $(\text{Sr}, \text{X})(\text{CO}_3)$

589 585 580 (578) 574 (571) 568 B.

⁵ Neodymium as the cause of the red-violet color in certain minerals. *J. Wash. Acad. Sci.*, 7, 143-146, 1917.

Greenish strontianite was discovered by Becquerel (*op. cit.*, p. 230) to show this absorption spectrum, although it is difficult to obtain any lines from this mineral by the microspectroscope.

Scheelite, neodymian, (Ca, X)(WO₄)

ω	595	593	589	587	585	580	575	533	529	527	B.
ε	...	593	589	587	585	580	575	532	528	...	B.

In specimens of this mineral from Traversella, Becquerel (*op. cit.*, p. 191) observed the lines tabulated. The microspectroscope shows only traces of the strongest.

Monazite, (Ce, X)(PO₄)

	675	622	590	—	—	—	570	(532)	523	512	485	...	W.
	586-582		580-576		574-568	K.
α	682	627	592	584	580	575	574	572	527	523	513	484	475 B.
β	682	627	592	584	580	575	574	572	527	522	513	484	475 B.
γ	682	627	592	584	580	575	574	572	527	522	513	...	B.

This mineral, the commonest rare earth phosphate, yields a very intense absorption spectrum, and can readily be identified by this means even when present as minute grains in a sand. Its bands in the yellow region are so intense as to tend to coalesce, to an extent differing with the source of the material. The specimens studied by Keeley showed rather evenly spaced light and dark bands. That examined by Becquerel (*op. cit.*, p. 227) with the large spectroscope gave rather different wave-lengths for several bands from that available to me.

Britholite, (Ce, X)+(PO₄)+(SiO₄)

(675)	(590)	588-578	...	530	(520)	(512)	(485)	W.
...	...	589-576	570-568	K.

This mineral, supposed to be a silicato-phosphate, shows much weaker absorption than monazite, but like the latter varies from one specimen to another, as the stronger band observed by Keeley did not show up in my specimen at all.

Rhabdophanite, (Ce, X)(PO₄) · H₂O

675	622	595	—	—	—	570	533	524	512	485	(470)	(445)	W.
...	...	(586-581)	581-578	(578-568)	K.
...	625	595	592	580	(576-571)	526	524	(512)	(484)	(477)	B.

As might have been expected, this mineral shows nearly the same spectrum as its anhydrous representative monazite, although

the bands in the yellow are more completely coalesced, with maximum absorption near 580. (See Becquerel, *op. cit.*, p. 228.)

Churchite, $\text{HCa}(\text{Ce, X})_3(\text{PO}_4)_4 \cdot 7\text{H}_2\text{O}$
(675) (620) **590** || **578** (535) 524 (510) (485) W.

There can be no doubt as to the distinctness of this from the preceding mineral, as all its bands are weaker, and the two in the yellow are clearly separated, with transmission at 588–581.

Pyrochlore, Na-Ca-(Ce,X)-Ti columbate
588–578 (525) W.

The single strong band in the yellow is characteristic of this mineral. The corresponding tantalate, microlite, differs in that its bands, while identical in position, are much weaker.

Samarskite, Fe-U-(Ce, X) columbate
(585) (525) W.

In my earlier article this compound was reported to show no absorption spectrum, but more translucent material was subsequently found to exhibit faint Nd bands. The same effect is shown by eschynite, which differs in containing also titanium, but the remainder of the columbates seem too opaque for study in this manner.

Cerite, $(\text{Ce, X})_2(\text{SiO}_3)_3 \cdot \text{H}_2\text{O}$ (?)
(675) (620) **590–570** (533) (525) (512) (485) W.

The bands of this, the silicate with the highest known cerium earth content, are rather distinctive, although all except the broad one in the yellow are faint.

Freyalite, $(\text{Th, Ce, X})(\text{SiO}_4) \cdot \text{H}_2\text{O}$ (?)
(675) (590) **585** || **575 530** (525) (512) (485) W.

The three strong bands, with transmission in the yellow at 582–578, are characteristic of this little known mineral.

Rinkite, Na-Ca-(Ce, X) titanosilicate
590–582 || 578–568 K.

This rare mineral has been found by Keeley (*loc. cit.*) to show two broad absorption bands in the yellow spectrum zone, the gap

between them lying at 582-578, a different position from that of any other member of the division.

Other silicates

A specimen in the National Museum collection labelled rowlandite, supposedly $Y_4(SiO_4)_3$, yielded bands corresponding to moderate amounts of Nd, with a rather intense one at 585-575; its composition evidently needs further investigation.

The remaining cerium-earth silicates tried, comprising mosandrite, sphene, tritomite, and woehlerite, show faintly the two Nd lines at 585 and 525. In addition, Becquerel (*op. cit.*, p. 229) found in leucophanite strong lines at 589 and 587.

In concluding the discussion of the cerium-earth minerals, it should be noted that secondary uranium compounds derived from primary ones containing these earths may show in addition to the uranium bands one or more of those due to neodymium.

GROUP 2. THE YTTRIUM EARTHS, SAMARIUM AND ERBIUM.

The approximate positions of the bands shown under the micro-spectroscope by minerals containing these elements are as before tabulated first. Four of them are obviously due to the metals indicated, but the lists of absorption spectra of known rare earth metals do not include a band in the orange spectrum zone, in the neighborhood of 605, so the source of this line is indeterminate.

Spectrum-zone	red	orange	yellow	green	blue
Wave-length.....	645	605	555	522	485
Element.....	Er	?	Sm	Er	Sm

Fluorite, yttrian, (Ca, X)F₂

(650) (605) 555 (522) W.

The brownish-green fluorite from Amelia, Virginia, which is known as chlorophane because of its green thermoluminescence, shows bands indicating the presence of traces of yttrium earths.

Xenotimite, (Y, X)(PO₄)

(660)	645	605	555 (545)	522	...	(485) W.
ω 657 653 651 644	...	552	546	...	539	524	521	492	489 B.
ε 658 655 652 644	...	550	545	542	539	524	521	494	488 B.

The spectrum of this mineral is intense and highly diagnostic. Becquerel (*op. cit.*, p. 194) observed lines due to several other metals than those here listed.

Fergusonite, (Y, X)(CbO₄) and related minerals.

(555) (522) W.

Most of the columbate minerals are too opaque to show any absorption spectrum, but fergusonite, inclusive of sipylite, (which is evidently the same, the analysis being untrustworthy) yields the faint bands tabulated.

Yttrotantalite, HCa(Y, X)₂(TaO₄)₄ (?)

(650) (600) (555) 522 W.

The absorption band at 522 is so strong in this mineral, as well as in the related if not identical risoerite, that its identification can be based on this feature.

Yttrialite, (Y, X)₂Si₂O₇

(645) (600) (555) (522) (485) W.

The bands in this compound are fainter than would be expected. Rowlandite, which is supposed to be related, shows the same bands together with a strong one at 580 which appears to be due to neodymium, but the specimen studied may not have been correctly labelled. Faint yttrium-earth bands are also shown by some minerals characterized particularly by cerium-earths, such as monazite.

GROUP 3. URANOUS URANIUM.

Spectrum-zone	red		orange		yel.		green		blue	
Wave-lengths	686	660	652	618	589	561	539	511	482	458

Zircon, uranoan, (Zr, U''''')(SiO₄)

	687	...	650	615	586	561	538	508	478	455	K.
	685	(660)	651	618	588	560	537	512	483	(460)	W.
ω	691	658	654	...	590	562	538	512	483	...	B.
ϵ	682	659	652	621	589	...	543	B.
	685	661	651	(619)	591	(560)	539	(511)	(483)	...	K. & H

The only mineral in which these bands have thus far been observed is transparent zircon; they are most intense in bluish colored types.⁶ The wave-lengths differ slightly from one specimen to another, as brought out by tabulating the values reported by Keeley (paper of 1911, p. 107), the writer, (*op. cit.*, p. 9), Bec-

⁶ They are said to have first been noted by Sorby, *Phil. Mag.*, **39**, 35, 1860.

querel (*op. cit.*, p. 196, and⁷) and Kraus and Holden.⁸ They are still different in uranous salts, obtained by reducing uranyl compounds with zinc and an acid, but not sufficiently so to raise any question as to their being due to this form of the element in the mineral.

GROUP 4. URANYL URANIUM.

Spectrum-zone	yel.	green			blue			v-b.
Wave-lengths	550	535	515	500	485	465	455	445

This spectrum, characterized by several nearly equally spaced absorption bands in the green and blue, is shown by the more transparent of the secondary uranium minerals, although so many earthy ones do not give it, that its failure to appear can not be considered as proof of the absence of the element.

Liebigite, $\text{CaCO}_3 + (\text{UO}_2)(\text{CO}_3) + \text{H}_2\text{O}$

(535) (515) 495 (480) 463 455 (440) W.

This is the only mineral observed in which the band in the blue, at 465-461, is most intense, this feature being thus diagnostic. Material labelled uranothallite gives the same bands, confirming the suspected identity of the two.

Voglite, $(\text{Ca}, \text{Cu})(\text{CO}_3) + (\text{UO}_2)(\text{CO}_3) + \text{H}_2\text{O}$

504 488 472 458 447 W.

The presence of a small amount of copper changes the spectrum markedly from that of the related compound, next preceding. The lines here tabulated are similar to those of torbernite, but otherwise more or less diagnostic.

Johannite, $\text{Cu}(\text{UO}_2)(\text{OH})_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$

497 479 (466) (450) W.

This mineral is interpreted as including gilpinite, uranochalcite, and voglianite. Its spectrum is unique in containing but two really well-marked bands, in blue-green and blue.

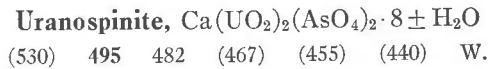
Autunite, $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 \pm \text{H}_2\text{O}$

(550) (532) 515 499 484 (468) (455) 445 W.
 504 487 472 457 445 R.

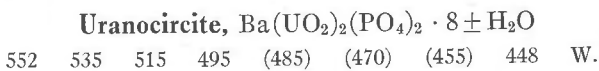
⁷ Relations between absorption of light and phosphorescence in uranium compounds. *Compt. rend.*, 101, 1252-1256, 1885.

⁸ Gems and Gem Materials, p. 60, 1925.

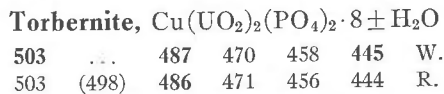
The second set of wave-lengths tabulated was that obtained by Rinne.⁹ The prominence of the bands in the green, blue-green, and violet-blue is diagnostic; the most intense shown by my specimens was the second noted, running from about 501 to 497.



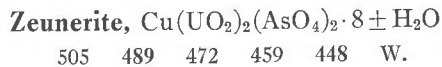
This mineral can be distinguished from the other members of the group by the presence of but a single intense band in the blue-green, at wave-lengths 497-493.



None of the bands in this mineral are sufficiently intense to indicate in bold-face type, but the two in the yellow and green are better marked than in any other mineral of the group.



The absence of bands in the yellow and yellow-green, but the presence of three strong ones elsewhere, is diagnostic of this species (see Rinne¹⁰).



The diagnostic features of this spectrum are the relative weakness of the band in the green and the intensity of the one in the violet blue at a slightly different point from its relative, next preceding, namely at 450-446.

Commercial uranium glass exhibits all of the absorption bands shown by any of the minerals containing uranyl, with an additional one in the orange at 595. Those in the blue-violet, however, are so broad as to coalesce, from about 455 to 435, or to the end of the visible spectrum. Uranyl salts behave similarly, although the details vary considerably with the composition.

(To be concluded)

⁹ Autunite and its dehydration product (metaautunite). *Centr. Min. Geol.*, 1901, 709-713.

¹⁰ Torbernite and its dehydration product (metatorbernite). *Centr. Min. Geol.*, 1901, 618-626; especially p. 622.