

A solid solution series between xenotime (YtPO_4) and chernovite (YtAsO_4)

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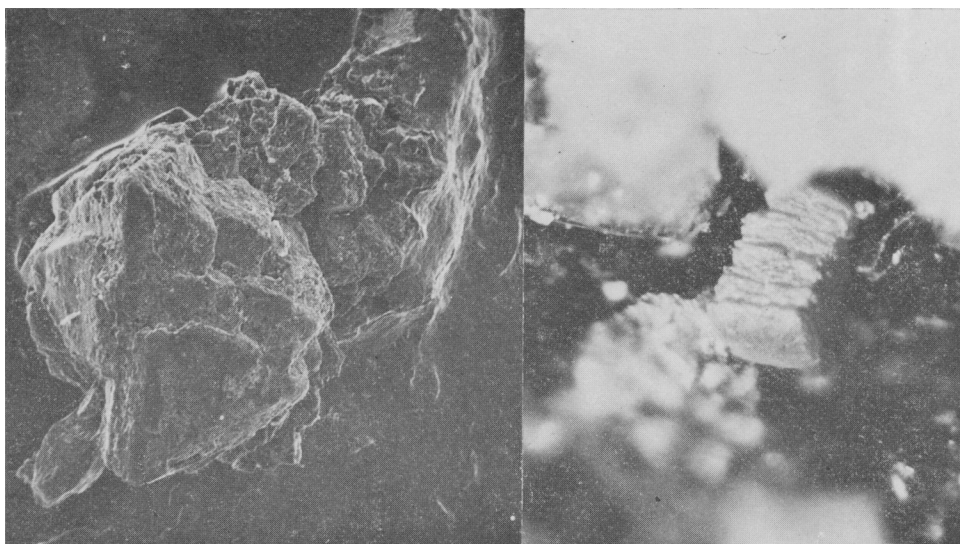
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SUMMARY. The mineral chernovite, described as a new mineral from the Urals by Russian mineralogists in 1967 (Goldin *et al.*, 1967), has been found at three different localities in mineral fissures in the Binnatal, Switzerland, and a little to the south, in Italy. The mineral occurs in greenish-yellow bipyramidal crystals up to about 1 mm. A detailed single-crystal study of several specimens showed that the lattice constants vary considerably on either side of those published for the original chernovite. The refractive indices, too, display some variation. Microprobe analyses of this material, and of xenotime specimens from the same region, revealed that there exists at least partial solution between chernovite and xenotime. The three chernovite samples have molar percentages of 63.2, 73.2, and 82.0% YtAsO_4 (the Urals chernovite has about 95.2%). These studies prove the existence of an isomorphous series between xenotime and chernovite, at least in the As-rich portion.

DURING the summer of 1966 the mineral collector Fritz Stettler of Berne found some mineral specimens in the southern part of Binnatal that were unknown to him; he sent them to the Natural History Museum in Berne for identification. One of us (H. A. St.) studied the minerals by Debye-Scherrer diagrams and optical methods. He found one of the minerals was identical with the artificial compound YtAsO_4 , for which *d*-values were published in the Powder Data File. As he possessed only a few minute grains of the material he did not continue the study, but hoped to get additional material for the description of the new mineral, which—at that moment—the compound really was. But in the meantime the same material was found in the near Polar Urals by Russian scientists, and the new mineral YtAsO_4 was described in 1967 under the name chernovite (Goldin *et al.*, 1967).

In 1970 and 1971 two more chernovite samples were found at other localities and identified by Weissenberg techniques by the first author (S. G.). As the X-ray data varied considerably it became interesting to start a comprehensive study on this mineral group. In addition to the three chernovites we also had two samples of xenotime from other localities in the same region (found by the professional mineral collector Toni Imhof at Binn).

Morphological description. The Binnatal chernovite occurs in very small bipyramidal crystals of pseudo-octahedral shape (fig. 1); sometimes they form aggregates along the c -axis (fig. 2); their size seems not to exceed about 1 mm. The colour of the inner zones is greenish-yellow, in the outer zones changing to bright yellow, probably due to weathering processes. Cleavage parallel to $\{100\}$ seems to be very indistinct. Xenotime from the same region is yellow transparent and forms elongated prismatic crystals with small bipyramidal faces. The $\{100\}$ -cleavage is clearly recognizable. Their size may reach about 5 to 6 mm along the c -axis.



FIGS. 1 and 2: FIG. 1 (left). Chernovite, sample SG 1227. Bipyramidal crystal of pseudo-octahedral habit. Stereoscan photograph; size of crystal about 0.5 mm along the a -axis. FIG. 2 (right). Chernovite crystal Be, showing aggregation in direction of the c -axis. Length of crystal about 0.75 mm along c -axis.

Optical data. The refractive indices of the two xenotime and three chernovite samples have been determined by the immersion method. As it was quite difficult—especially in the case of the chernovites—to get good material for the determination of refractive indices we measured only ω . The refractive indices of both xenotimes and chernovites from Binnatal are listed in table I. The probable existence of a solid solution series, at least on the chernovite side, is clearly outlined by the variation of the refractive indices. The correlation of optical data and chemical composition is considered below.

X-ray determinations. The first determinations on the Binnatal samples were carried out by the Debye-Scherrer method, which led to the identification of the compound YtAsO_4 , at that time not known as a mineral. When the additional mineral samples became available and showed very similar powder patterns it seemed important to study the minerals by single-crystal methods; so all the xenotime and chernovite samples were examined by Weissenberg techniques (table I). The cell parameters of artificial YtAsO_4 are noticeably smaller than those of natural material, which may be

TABLE I. *Chemical and physical data for chernovite and xenotime. All specimens are optically negative and have space-group $I4_1/amd$*

	I	II	*	Be	SG 1227	SG 1053	U	†
Yt ₂ O ₃	52.7	51.8	—	38.7	37.5	36.9	—	—
Ln ₂ O ₃	10.0	12.9	—	15.5	15.8	15.1	—	—
P ₂ O ₅	37.7	38.6	—	11.9	8.5	5.5	—	—
As ₂ O ₅	0.2	—	—	33.2	37.6	40.3	—	—
Sum	100.6	103.3	—	100.3	99.4	97.8	—	—
(Yt, Ln)AsO ₄ } mol. %	0.4	0	0?	63.2	73.2	82.0	95	100.0
ω	1.716	1.718	—	1.753	1.764	1.772	1.783	—
<i>a</i> , Å	6.90 ₁	6.90 ₂	6.89	6.99 ₃	7.04 ₈	7.09	7.03 ₉	7.03 ₉
<i>c</i> , Å	6.05	6.02	6.04	6.16 ₇	6.26 ₂	6.32	6.27 ₂	6.29 ₈
<i>c/a</i>	0.8767	0.8722	0.877	0.8819	0.8891	0.8914	0.8910	0.8939

* Xenotime, data from Strunz, 1970. SG 1227, Chernovite, Cherbadung.
 I, Xenotime, Cherbadung. SG 1053, Chernovite, Wannigletscher.
 II, Xenotime, Gibelalpe. U, Chernovite, Urals (Goldin *et al.*, 1967).
 Be, Chernovite, Gischihorn. † Synthetic YtAsO₄, Powder Data File card 13-429.

TABLE II. *X-ray powder data for xenotimes and chernovites. Fe-K_α radiation*

<i>hkl</i>	Xenotimes				Chernovites						
	I		II		Be		SG 1227		SG 1053		Urals
	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>d</i> _{meas}	<i>d</i> _{calc}	<i>d</i>
101	4.55Å	4.54Å	4.56Å	4.55Å	—	4.63Å	4.68Å	4.67Å	4.72Å	4.72Å	—
200	3.45	3.45	3.46	3.45	3.48Å	3.49	3.52	3.52	3.56	3.55	3.519Å
112	2.567	2.562	2.57	2.571	2.623	2.616	2.65	2.651	2.673	2.673	2.644
220	2.435	2.440	2.447	2.440	2.474	2.472	2.489	2.490	2.509	2.507	—
301	2.145	2.149	2.150	2.150	2.179	2.180	2.193	2.198	2.211	2.213	—
312	1.765	1.767	1.767	1.769	1.796	1.797	1.813	1.815	1.830	1.829	1.811
400	1.722	1.725	1.723	1.725	1.740	1.748	1.758	1.761	1.776	1.773	—
420	1.539	1.543	1.541	1.543	1.562	1.564	1.569	1.575	1.586	1.585	—
332	1.430	1.431	1.429	1.432	1.453	1.454	1.461	1.467	1.477	1.477	—
512	1.233	1.234	1.233	1.237	1.252	1.253	1.259	1.264	1.272	1.272	1.261
404	1.134	1.135	1.135	1.137	—	—	1.169	1.170	—	—	—
424	—	—	1.089	1.080	—	—	1.108	1.108	1.120	1.119	1.109

Key as Table I.

explained by the relatively high content of lanthanons in natural chernovite (up to 15 wt. %).

Chemical composition. Part of the same material as was used for the X-ray determinations was analysed on a JEOL microprobe (table I). The following materials served as standards: Yt-garnet (artificial), two yttrium glasses, and the minerals cafarsite and asbecasite, two arsenate minerals (Graeser, 1966). The relatively high

content of lanthanons was determined only semiquantitatively; the exact content in the xenotimes and chernovites as well as in a number of associated minerals will be determined in a comprehensive study of the rare earths in minerals from the region.

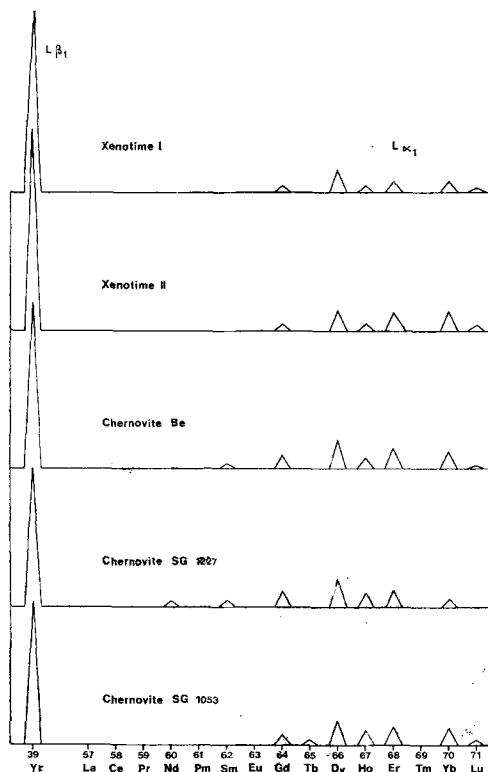


FIG. 3. Relative abundances of lanthanons in xenotimes and chernovites from Binnatal. $L\alpha_1$ signals for the lanthanons, compared with $L\beta_1$ for yttrium.

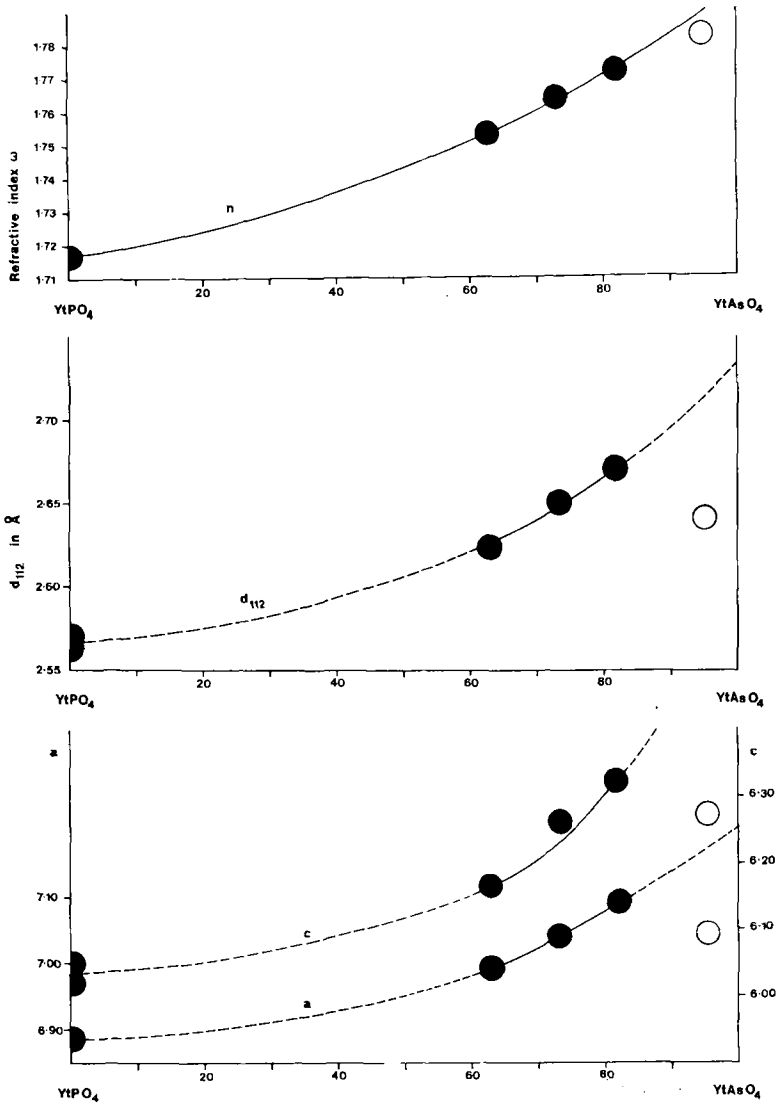
on a presumable existence of mix-crystals between torbernite and zeunerite from Menzenschwand. The material was put at our disposal, and will be studied by the first two authors (the note by Schatz was based on simple chemical tests, X-ray study or microprobe analyses were lacking).

The chemical composition has a very strong influence on optical and X-ray data: with increasing arsenate content the refractive indices and cell dimensions increase. By plotting the chernovite molecular percentage against refractive index and cell dimensions, it is possible to estimate the arsenate content by simple determination of optical or powder data. From the diagrams in fig. 4, and especially figs. 5 and 6, it becomes obvious that there exists some contradiction between the data of the present paper and those of Goldin *et al.* (1967): from the chemical analysis, the Russian chernovite has about 95 mol % $YtAsO_4$; the refractive index graph (fig. 4) yields about

The lanthanon concentrations in the chernovites are notably higher than in the xenotimes. The most abundant lanthanons are Gd, Dy, Ho, Er, and Yb (see fig. 3).

If we consider also the Russian chernovite, for which the $YtAsO_4$ content is about 95 mol %, we have a solid solution series in the arsenate-rich portion between xenotime and chernovite extending from about 60 % to almost 100 %. The formation of mix-crystals on the xenotime side seems to be slight; no xenotime analyses reporting As_2O_5 were found in the literature. However, the xenotime found near the chernovite localities in Binnatal shows a small As concentration, so it is possible that arsenate-bearing xenotimes have not been identified because of too small optical and physical differences from pure xenotime.

According to Strunz (1970), this result would represent the first and only case of an isomorphous solid-solution series between phosphate and arsenate minerals. Schatz (1971) reported some very interesting data



FIGS. 4 to 6. ●, Binnatal samples; ○, Russian chernovite. FIG. 4 (top). Variation of refractive index ω with AsO_4^{3-} content. FIG. 5 (middle). Variation of d_{112} with AsO_4^{3-} content. FIG. 6 (bottom). Variation of a and c with AsO_4^{3-} content.

92 %, but from figs. 5 and 6 percentages of 73 or 71 % result, very close to sample SG 1227 of this study. Perhaps this contradiction may be due to a much lower lanthanon content in the Russian chernovite (Goldin *et al.* give no Yt:Ln ratio). The accordance in X-ray data between the Russian chernovite and artificial YtAsO_4 is unexpected. A slightly better accordance is achieved by plotting the axial ratio $c:a$ against chemical

composition (P:As ratio); in this case it becomes possible to determine an approximate molar percentage from X-ray data independently of the lanthanon concentration (fig. 7).

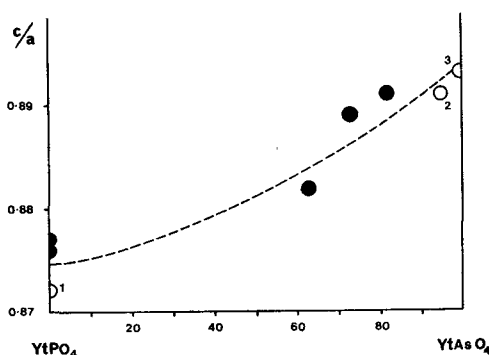


FIG. 7. Correlation of axial ratio c/a with chemical composition. ●, Binnatal samples; 1, xenotime (Strunz, 1970); 2, chernovite from Urals; 3, artificial $YtAsO_4$.

Genesis, paragenesis. Whereas the formation of the Russian chernovite is bound to the occurrence of subvolcanic liparite porphyries of Rhiphaean age, the Binnatal chernovites are a typical product of Alpine fissure-mineral formation in connection with Alpine metamorphism. The material that formed the minerals originates—as for the two new arsenate minerals cafarsite and asbecasite (Graeser, 1966)—from an old Cu-As deposit of presumably Hercynian age, which was partly remobilized by Alpine metamorphism. These As-rich solutions

moved in the direction of lower temperatures, and from them crystallized by further cooling the rare and uncommon arsenate minerals cafarsite, asbecasite, chernovite.

The Cu-As deposit (chalcopyrite, tennantite, etc.; Graeser, 1965) lies in the gneisses of the Monte Leone nappé (one of the lower Pennine nappes), as do the fissure minerals described. The whole region is extraordinarily rich in rare and interesting minerals. The chernovites here are associated with smoky quartz, adularia, sphene, anatase, rutile, magnetite, apatite, monazite, cafarsite, asbecasite, metatorbernite (Graeser, 1972), fluorite, synchysite, tourmaline, and some hitherto unknown minerals. Some of these minerals, including the monazite, synchysite, and chernovite, will be studied in a future work in respect of their content and distribution of rare earths, which has already turned out to be very unusual.

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Addendum. After this manuscript had been completed we found a work by Walenta (1972), who describes the mineral occurrences at Wittichen, Schwarzwald, Germany. Among the minerals described Walenta mentions an unknown species, which he supposes to be some variety of xenotime. By qualitative microprobe analysis he found as major constituents Yt, Ln, Ba, Fe, As, and P. Whether As or P dominates he could not decide, but presumably P. The reported X-ray diffraction data are quite close to those of xenotime, but significantly shifted to higher values. If it is really a mineral between xenotime and chernovite, it would fall—according to figs. 4 and 5—into the field of As-rich xenotimes (between 20 and 50 % chernovite mol), and could step into the breach between xenotime and phosphate-rich chernovite.

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