Delorenzite is tanteuxenite.

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Summary. Specimens of delorenzite from the type locality, Craveggia, Val Vigezzo, Piemont, have been examined and found to be close to tanteuxenite from Australia. The X-ray powder patterns are virtually the same, and the chemical analyses (including the relative abundances of the rare earths) are closely similar.

Zambonini's original (1908) specimens have not been re-examined, but are without reasonable doubt the same as the specimens now described; the considerable discrepancies between the old and new analyses can be explained by the difficulty of the separations. It is suggested that the name delorenzite be abandoned despite its priority because of its association with an incorrect analysis.

C. M. GRAMACCIOLI (1958) has described his rediscovery in 1957 of delorenzite at the type locality, Piano del Lavonchio, Craveggia, Val Vigezzo, Piemont. He submitted a specimen to the British Museum (Natural History) for exchange, and later kindly presented the fragments of a large crystal, which had broken on removal from the matrix; the present paper is based on this latter material (B.M. 1958,397).

Delorenzite was originally described by Zambonini (1908), and the new material agrees very well with his description except for the chemical composition and the specific gravity. A pyknometric determination on the new material gave 5-68, which is close to the published specific gravity (5.77) of tanteuxenite from Cooglegong, Western Australia, but differs considerably from Zambonini's value of about 4.7; this latter value was obtained by comparing the rates of fall of delorenzite fragments in a column of acetylene tetrabromide with those of similar fragments of xenotime, and the inaccuracy of the method could easily account for the difference.

As noted by Zambonini, delorenzite crystals are deeply striated in the prism zone; measurement of many fragments of the new material yields interfacial angles in agreement with the originally described values, but also shows that several vicinal forms are developed and hence that no DELORENZITE

reliance may be placed on any crystallographic distinction drawn between the present material and euxenite as was done by Zambonini for the type delorenzite. Delorenzite and tanteuxenite are both metamict, but X-ray powder photographs of heated specimens of the two are virtually the same—as may be expected from their similarity of com-

| | | | | 1. | 2. | 3. |
|--------------------------------|--------------------------------|-----|-----|-------|--------|--------|
| Na ₂ O | ••• | | | | * | tr. |
| MgO | | | | _ | 0.19 | |
| FeO | | | ••• | 4.25 | м | _ |
| MnO | | | | | m | .35 |
| CaO | | | | _ | 2.17 | 2.22 |
| PbO | | | | | tr. | tr. |
| Al_2O_3 | | | ••• | _ | m | nil |
| Fe ₂ O ₃ | | ••• | | | 1.8 | 1.18 |
| (Yt,Lr | ı) ₂ O ₃ | | | 14.63 | 24.35 | 24.70 |
| SiO ₂ | | | | | м | 0.90 |
| TiO ₂ | | | ••• | 66.03 | 16.2 | 14.17 |
| SnO_2 | | | | 4.33 | tr. | 0.14 |
| ThO ₂ | | ••• | | | * | tr. |
| UO_2 | | | ••• | 9.87 | | — |
| UO | | | | | | 3.35 |
| U ₃ O ₈ | | | ••• | | 7.75 | |
| Nb205 | | | | _ | 4.45 | 3.83 |
| Ta ₂ O ₅ | | | | _ | 36.4 | 47.31 |
| Ign | | | | · | n.d. | 2.40 |
| | | | | 99.11 | (92.3) | 100.55 |
| | | | | | (== •) | |

TABLE I. Analytical data for delorenzite and tanteuxenite.

1. Delorenzite, Piano del Lavonchio, Craveggia, Val Vigezzo, Piemont, Italy. Anal. Štěrba, in Zambonini, 1908. State of oxidation of U and Fe not known.

2. Delorenzite, locality as 1. Anal. Butler and Hall. Total iron as Fe_2O_3 determined by D. I. Bothwell. Optical spectrographic data indicate that Fe and Si exceed 1 %, Al exceeds 0.1 %, and Mn exceeds 0.01 %; Pb and Sn are below 0.01 %; *=not detected spectrographically. (B.M. 1958,397.)

3. Tanteuxenite, Eleys, 10 miles south of Cooglegong, Pilbara goldfields, W. Australia. Anal. Simpson, 1928. (B.M. 1928,341, type material.)

position. The type tanteuxenite consists of worn fragments with no measurable faces, and so its morphology cannot be compared with euxenite on the one hand or delorenzite on the other.

On the basis of the analysis of Štěrba (Zambonini, 1908) there is no doubt that delorenzite was rightly considered to be a new mineral (table I, col. 1); present-day correlation of that analysis reveals some *chemical* similarity between delorenzite and davidite in terms of Ti, Ln, and U contents, but the presence of Sn in delorenzite is a contrasting property. It is not clear what methods were used in the original analysis but it seems certain that chemical precipitates were not checked spectrographically for purity. Ti, Nb, and Ta occurring together presented many difficulties to analysts in the early part of the century, and it is suggested that Štěrba's TiO₂ value is one that should be correlated with the value of TiO₂+Nb₂O₅+Ta₂O₅ now found (table I, col. 2). If oxalate ion was originally used to keep the decomposed mineral in solution then part of the rare-earths will have been reckoned as TiO₂, and this may explain the discrepancy between the old and new values for the rareearths. Thus Štěrba's summation of TiO₂ and Ln₂O₃ approximates within 1 % to our value of TiO₂+Nb₂O₅+Ta₂O₅+Ln₂O₃. The figures for U are not too dissimilar; delorenzite was noted to be the only radioactive mineral at the type locality and it is suggested that the identity of the mineral now analysed is certainly delorenzite.

Analytical methods. About 600 mg. of the mineral was decomposed by prolonged attack with conc. HNO₃-40 % HF mixtures and the rare-earth oxides plus thoria separated via the fluorides and oxalates (Butler, 1957a); individual rare-earths were determined on these separated oxides using optical spectrographic methods (Butler, 1957b). $(Ta,Nb)_2O_5$ was determined in the filtrate from the Ln+Th fluoride precipitation by evaporating down to dryness twice with conc. HNO₃, taking up in NH_4F and water, and treating chromatographically (Mercer and Wells, 1954). Ti and W were confirmed as below 0.1 and 0.5 % respectively on the separated (Ta,Nb)₂O₅ by normal optical spectrographic methods; the spectrogram showed clearly enough the preponderance of Ta over Nb. Ta and Nb were determined on the separated (Ta,Nb)₂O₅ by the pyrogallol method (Hunt and Wells, 1954). Ti was determined by the peroxide method on a separate portion of the mineral (10 mg.). U was determined on 100 mg. mineral using the colorimetric ascorbic acid method. A radiometric assay by Mr. E. F. Bunt of the Geological Survey (Atomic Energy Division) gave $eU_3O_8 = 7.3$ %. Optical spectrography was used to determine elements in the mineral; conditions were as for the rare-earths determination except for the recording range $(3600-2700 \text{ \AA})$ and the spectrograph (Hilger no. 471; quartz prism). Sn and Pb were judged to be below 0.01 %, Mn and Al below 0.2 %, and Si above 1 %.

Relationship of delorenzite to tanteuxenite. Table I (cols. 2 and 3) shows the new analysis of delorenzite compared with that for the type tanteuxenite (Simpson, 1928). The total for the new analysis is below 100 in that Mn, Al, Si, and H_2O were not determined. It will be seen that total rare-earths, CaO, and TiO₂ are closely similar in both minerals; Nb values are reasonably similar and Ta values somewhat different. U differs by a factor of two and is lower in the type tanteuxenite. Despite the Ta and U differences the new analysis of delorenzite is difficult to reconcile with that of any mineral other than tanteuxenite. Additional evidence for the identity of delorenzite with tanteuxenite is the remarkable similarity of their rare-earth distribution patterns. The

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rare-earths may be nominally described as Yt-earths as Yt comfortably exceeds the sum of the lanthanons. The lanthanons, however, instead of being Dy-rich (on the basis of Yt and Dy having identical radii) are Nd-rich (fig. 1). It is quite abnormal for Nd to exceed other individual lanthanons in minerals containing essential rare-earths. Lyndochite (Butler, 1957c), and æschynite from an alkali syenite pegmatite (Semenov and Barinsky, 1958), show Nd peaks in their lanthanon distribution

TABLE II. Individual rare-earth concentrations in $(Yt,Ln)_2O_3$ separated chemically from the minerals. Eu₂O₃ below 0.1 %; no data for Ho₂O₃. σ , percentage standard deviations of individual rare-earths from duplicate spectrograms.

| | | 1. | 2. | σ. |
|---------------------------------|------|-------|-------|----------------|
| Yt ₂ O ₃ | | 44.5 | 56.8 | 5 |
| La ₂ O ₃ | | 0.83 | 0.51 | 8 |
| CeO ₂ | | 5.76 | 4.60 | 7 |
| Pr ₆ O ₁₁ | | 1.45 | 1.37 | 8 |
| Nd ₂ O ₃ | | 11.7 | 9.05 | 5 |
| Sm_2O_3 | | 6.30 | 6.10 | 5 |
| Gd ₂ O ₃ | | 9.70 | 6.30 | 6 1 |
| Tb407 | | 1.82 | 1.33 | 6 |
| Dy ₂ O ₃ | | 8.85 | 5.71 | 5 |
| Er ₂ O ₃ | | 4.68 | 2.34 | 13 |
| Tm_2O_3 | | 0.48 | 0.4 | 10 |
| Yb ₂ O ₃ | | 2.94 | 1.60 | 5 |
| Lu ₂ O ₃ | | 0.46 | 0.4 | 35 |
| Sum | | 99.47 | 96.51 | |

l. $(Yt,Ln)_2O_3$ from delorenzite. 2. $(Yt,Ln)_2O_3$ from tanteuxenite. Localities in table I.

pattern but the former has total lanthanons exceeding Yt in atomic ratio 2:1, and presumably the latter is also Yt-poor (otherwise it might have been described as priorite or æschynite-priorite). Similarly the Ce-poor rhabdophane from Salisbury, Connecticut, U.S.A. (Hildebrand *et al.*, 1957) has Nd the most abundant rare-earth with the atomic ratio Yt:Ln approximately 1:4. The only mineral showing Yt predominating in the rare-earths and Nd predominating in the lanthanons is yttrotungstite (Butler, 1957); Ce is almost as abundant as Nd. Other complete-assemblage type rare-earth minerals would be expected to have the possibility of containing high concentrations of Nd but with other Z-even lanthanons almost equally abundant; one gadolinite has been reported to contain $14 \% Nd_2O_3$ in total Ln_2O_3 (Semenov and Barinsky, 1958). The lanthanon distributions in delorenzite and tanteuxenite are to be regarded as uncommon; certainly the distribution pattern is distinct from those shown by members of the euxenite-polycrase series which are Nb- rather than Ta-rich (Butler, 1958).

Conclusions. It is clear from the foregoing paragraphs that the mineral now described as delorenzite agrees with the original descrip-



FIG. 1. Lanthanon distribution in delorenzite and tanteuxenite (Ho excluded).

tion, and that the discrepancies have a straightforward explanation. Moreover, no other radioactive mineral has been reported from Craveggia with which the old or the new delorenzite could be confused. The identity of delorenzite with tanteuxenite is certain, and Craveggia is thus the only known locality for tanteuxenite outside Western Australia. We recommend that the name delorenzite be abandoned in favour of tanteuxenite, despite its priority, both to make clear the close

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relationship to euxenite (of which it is a variety) and because of its association with an incorrect chemical analysis.

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References.

BUTLER (J. R.), 1957a. Geochimica Acta, vol. 12, p. 190.

----- 1957b. Spectrochimica Acta, vol. 9, p. 332.

----- 1957c. Amer. Min., vol. 42, p. 67.

----- 1958. Min. Mag., vol. 31, p. 763.

GRAMACCIOLI (C. M.), 1958. Natura (Milan), vol. 49, p. 110.

HILDEBRAND (F. A.), CARRON (M. K.), and ROSE (H. J., Jr.), 1957. Bull. Geol. Soc. Amer., vol. 68, p. 1744.

HUNT (E. C.) and WELLS (R. A.), 1954. Analyst, vol. 79, p. 345.

MERCER (R. A.) and WELLS (R. A.), 1954. Ibid., p. 339.

SEMENOV (E. I.) and BARINSKY (R. L.), 1958. Geochemistry, no. 4, p. 398.

SIMPSON (E. S.), 1928. Proc. Roy. Soc. Western Australia, vol. 14, p. 45.

ZAMBONINI (F.), 1908. Zeits. Kryst. Min., vol. 45, p. 76.