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EUXENITE FROM AMPANGABÉ, MADAGASCAR

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ABSTRACT

Wet-chemical and electron microprobe analyses, and X-ray diffraction analysis of material annealed in the temperature range 300°C and 1200°C (at 1100°C in air; *a* 5.567(3) *b* 14.460(7) *c* 5.199(3)Å) and differential thermal analysis (exotherm at 760°C) of an "ampangabéite" from Madagascar identify the specimen as euxenite. The composition of the euxenite is compared to orthorhombic AB_2O_6-type Nb-Ta-Ti oxides using the canonical plots of Ewing (1976). Specific gravity (4.92 to 5.32) and *n* (2.01 to 2.19) increase with heating.

SOMMAIRE

Un échantillon d' "ampangabéite" de Madagascar a été identifié comme euxenite par les moyens suivants: analyse chimique par voie humide et à la microsonde électronique, détermination de la maille par diffraction X sur matériau recuit dans le domaine de température 300-1200°C et ATD (exotherme à 760°C). A 1100°C, à l'air: *a* 5.567(3), *b* 14.460(7), *c* 5.199(3)Å. La composition de l'euxenite peut être comparée à celle des oxydes Nb-Ta-Ti du type AB_2O_6 orthorhombique, au moyen des courbes canoniques de Ewing (1976). La densité (4.92-5.32) et l'indice de réfraction (2.01-2.19) croissent avec la température.

(Traduit par la Rédaction)

INTRODUCTION

The complex, metamict Nb-Ta-Ti oxides of the type formula AB_2O_6 (where $A=RE$, Fe^{2+}, Mn, Ca, Th, U, Pb; $B=$Nb, Ta, Ti, Fe^{3+}, W) include three structure types: (1) orthorhombic euxenite structure, (2) orthorhombic aeschynite structure, and (3) the monoclinic (pseudo-orthorhombic) samarskite structure. Structural and chemical relations between euxenite and aeschynite have been summarized by Ewing & Ehlmann (1975) and Ewing (1976). Samarskite, which always occurs in the metamict state, shares many compositional similarities with euxenite, but exhibits a characteristic diffraction pattern on heating (Lima de Faria 1964; Komkov 1965; Nilssen 1970; Mitchell 1970). Relation of the samarskite structure to those of euxenite and aeschynite is poorly defined, and it is particularly important to determine whether metamict samarskites will recrystallize to either euxenite or aeschynite during annealing experiments. This study is a detailed examination of a specimen labelled "Samarskite Variety Ampangabéite" from Ampangabé, Madagascar (Malagasy Republic). The specimen was obtained from Minerals Unlimited in 1967 by K. G. Snetsinger.

COMPOSITION

The mineral was quantitatively analyzed wet-chemically and with an ARL-EMX electron microprobe; qualitative data were obtained with an ARL-IMMA ion microprobe. Results are listed in Table 1 together with details of the analytical method. The electron microprobe analysis showed the material to be remarkably homogeneous.

In comparing the present data with previous analyses of Nb-Ta-Ti oxides, it is important to note that a number of chemical formulae for samarskite have been proposed (Table 2). This situation is complicated by the fact that samarskite may be difficult to distinguish from euxenite compositions which have the general formula AB_2O_6. Variations in *A*-site and *B*-site cations may be considerable due to the great number of components and the possibility of cation deficiencies caused by primary or secondary alteration (Van Wambeke 1970; Ewing 1975).

On the basis of the ratio of *A*-site cations to *B*-site cations the "ampangabéite" could either be samarskite or euxenite. Assuming a euxenite-type structure, the question of the nomenclature of the orthorhombic AB_2O_6-type Nb-Ta-Ti oxides becomes important. Using the numerical methods of Ewing (1976) the present specimen would be compositionally classified as "euxenite" on the basis of Nb_2O_5 and TiO_2 content (Table 3). The exact position of the "ampangabéite" may be shown on a canonical plot (Fig. 1) where the classification variables are TiO_2, Nb_2O_5

and ΣCe_2O_3. The positions of aeschynite (A), "euxenite" (e) and "polycrase" (t) from the literature are also shown. A detailed explanation of the meaning and interpretation of this particular canonical plot is given in Ewing (1976). On the basis of the three classification variables, the "ampangabéite" composition is certainly compatible with euxenite compositions. It should be emphasized that the canonical plots of Ewing (1976) were made only for orthorhombic AB_2O_6-type Nb-Ta-Ti oxides. Using the triangular plot of Nilssen (1970) for samarskite compositions the "ampangabéite" compares well with the compositions of 18 samarskites.

Both previous plots address the question of

TABLE 1. ANALYSIS OF "AMPANGABÉITE" FROM AMPANGABÉ, MALAGASY REPUBLIC[1]

Oxide	wt.%	wt.% Without $H_2O^{+,-}$	Atoms[2] on Basis 6 $O^{=}$	
CaO	1.65	1.71	0.108	
MnO	0.18	0.19	0.011	
FeO	0.14	0.15	0.007	
Fe_2O_3	1.08	1.12	0.049	
MgO	0.01	0.01	0.004	
SnO_2	0.11	0.11	0.004	
PbO	0.37	0.38	0.007	
UO_2	7.97	8.24	0.108	
UO_3	0.08	0.08	0.004	
ThO_2	4.67	4.83	0.063	1.005
Y_2O_3	13.4[3]	13.9	0.43	
Gd_2O_3	2.1	2.2	0.04	
Dy_2O_3	1.7	1.8	0.04	
Er_2O_3	1.2	1.2	0.02	
Yb_2O_3	1.6	1.7	0.03	
Ce_2O_3	0.7	0.7	0.01	
Nd_2O_3	1.4	1.5	0.04	
Sm_2O_3	1.4	1.5	0.03	
Nb_2O_5	28.74	29.71	0.782	
Ta_2O_5	2.48	2.56	0.042	2.004
TiO_2	26.06	26.94	1.176	
WO_3	0.08	0.08	0.004	
Al_2O_3	0.16	0.17	0.014	
SiO_2	0.28	0.29	0.018	
H_2O^-	0.40	--	--	
H_2O^+	2.89	--	--	
Total	100.85	100.09[4]		

[1] Oxides reported to one decimal place (RE and Y) are electron probe determinations. Others are wet-chemical ones obtained by the Japan Analytical Chemistry Research Institute, Tokyo; values for Nb_2O_5, UO_2, ThO_2, TiO_2 and Ta_2O_5 were verified by electron probe analysis using an analyzed euxenite of similar composition from Eitland, Norway (Hongslo & Langmyhr 1960). Zr was found by wet chemistry or ion probe; traces of F and Cu were detected with the ion probe.

[2] Calculated from the water-free analysis.

[3] Y_2O_3 plus the rare-earth oxides, determined wet chemically as a group total 22.72 wt.%; the sum of these oxides, determined individually by the electron probe, is 23.5 wt.%. Qualitative ion probe data show that, as well as the RE listed in the analysis, all other RE are present in traces (less than ca. 0.05 wt.%) except for Eu, which, if present, is at a scant trace level. For Ce_2O_3, Sm_2O_3, Er_2O_3 and Yb_2O_3, RE glass standards (Drake & Weill 1972) were used. values for these oxides are corrected for all matrix effects. The other RE oxides, and yttrium, were done with the analyzed euxenite standard (Hongslo & Langmyhr 1960), and no matrix corrections have been applied.

[4] Owing to rounding-off effects, particularly in the RE group, summation after recalculation to eliminate water is higher than 100.85.

TABLE 2. PROPOSED CHEMICAL FORMULAE FOR SAMARSKITE AFTER NILSSEN (1970)

AB_2O_6	Palache et al. (1944)
$(RE,U,Fe^{+2},Ca)(Nb,Ta,Fe^{+3})_2O_6$	Gorzhevskaya (1964)
$(Fe,RE,U)_2(Nb,Ta,Ti)_2O_7$	Vlasov (1966)
$AB_{2+x}(O,OH_2)_{6+2.5x}nH_2O$ (altered samarskite)	Van Wambeke (1960)
ABO_4	Komkov (1965)

TABLE 3. COMPARISON OF "AMPANGABÉITE" TO THE MEAN VALUES OF CLASSIFICATION VARIABLES AFTER THE METHOD OF EWING (1976)

Classification	"ampangabeite"	"euxenite"	"polycrase"	(Nilssen 1970)*	(Lima-de-Faria 1964)†
TiO_2	26.06	22.28 ±3.06	32.47 ±4.01	2.02	2.55
Nb_2O_5	28.74	26.91 ±5.22	18.71 ±5.04	44.11	28
ΣCe_2O_3		2.13 ±1.28	2.47 ±1.17		

*mean values of four Norwegian samarskites.

†mean values of four Madagascar samarskites.

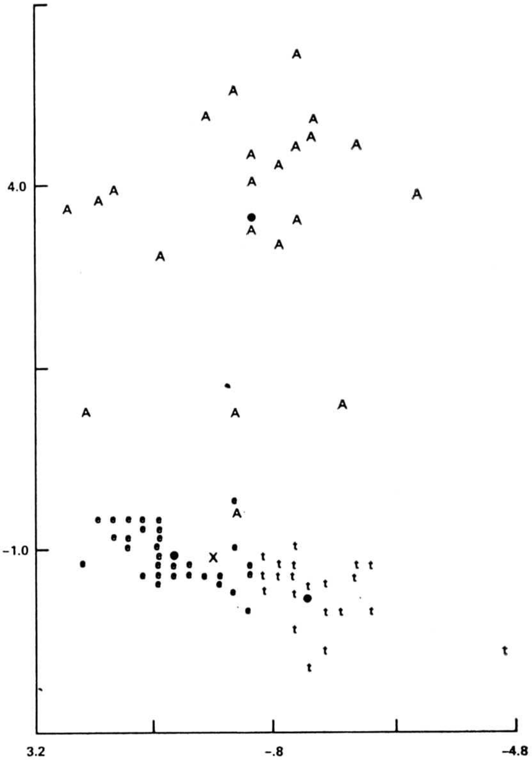

FIG. 1. Plot of the first (ordinate) and second (abscissa) canonical variables for the groups "euxenite" (e), "polycrase" (t) and aeschynite (A) using TiO_2, Nb_2O_5 and ΣCe_2O_3 as classification variables after the method of Ewing (1976). The position of "ampangabéite" is indicatede by an X.

the molecular ratio of *A*-site and *B*-site cations after the analysis has been normalized to O=6. Thus, it is not surprising that "ampangabéite" may be accommodated in either classification scheme. A detailed oxide comparison of the "ampangabéite" to euxenite and samarskite compositions suggests significant descrepancies. The TiO_2 content of the "ampangabéite" is approximately ten times as great as values cited by Nilssen (1970) for Norwegian samarskites and by Lima-de-Faria (1964) for ampangabéite from Madagascar (Table 3). The Nb_2O_5 content of the "ampangabéite" is lower than one would expect of typical samarskites (Nilssen 1970), but comparable to the mean values for samarskites from Madagascar analyzed by Lima-de-Faria (1964).

Further details of the oxide compositions are less definitive. The markedly yttrium-earth-rich *RE* distribution of the "ampangabéite" is comparable to distributions found in samarskites (Nilssen 1970) and euxenites (Ewing 1975). Values for other *B*-site cations fall well within the ranges of variation for both samarskite and euxenite.

TABLE 4. X-RAY DATA FOR HEATED METAMICT "AMPANGABÉITE"[1]

hkl[2]	*d*(calc.)[3]	*d*(obs.)[4]	*hkl*[2]	*d*(calc.)[3]	*d*(obs.)[4]
110(f)	5.20	5.22	042(r)	2.12	2.11
040(f)	3.66	3.67	142	1.981	1.980
121(f)	3.37	3.37	071	1.940	1.940
131(f)	3.00	3.00	202	1.900	1.900
050(r)	2.93	2.96	080(r)	1.830	1.830
200(f)	2.78	2.78	320	1.799	1.800
141(f,r)	2.64	2.62	232	1.771	1.771
002(f)	2.60	2.60	330(r)	1.735	1.734
012(f)	2.56	2.56	081	1.726	1.725
022(r)	2.45	2.45	023(r)	1.686	1.690
211(r)	2.42	2.43	113(r)	1.644	1.640
151(r)	2.32	2.31	090(r)	1.627	1.622
061	2.21	2.21	123(r)	1.614	1.610
231	2.19	2.19	350(r)	1.568	1.570

[1] Heated at 1100°C for 24 hours in air.

[2] The (f) indicates indices that were assigned from data in the literature and held fixed during computer refinement; (f,r) indicates a fixed index that was rejected by the computer and not used in the final cycle of cell refinement. Unqualified indices are ones selected by the computer and used in the final cycle of refinement; (r) indicates indices assigned by computer, but not used in the final cycle of cell refinement.

[3] Calculated from the computer-refined unit-cell dimensions *a* 5.567±0.003, *b* 14.640±0.007, *c* 5.199±0.003Å; cell volume is 423.8±0.3Å^3. The computer program of Evans *et al.* (1963) was used for the calculations.

[4] Silicon-standardized diffractometer data, using Ni-filtered Cu radiation.

TABLE 5. VARIATION OF SPECIFIC GRAVITY AND INDEX OF REFRACTION WITH TEMPERATURE

	Prior to heating	500°C	1200°C
specific gravity	4.92±.02	5.29	5.32
refractive index*	2.01±.01	2.14	2.19

*Each value is the mean of five determinations after the method of Merwin & Larsen (1912).

ANNEALING AND DTA STUDY

The mineral was heated over the range of 300°C to 1200°C after the method of Ewing (1975). At each 50°C interval, the sample was air-quenched and examined by Debye-Scherrer X-ray powder camera (114.6 mm; Cu/Ni radiation).

Prior to heating no X-ray diffraction pattern was obtained, indicating that the specimen was completely metamict. Recrystallization was initiated at 450°C. Phases identified during the recrystallization sequence included: (1) an isometric pyrochlore-type phase with $a_o \cong 10$Å, (2) monoclinic $YNbO_4$ (3) monoclinic $FeNbO_4$ (?) (4) Nb_2TiO_7 and (5) $YNbTiO_6$–euxenite structure.

X-ray data for the 1100°C interval are summarized in Table 4. The indexed pattern compares well to the indexed pattern of Mitchell (1972) for heated euxenite and the refined unit-cell parameters are comparable to those determined by Ewing (1975) for euxenites crystallized at 900°C. Despite the apparent X-ray identification of the "ampangabéite" as euxenite, caution is advised. Correct indexing of the pattern requires the identification and elimination of diffraction maxima which are associated with decomposition phases. In this study, it was particularly difficult to identify and exclude all of the lines associated with the monoclinic $YNbO_4$ and the isometric pyrochlore phases. It should be noted that the same data set may be refined successfully in the monoclinic system but neither the indexing nor refined unit-cell parameters are comparable to the monoclinic cell of samarskite defined by Komkov (1965). Note that the appearance of orthorhombic euxenite as a phase during recrystallization does not indicate that the pre-metamict phase was euxenite. Indeed, examination of a large subhedral fragment of this specimen suggests a monoclinic symmetry.

The variations in specific gravity and index of refraction before heating and at 500°C and 1200°C are tabulated in Table 5. The dramatic increase in specific gravity and index of refraction at 500°C is due largely to the loss of water. The less dramatic increase in specific gravity and index of refraction between 500°C and 1200°C is due to continued crystallization of Nb-oxide phases rather than loss of water.

The DTA curve (Fig. 2) displays a major exo-

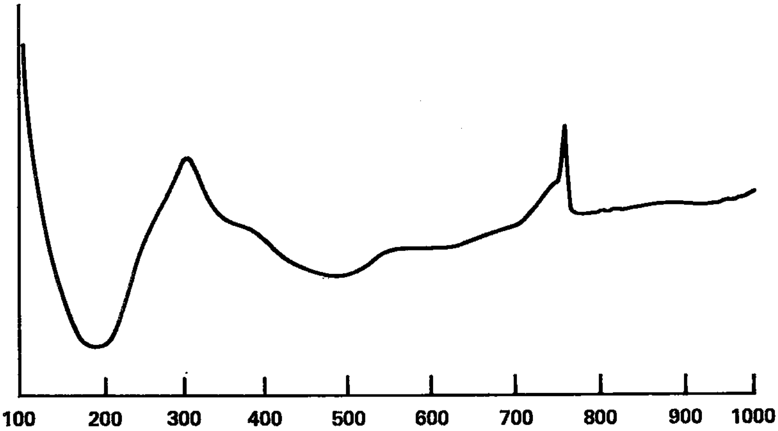

FIG. 2. DTA curve for "ampangabéite". Temperature is given in °C. Air ignition with a heating rate of 25°C/min.

therm at 760°C which represents the recrystallization of the euxenite phase. The large endotherm below 300°C is a common feature of metamict minerals and is the result of dehydration. The DTA curves of both euxenites and samarskites display similar features (Nilssen 1970; Ewing 1975).

CONCLUSIONS

The composition, X-ray diffraction data, DTA and physical properties identify this specimen of "ampangabéite" as euxenite. The very high values of TiO_2 as compared to other ampangabéites from Madagascar suggests that the specimen may have been incorrectly labeled or located. The possibility that the pre-metamict phase was a Ti-rich samarskite has not been eliminated, and thus clearly points to need for a determination of the phase relations between the monoclinic samarskite structure and the orthorhombic euxenite stucture. Knowledge of the effect of Nb/Ti ratio on the stability ranges of euxenite and samarskite would be of particular interest.

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