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 “ampangabeite” 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.

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 & Ehmann (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 Ampangabe, 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$_2$O$_5$ 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$_2$O$_5$.
TABLE 1. ANALYSIS OF "AMPANGABÉITE" FROM AMPANGABÉ, MALAGASY

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt.%</th>
<th>wt.% Without H₂O 4-</th>
<th>Atoms² on Basis 6 O³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>1.65</td>
<td>1.71</td>
<td>0.108</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>0.19</td>
<td>0.011</td>
</tr>
<tr>
<td>FeO</td>
<td>0.14</td>
<td>0.15</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.08</td>
<td>1.12</td>
<td>0.049</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.004</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.11</td>
<td>0.11</td>
<td>0.004</td>
</tr>
<tr>
<td>PbO</td>
<td>0.37</td>
<td>0.38</td>
<td>0.008</td>
</tr>
<tr>
<td>UO₂</td>
<td>7.97</td>
<td>8.24</td>
<td>0.108</td>
</tr>
<tr>
<td>UO₃</td>
<td>0.08</td>
<td>0.08</td>
<td>0.004</td>
</tr>
<tr>
<td>ThO₂</td>
<td>6.67</td>
<td>6.83</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Notes:
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 Nb₂O₅, UO₂, ThO₂, TiO₂ and Ta₂O₅ 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. Y₂O₃ plus the rare-earth oxides, determined wet chemically as a group total 22.22 wt.%; the sum of these oxides, determined individually by the electron probe, is 23.57 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 CeO₂, SmO₂, ErO₂ and YbO₃, 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. Onion to rounding-off effects, particularly in the RE group, summation after recalulation to eliminate water is higher than 100.85.

and ΣCe₂O₅. The positions of aëschynite (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 ABO₄ 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

FIG. 1. Plot of the first (ordinate) and second (abscissa) canonical variables for the groups "euxenite" (e), "polycrase" (t) and aëschynite (A) using TiO₂, Nb₂O₅ and ΣCe₂O₅ as classification variables after the method of Ewing (1976). The position of "ampangabéite" is indicated 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 discrepancies. The TiO₂ 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 Nb₂O₅ 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. The less dramatic increase in specific gravity and index of refraction before heating and at 500°C is due largely to the loss of water. 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-

### TABLE 5. VARIATION OF SPECIFIC GRAVITY AND INDEX OF REFRACTIVE TEMPERATURE

<table>
<thead>
<tr>
<th>Prior to heating</th>
<th>500°C</th>
<th>1200°C</th>
</tr>
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<tbody>
<tr>
<td>specific gravity</td>
<td>4.92±.02</td>
<td>5.29</td>
</tr>
<tr>
<td>refractive index*</td>
<td>2.01±.01</td>
<td>2.14</td>
</tr>
</tbody>
</table>

*Each value is the mean of five determinations after the method of Merwin & Larsen (1912).
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 TiO₂ 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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REFERENCES


Mitchell, R. S. (1972): Virginia metamict minerals:


VLASOV, K. A. editor (1966): Geochemistry and Mineralogy of Rare Elements and Genetic Types of Their Deposits. II, Mineralogy of Rare Elements. Israel Program Sci. Transl., Jerusalem.

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