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NATURAL GAMMA-RAY SPECTRA OF EUXENITE, POLYCRASE AND AESCHYNITE

RODNEY C. EWING and JAMES L. KRUMHANSL
Department of Geology, Stanford University, Stanford, California 94305

INTRODUCTION

Prior to the work of Charlet (1968), the natural gamma-ray spectra of metamict minerals had not been recorded or studied. Charlet suggested that the low-energy gamma-ray spectra (20 - 610 kev) would be a quick, non-destructive, method of identification of small amounts of radioactive minerals (*e.g.* stream concentrates) and accordingly recorded the spectra of metamict betafite, euxenite and ampangabeite. The differences in the energy spectra of U^{238} and Th^{232} as well as the differential absorption by the mineral's matrix would be characteristic of particular minerals. Variations in the uranium content between samples could be corrected by dividing the intensities of strongly absorbed low-energy peaks (47 and 74 kev) by the much less absorbed intensity of the 352 kev peak. The lower energy peak intensities are affected by matrix absorption, but the intensity of the 352 kev intensity is a function of uranium concentration. Plots of the normalized 47 and 74 kev intensities against one another result in clustering of samples with similar compositions. Charlet (1968) suggested that such methods would be useful in discriminating between end members of the isomorphous euxenite (Nb>Ta; Nb+Ta>Ti) and polycrase (Ti>Nb+Ta) solid solution series. The purpose of this study is to test Charlet's thesis and determine the limiting factors of the technique.

Calculation of gamma-ray absorption for theoretical compositions

In dealing with the orthorhombic rare earth AB_2O_6-type Nb-Ta-Ti oxides (A = *RE*, Ca, U, Th, Fe^{2+}, Mn; B = Nb, Ta, Ti, Fe^{3+}), the immediate question is whether the variations in the matrix absorption for low energy gamma-rays (47 and 74 kev) can be related to unique compositions of A- and B-site cations. Charlet's suggestion that end members of the euxenite - polycrase series can be separated on the basis of matrix absorption assumes a minimal contribution of A-site cations to variation in matrix absorption; and thus, matrix absorption is a function of the Nb + Ta : Ti ratio. The following calculations consider the relative effects of A- and B-site cations on the matrix absorption of low energy gamma-rays.

Using 91 analyses from the literature for euxenite (=priorite), polycrase (=blomstrandine) and aeschynite, means and standard deviations were calculated for principal chemical components and from these data, seven idealized but plausible compositions were constructed (Table 1). Three represent typical compositions for euxenite, polycrase and aeschynite. Four represent compositions of the lowest-absorbing and highest-absorbing matrix compositions for euxenite and polycrase. The compositions are calculated so that one may compare the absorptions of a matrix in which A-site cations are identical but B-site cations vary (*e.g.* euxenite and polycrase). Similarly, A-site cations for a low-absorbing matrix of euxenite and polycrase are identical, as is their high-absorbing matrix. Such a scheme of compositions gives the lowest and highest absorption characteristics of euxenite and polycrase and allows the determination of whether there is any significant overlap of the absorption characteristics. For each composition the ratio of the transmitted

TABLE 1. THEORETICAL COMPOSITIONS OF EUXENITE, POLYCRASE AND AESCHYNITE USED IN CALCULATION OF I/I_0 IN FIGURE 1

	EUXENITE			POLYCRASE			AESCHYNITE
	low	av.	high	low	av.	high	
TiO_2	25	22	19	36	33	30	22
Nb_2O_5	25	27	29	17	19	21	27
Ta_2O_5	4	5	6	1	2	3	5
B-site total	54	54	54	54	54	54	54
Y_2O_3	22	20	18	22	20	18	5
Ce_2O_3	6	5	6	6	5	6	20
CaO	3	2	1	3	2	1	2
U_3O_8	4	10	8	4	10	8	3
ThO_2	4	3	8	4	3	8	10
H_2O	7	6	5	7	6	5	6
A-site total+H_2O	46	46	46	46	46	46	46

Compositions are in wt %. For euxenite and polycrase the low, average and high-absorbing compositions are listed.

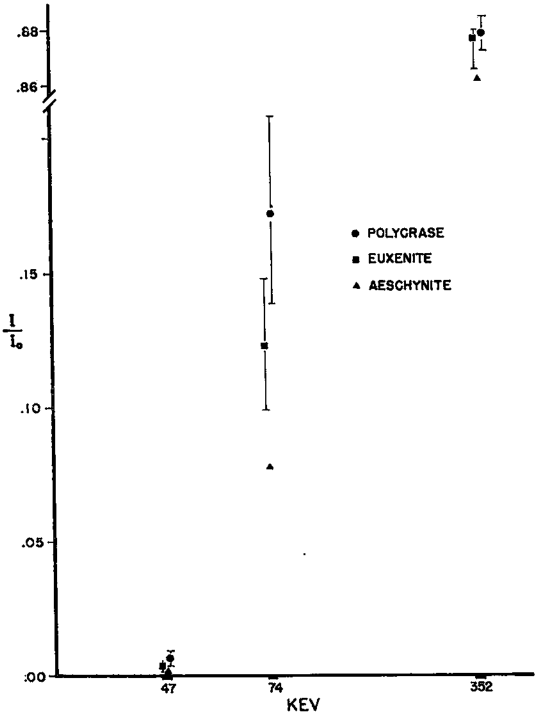

Fig. 1. Matrix absorption as a function of gamma-ray energy (kev) for the compositions listed in Table 1. Error bars for euxenite and polycrase compositions give the I/I_o range for low- and high-absorbing compositions.

intensity (I) to the original intensity (I_o) for 47, 74 and 352 kev gamma-ray energy after passing through a one gram sample spread uniformly over one square cm was calculated from the following expression:

$I/I_o = exp \sum_i (u/p)_i m_i$ where $(u/p)_i$ = mass absorption coefficient (Storm & Israel 1967), and m_i = weight % element. The results of these calculations are shown in Figure 1. The range bars for euxenite and polycrase at each energy represent the values for the high- and low-absorbing compositions and as shown there is a considerable overlap at the 47 and 74 kev energies. This overlap is due in part to A-site cation variation and natural samples could easily fall in this range. In the cases where there is no difference between the A-site cations, euxenite and polycrase can be distinguished at low gamma-ray energies. As gamma-ray energy increases (352 kev), absorption decreases by several orders of magnitude. The aeschynite composition (Ce-rich) has the highest absorption of all compositions and at low energies its absorption characteristics are clearly out of the range of euxenite and polycrase.

Natural gamma-ray spectra of euxenite, polycrase and aeschynite

Natural gamma-ray spectra were recorded for specimens of euxenite (10), polycrase (12) and aeschynite (1) using a 400 channel analyzer with a 3″ × 4″ NaI scintillation crystal and one gm samples. The normalized intensities of the 47 and 74 kev energies are plotted in Figure 2. As one would expect from the calculated intensities, there is an overlap of the euxenite and polycrase fields. Furthermore, one specimen of polycrase is clearly in the euxenite field. The average composition of the three least-absorbing and three most-absorbing natural compositions were determined by microprobe analysis and the average weight percentages are summarized below:

	least-absorbing compositions	most-absorbing compositions
Nb_2O_5	15.9	21.0
Ta_2O_5	2.6	4.6
TiO_2	34.3	27.4
U_3O_8	3.9	10.8
ThO_2	7.8	4.1

The samples with the highest absorption characteristics have the greater average concentration of Nb, Ta and U, whereas the samples with the lowest absorption characteristics have the greater average concentration of Ti and Th.

The single aeschynite composition clearly plots away from the euxenite and polycrase fields, but its position is directly opposite to what one would expect from the absorption values calculated from the theoretical compositions; that is, aeschynite should have a more absorbing matrix than either euxenite or polycrase. Also, for this particular aeschynite, $Ce_2O_3 > Y_2O_3$ and $Nb_2O_5 > TiO_2$, so that its matrix absorption should be at least as great as that of the theoretical composition. The explanation of this effect lies in the fact that in aeschynite $ThO_2 \gg U_3O_8$, so that all the gamma-ray radiation originates from the decay of Th^{232}. Although decay of U^{238} results in gamma-ray peaks at 47, 74 and 352 kev, the decay of Th^{232} results in peaks at 47, 74 and 240 kev. The data in Figure 2 have been normalized by the 352 kev peak, but in the case of aeschynite with the Th^{232} decay scheme, there is no peak at 352 kev and the normalization factor used is simply background. This effect will complicate any spectrum that is a combination of U^{238} and Th^{232}, as both decay schemes will contribute to the intensity of the 47 and 74 kev peaks whereas the 352 kev normalization will only correct for the variation in U^{238} content and not Th^{232}.

Summary

Gamma-ray spectra are only a qualitative tool in the identification of Nb-Ta-Ti oxides.

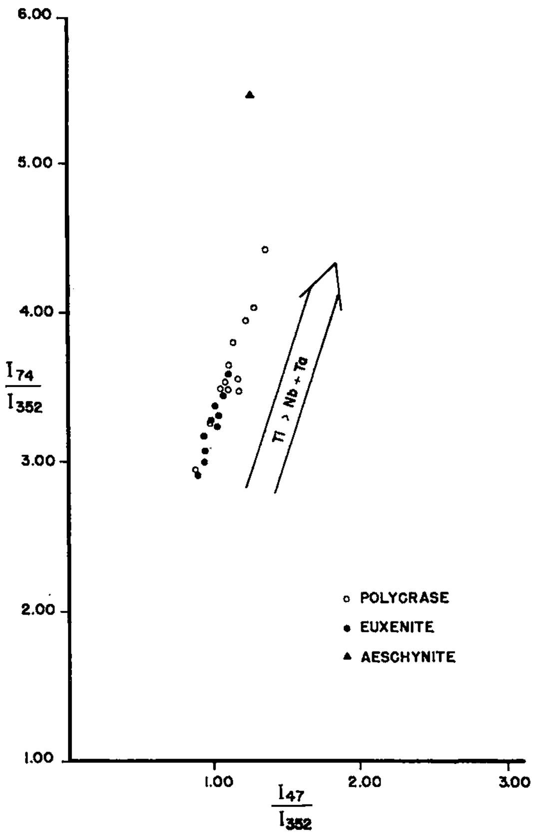

FIG. 2. Normalized (to 352 kev) intensities for 74 and 47 kev peaks plotted against one another. Arrow indicates a decrease in absorption as titanium content increases.

For extreme compositions (*e.g.* Nb + Ta≫Ti), polycrase and euxenite may be distinguished from one another, but for less extreme compositions, *A*-site cationic variations may make this difficult or impossible. In such cases, it is not possible to relate the absorption data to unique compositions and the results are always subject to a certain degree of ambiguity. In stream concentrates, where one might expect to find other complex Nb-Ta-Ti oxides besides euxenite and polycrase, the problem of interpretation becomes even more difficult. Considering the ambiguities that may still remain with complete chemical analysis, the absorption spectra can never be expected to yield more than very limited and qualitative identification data.

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