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An indication of universal linear variation of K_2O percentage with beta dose rates in ceramics : preliminary results

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Introduction

In geology it has been repeatedly documented that there is an almost universal tendency for an increase in the concentration of uranium and thorium in proportion to the concentration of later members - potassium, for example - in any "igneous differentiation series" (the migration and concentration of elements during metamorphism so as to produce an inhomogeneous rock from an originally homogeneous one). (Peterman, 1963; Hamilton, 1959; Gottfried, 1959; and Heier and Rogers, 1978, in Handbook of Geochemistry, Vol. II, 5 (1978), ed. K. H. Wedepohl.) Accordingly it was thought interesting to look for such a relationship in archaeological clay artifacts.

When thorium ppm values are plotted against those of their counterpart potassium, the above-mentioned tendency is illustrated (see Fig. 1a). These data were derived from geological materials, from Skaergaard intrusion Greenland, Dillsburg sill, Pennsylvania and Duluth Complex, Minnesota (Peterman, 1963), and from archaeolgical materials from Greece (Liritzis, 1979).

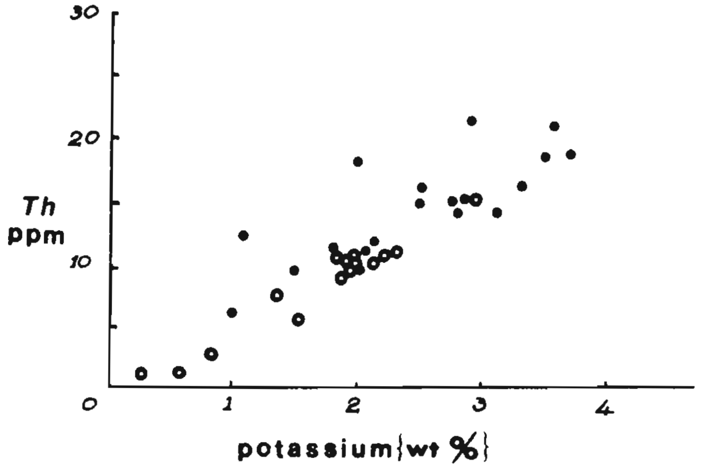

Figure 1a: Thorium (ppm) vs K for geological materials; opens circles (after Peterman, 1963) and from present studies (black dots).

As a result of this observation, it was thought of interest to extend such a study to learn if the K_2O percentages from the samples, plotted against their beta dose-rates (derived from their respective uranium, thorium, and K_2O values), are in proportion. It was considered worthwhile to plot the potassium content of each pottery and well-fired clay sample used in a TL-dating project (from materials throughout Greece), against its respective beta dose-rate values (mrads/yr) (Liritzis, 1979; Liritzis and Galloway, 1980; Liritzis, 1981). The beta dose-rates were measured by both the alpha-counting and potassium determination (α + K) as well as the TLD methods. But before discussing these plottings, some geochemical aspects of the distribution/correlation of uranium, thorium, and potassium in nature will follow.

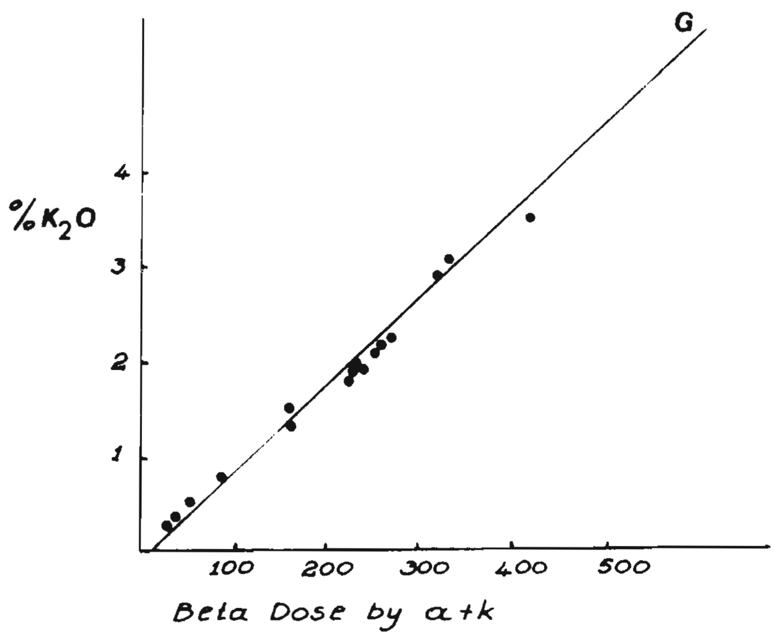

Figure 1b: β *dose-rate and* K_2O *for geological materials.*

Uranium, Thorium and Potassium Distribution/Correlation in Nature

Few studies directly examine the behaviour of thorium, uranium, and potassium during weathering and alteration. It is, however, known that the tendency of uranium to be oxidized to the comparatively soluble uranyl ion (UO_2^{++}) permits uranium to be mobilized easily in surficial processes. This oxidation is primarily responsible for the wide variations in Th/U ratios shown in surficial material - e.g. clays, sands, soils. The comparatively insoluable thorium is concentrated in resistate minerals or is adsborbed on clays, whereas uranium is redistributed in surface and ground waters.

The almost universal tendency for the concentration of uranium to increase toward the later members of an igneous differentiation series has been documented mainly from plots of uranium content against some type of differentiation index such as the potassium content. The consistent trends are shown by most extrusive series than by instrusive rocks (plutonic, i.e., deeply buried igneous structures).

Similar observations have been made for the K/Th ratio, which has been found to have a nearly constant value in a large variety of igneious rocks, sediments, and surficial materials. Although the precise location of uranium and thorium in rock-forming minerals - e.g. allanite, monazite, feldspars, epidote and zircon is yet uncertain, for geochemical reasons these three radio-elements are highly correlated in these rock-forming minerals. The weathering that follows diagenesis, transportation, mobilization/differentiation of radioisotopes and sedimentation presumably controls the abundance of these radioactive elements, and one may expect a correlation of their distribution/concentration with climatological variations.

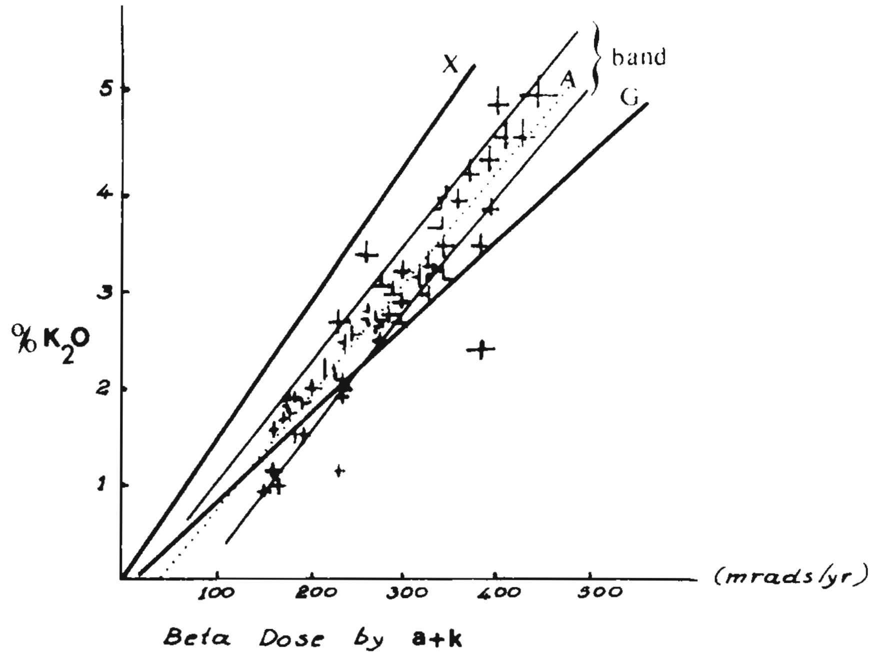

Figure 2: Plotting β-dose rate (α + K) vs K_2O.

Discussion

Fig. 2 plots the K_2O percentages against the beta dose-rates - derived by (α + K) - and exhibits a linear distribution, as most of the points with their standard errors lie along curve A (drawn from the least square method). There appears to be a higher scatter in the case of the beta dose-rates measured by TLD - that is, curve T, Fig. 3. For curves A and T, however, a quadratic fit is better than a linear - that is, the chi-square is lower. Nevertheless an exponential initial rise with subsequent linear response is more realistic in view of the shape of the curve, due mainly to the lack of points of low K_2O percentages. Scattered points might imply systematic errors due to some prior assumptions regarding the method (Liritzis and Galloway, 1981).

If there were no thorium and uranium present in a sherd, the X-curve - that is, the beta dose derived from ^{40}K against K_2O% - of Figs. 2 and 3 would indicate the lower linear boundary of the expected uniform distribution. With the presence of thorium and uranium, the corresponding distribution would incline toward higher beta dose values. There is no reason to suppose that typical clay minerals have depleted thorium and uranium and NAA has shown the opposite for clays, worldwide. Thus there should be no scattering of points to the left - that is, the lower part of the distribution curves - but only toward the right, or upper, parts. For excessive thorium and uranium, the points, then, would be expected to lie even further from the line of the "band" - that is, the curves A and T plus their associated error bars.

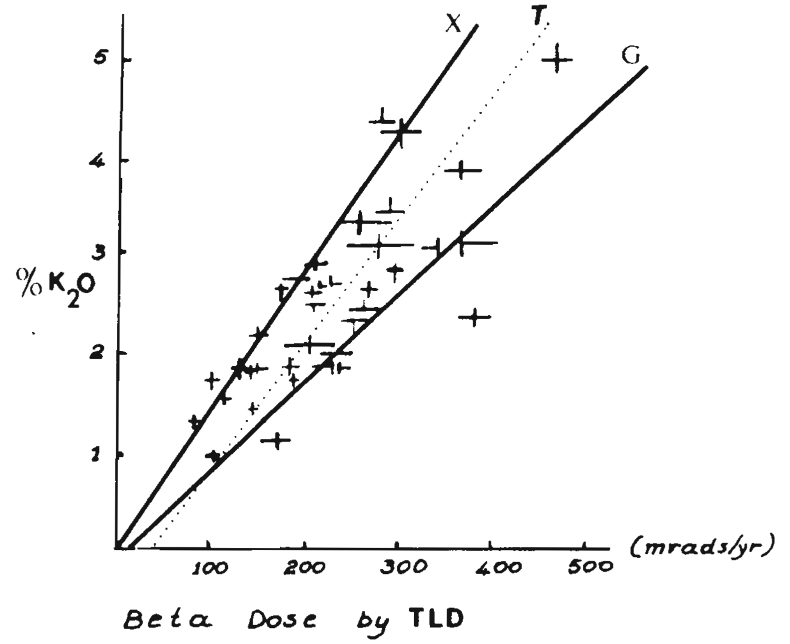

Figure 3: *Plotting of β-dose rate (TLD) vs K_2O.*

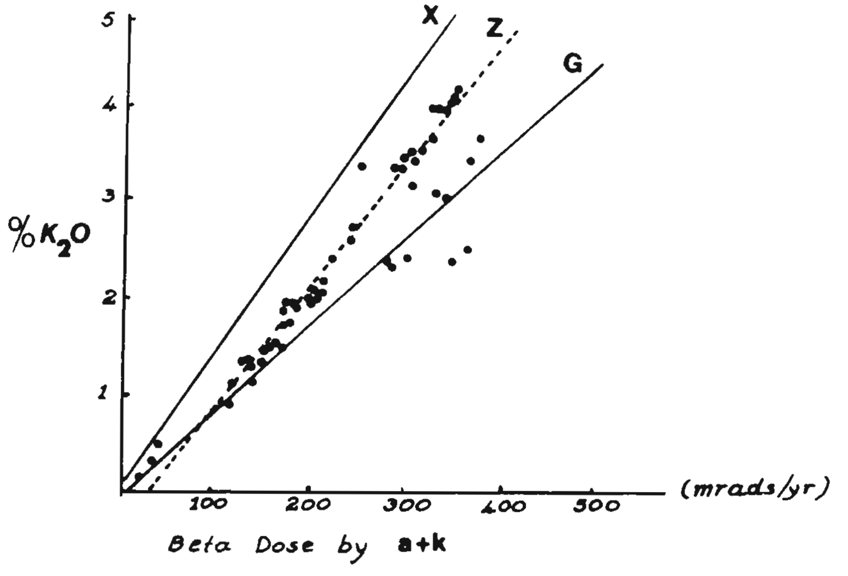

Figure 4 *Plotting of β-dose rate (α + K) vs K_2O. Data taken from Zimmerman, Ph.D. thesis (1970).*

In all of the above the line G is the best fit to the geological data of Fig. 1B.

Generally, the thorium and uranium correlate with the potassium in such a way that the result would be a curve with a slightly reduced slope compared to the X-curve, as the geological data (Fig. 1b) do not support a dose-rate from thorium and uranium which could be expressed as a curve parallel to X.

The above linear distributions were further substantiated by plotting the potassium contents of sixty-two sherds against their respective total beta doses (derived by α + K), the data being taken from Zimmerman (1970). His ceramics came from England, France, and Greece. For this the linear curve Z was obtained (Fig. 4). The geological curve (Fig. 1b) has a slightly lower slope that curves A, T, and Z, explainable as:

1. a result of the small number of geological samples analysed; or

2. because the geological analyses relate to variations of U, Th and K concentrations in three gabbro-granophyre sequences, which could obey different mechanisms than those in clays.

Overall, a linear distribution of K_2O percentage against beta dose-rates, with "narrow bands", could be considered as an indicator of their relationship, which can be used as a reference curve, in the sense that fairly satisfactory beta dose-rate values can be readily assessed by knowing only the potassium content of the sample. The novelty of this observation is that it can aid preliminary TL-dating by giving an approximation of the beta dose-values, thereby reducing the number of needed experimental measurements. (Note an unusually high beta value in Figs. 2 & 3.)

From the present preliminary results, besides the level of significance attached to each data point, the likely error resulting from use of the relationships of Table 1 can be evaluated. Thus for a value b of the true beta dose, the predicted one (at the 68% level of confidence) is given with a $\pm$ 4-5% error based on the error of the dose co-efficient of the relationships in Table 1. Drawing arbitrarily "narrow" bands around the A, T and Z curves that include most ($\geq$ 95%) of the experimental points, the errors in the beta-dose lie between approximately $\pm$ 6 to $\pm$ 15% for around 4% and 1% K_2O values respectively. Although this distribution has been approached by linear and by quadratic fitting (as well as for other function degrees for a more accurate functional representation), at present it is not possible to define a function that would take into account the lower regions of curve A.

Further data are, of course, needed to confirm such a correlation for the lower regions of the curve. At present this observation is further encouraging since the samples cover a wide range of provenance and they are not of local or limited origin.

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Table 1

Data Function	Geological	α + K	TLD	Zimmerman
Linear fit	$Y = 0.23 + 0.83\,x$ $\pm 0.10 \quad \pm 0.038$	$Y = 0.604 + 0.76\,x$ $\pm .01 \quad \pm .04$	$Y = 0.23 + 0.71\,x$ $\pm .17 \quad \pm .08$	$Y = 0.36 + 0.80\,x$ $\pm .1 \quad \pm .04$
χ^2	0.658×10^0 (8.7)	0.103×10^3 (37)	0.15×10^2 (23.2)	0.87×10^3 (34)
Quadratic fit	$Y = -0.17 + 1.88x - 0.054x^2$ $\pm 0.85 \pm .058 \pm .008$	$Y = 0.57 + 0.79x - 0.005x^2$ $\pm .22 \pm .18 \pm .03$	$Y = 0.43 + 0.52x + 0.04x^2$ $\pm .39 \pm .34 \pm .07$	$Y = -0.086 + 1.27x - 0.1x^2$ $\pm .17 \pm .15 \pm .03$
χ^2	0.159×10^0	0.105×10^2	0.154×10^2	0.75×10^3

Notes

The sets of points for the four figures were fitted to both linear and quadratic fits with the use of a program written in Fortran IV. The best fit amongst different degree polynomials was that of the second degree. The term x (β-dose, $D\beta$) is given as $10^{-2} x D\beta$ and Y is given as % K_2O. Numbers in parenthesis are the critical ^{2} values at 95% confidence level. For $\chi^2_{calc.} < \chi^2_{crit.}$ the null hypothesis (i.e. calculated value close to a sample value) is not rejected, but the fitting function upon which the calculated values were obtained have a level of significance of 95%.

References

Liritzis, Y. (1979) Ph.D. Thesis, Edinburgh University (unpublished).

Liritzis, Y. and Galloway, R. B. (1982) "Thermoluminescence Dating of Neolithic Sesklo and Dimini, Thessaly, Greece". PACT J., 6, 450-459.

Liritzis, Y. and Galloway, R. B. (1981) "A Comparison of Two Techniques for the Determination of the Beta Dose-Rate in Ceramics for Thermoluminescence Dating", Nucl. Inst. and Methods, 192, 555-8.

Liritzis, Y. (1981) "A Chronological and Operational Reappraisal of Minoan Kilns by Thermoluminescence Dating and Neutron Activation and XRF-Analyses", Revue d'Archaeometrie (in press).

Zimmerman, D. (1970) Ph.D. Thesis, Oxford University (unpublished).

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