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A Gamma Spectrometric Study of Mont Blanc Granite Samples

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des Arbeitsausschusses für die Untersuchung schweizerischer
Mineralien und Gesteine auf Atombrennstoffe und seltene
Elemente**

Die vorliegende Arbeit von L. Rybach, J. von Raumer und J. A. S. Adams "A Gamma Spectrometric Study of Mont Blanc Granite Samples" befasst sich einerseits mit der Methodik der Bestimmung von U, Th und K in Gesteinen mit der sehr rasch und genau arbeitenden Gamma-spektrometrie, anderseits vermittelt sie die Gehalte an den genannten Elementen in einem Granitprofil im schweizerischen Teil des Mont Blanc Massivs. Die Untersuchung wurde zum Teil durch den Arbeits-ausschuss im Rahmen seines Programmes, aus Mitteln, welche ihm der Schweizerische Nationalfonds zur Durchführung seiner Aufgaben gewährte, finanziert. Den Autoren sei für ihren interessanten Beitrag an das neue und erfolgversprechende Analysenverfahren vielmals gedankt.

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Der Präsident der
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Prof. F. DE QUERVAIN

A Gamma Spectrometric Study of Mont-Blanc Granite Samples

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Summary – Gamma-ray spectra of the samples were measured by standard laboratory multi-channel spectrometry. The weighted least squares method was applied to the digital output data in order to determine the concentrations of U^{238} , Th^{232} and K^{40} present. U and Th increase towards the rim of the massif (from 4 ppm U and 20 ppm Th in the coarse-grained central facies to 23 ppm U and 42 ppm Th in the fine-grained rim variety), whereas K remains fairly constant at $\sim 3.85\%$.

1. Introduction

In addition to several economic aspects many significant conclusions can be drawn in various geological problems (magmatic differentiation, hydrothermal alternation, terrestrial heat flow, etc.) from the knowledge of the concentration of the natural radioisotopes in rocks. The determination of these concentrations by measuring the gamma radiation from members in the U^{238} and Th^{232} decay series (mainly Bi^{214} and, Tl^{208} , respectively) and of K^{40} by standard scintillation spectrometry is a widely used analytical method. In most cases the assumption of radioactive equilibrium was found to be valid.

The analysis is usually carried out on finely ground rock samples [1, 2, 3, 4]⁴⁾. In all these works the U, Th and K concentrations have been calculated from the measured gamma ray spectra by the 'stripping' method which was established for single channel spectrometry [5, 6]. More recently the spectra are routinely obtained with multichannel pulse height analyzers. Computer data reduction applying the *weighted least squares method* to the measured spectra is described in this paper. The advantages of this method are demonstrated on a number of samples from the Mont-Blanc massif, Switzerland.

2. Geology

The Mont-Blanc massif (figure 1) consists mainly of a central granite core emplaced discordantly inside a metamorphic terrane. The northern border of the granite is composed of a broad mylonite zone. Herzynian ages ($242\text{--}355 \cdot 10^6$ years) have been found by the 'total Pb' method on zircons from the granite [7].

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⁴⁾ Numbers in brackets refer to References, page 160.

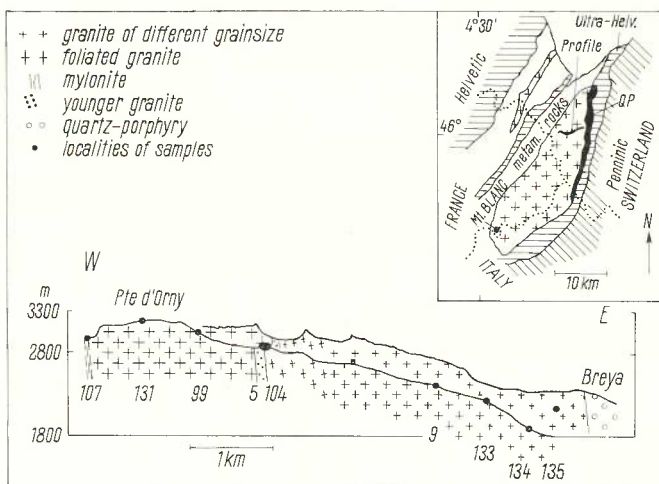


Figure 1

Geological map of the Mont-Blanc region and geological section of the profile studied (sample locations marked; geographical longitude $4^{\circ} 30'$ refers to Paris)

The central facies (samples 131, 99) displays a very coarse granite; the tabular (010) potash feldspar grains reach a maximum length of 6 cm and the quartz grains a diameter of 1.6 cm. Primary structures like schlieren flows and domes are visible. Towards the rim the grain size decreases gradually (samples 104, 9), turning into a fine-grained granite as the rim facies (samples 133, 134). Both potash feldspar and quartz reach here a size of 5 mm. A younger fine-grained granite (sample 5) follows in the intrusion sequence after the main phase. Microgranitic veins (sample 135) are quite abundant in the rim zone. A broad quartz-porphyry zone marks the eastern border.

The main tectonic directions were already in evidence during the final stages of the granite emplacement. Later the whole region underwent the Alpine metamorphism (lowest greenschist-facies, new formation of stilpnomelane [8]) in the course of which the old tectonic lines have been rejuvenated.

3. Experimental⁵⁾

Annular cylindrical cannisters constructed of plastic were used as sample containers for the powdered rocks in order to obtain favorable geometry. The detector contained a $3'' \times 3''$ NaI (Tl) crystal. A stabilized HV unit (M. 4052, John Fluke Mfg. Co. Inc., Seattle, Washington) supplied 940 V for the RCA 8054 multiplier phototube. The detector was surrounded by an inner shield of triply distilled mercury

⁵⁾ The spectrometric measurements were performed at the Physik-Institut, Universität Freiburg (Switzerland). Preliminary gamma measurements (integral counting) have been carried out at the Institut für Geophysik, Eidgenössische Technische Hochschule, Zürich, with the apparatus described in [9].

(1") and an outer shield of lead (6"). The gamma ray spectra were measured with an RCL 512-channel pulse height analyzer, using 128 channels effectively. The photopeaks of Cs^{137} , K^{40} , Bi^{214} and Tl^{208} were used for energy calibration. There was no zero intercept in the calibration graph. The channel width was rather wide (24 keV) and the overall drift much less than one channel. The background is relatively low and constant. The samples were counted for 1000 seconds (average sample weight: 500 g). With the array described above the signal/noise ratio is better than 20:1 over the whole spectrum for an average granite sample.

4. Data reduction

For quantitative data reduction the background must be subtracted. Most data reduction methods are based on the comparison with standards measured under exactly the same experimental conditions. In a composite spectrum photopeaks are characteristic of the corresponding radionuclides. In simple cases where photopeaks are superposed on a 'smooth', horizontal continuum the method of COVELL [10] can be applied. The spectrum of a rock sample measured under the experimental conditions described above is, however, of complex nature (figure 2). Such a spectrum represents the linear sum of the contributions from the uranium series, the thorium series, and K^{40} .

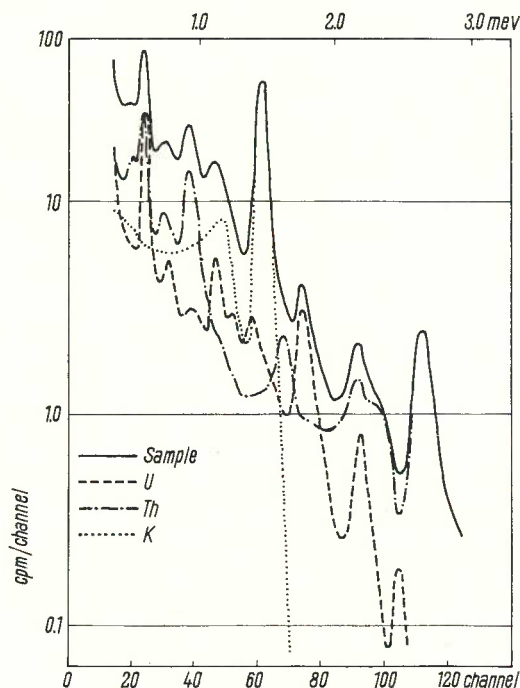


Figure 2

A typical gamma-ray spectrum of a rock sample (solid line) with contributions from U (---), Th (-.-) and K (···)

The easiest way to take the different contributions in consideration is the 'stripping' in regions of characteristic photopeaks (2.62 MeV Ti^{208} , 1.76 MeV Bi^{214} and 1.46 MeV K^{40}). This method gives relatively accurate results and does not require too much calculation (solving 3 linear equations for 3 unknowns). But on the other hand it utilizes only a *fraction* (< 25%) of the information held by the recorded 'multichannel' spectrum which therefore must be measured with a relatively high statistical accuracy for long counting times.

In recent years the availability of computers facilitates the analysis of gamma ray spectra and this analysis can be extended to the *whole* spectrum. The data obtained by multichannel analyzers offer an excellent opportunity for the application of least square methods. SALMON [11] used the unweighted least squares method for the unscrambling of relatively simple gamma ray spectra of monoenergetic, artificial radioisotopes. In our case, however, there is in addition to the complex components another complication present: the spectra are extending over several orders of magnitude due to scattering effects (higher count rates in the low energy channels). This fact suggests the introduction of *weights*.

Let us define the following symbols:

n	= number of channels,
a_i	= count rate of the U standard in channel i (cpm),
b_i	= count rate of the Th standard in channel i (cpm),
c_i	= count rate of the K standard in channel i (cpm),
d_i	= count rate of the sample in channel i (cpm),
v_i	= a random error,
w_i	= weight of d_i ,
m_U	= U in the sample (gm),
m_{Th}	= Th in the sample (gm),
m_K	= K in the sample (gm),
M_U	= U in the U standard (gm),
M_{Th}	= Th in the Th standard (gm),
M_K	= K in the K standard (gm),
x	= the ratio m_U/M_U ,
y	= the ratio $m_{\text{Th}}/M_{\text{Th}}$,
z	= the ratio m_K/M_K ,
$\sigma_x, \sigma_y, \sigma_z$	= the corresponding standard deviations,
Q_x, Q_y, Q_z	= 'weight factors',
W	= sample weight (gm).

Due to the linear superposition of the U, Th and K contributions we can write for each channel (error equations)

$$d_i = a_i x + b_i y + c_i z + v_i, \quad \text{weight } w_i. \quad (1)$$

Having n such equations for only three unknowns the application of the weighted least squares method means the determination of the 'best values' for x , y , z in the sense of

$$\sum_{i=1}^n w_i v_i^2 = \sum_{i=1}^n w_i [d_i - (a_i x + b_i y + c_i z)]^2 = \text{minimum}. \quad (2)$$

It is easy to show that for multichannel operation (constant counting time for each channel)

$$w_i = \frac{1}{d_i}, \quad (3)$$

where with the normal equations [12] are:

$$\left. \begin{aligned} x \sum_{i=1}^n \frac{a_i^2}{d_i} + y \sum_{i=1}^n \frac{a_i b_i}{d_i} + z \sum_{i=1}^n \frac{a_i c_i}{d_i} &= \sum_{i=1}^n a_i, \\ x \sum_{i=1}^n \frac{a_i b_i}{d_i} + y \sum_{i=1}^n \frac{b_i^2}{d_i} + z \sum_{i=1}^n \frac{b_i c_i}{d_i} &= \sum_{i=1}^n b_i, \\ x \sum_{i=1}^n \frac{a_i c_i}{d_i} + y \sum_{i=1}^n \frac{b_i c_i}{d_i} + z \sum_{i=1}^n \frac{c_i^2}{d_i} &= \sum_{i=1}^n c_i. \end{aligned} \right\} \quad (4)$$

The matrix solution which is especially suitable for computer data processing gives the values x , y , z with which the 'best fit' can be computed:

$$d'_i = a_i x + b_i y + c_i z. \quad (5)$$

With

$$\mu = \pm \left[\frac{1}{n-3} \sum_{i=1}^n \frac{(d'_i - d_i)^2}{d_i} \right]^{1/2} \quad (6)$$

the standard deviations of the unknowns are:

$$\sigma_x = \pm \mu Q_x^{1/2}, \quad \sigma_y = \pm \mu Q_y^{1/2}, \quad \sigma_z = \pm \mu Q_z^{1/2}. \quad (7)$$

The Q 's can be calculated [13] from the matrix elements (normal equations).

Finally we obtain the U, Th and K concentrations in the sample:

$$\left. \begin{aligned} \text{ppm U} &= (x \pm \sigma_x) \frac{M_U}{W} \cdot 10^6, & \text{ppm Th} &= (y \pm \sigma_y) \frac{M_{\text{Th}}}{W} \cdot 10^6, \\ \% \text{ K} &= (z \pm \sigma_z) \frac{M_K}{W} \cdot 10^2. \end{aligned} \right\} \quad (8)$$

Experimental precautions have been made to fulfill the assumptions necessary for this method: i) the standard spectra are measured to high statistical accuracy; ii) there is no drift; iii) the background is constant. The standards used were pure KCl and a 0.01% U and a 0.05% Th standard purchased from the USAEC, New Brunswick Laboratory.

5. Results

A Fortran program was written for the calculation of the U, Th and K concentrations from the spectra recorded in digital form, using channels 15 to 125. The computer⁶⁾ plots the original spectrum and the least squares fit for each sample. Measured spectrum and computed best fit for sample 107 are displayed in figure 3.

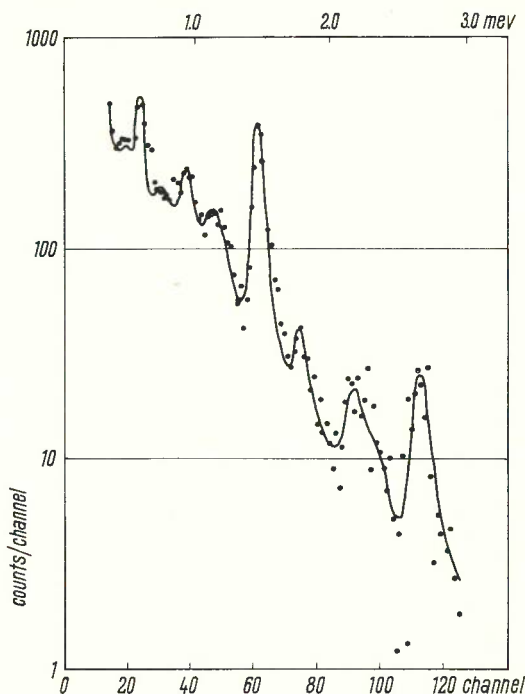


Figure 3

Measured gamma-ray spectrum of sample 107 and computed best fit. Dots: counts in 1000 sec (background subtracted), solid line: best fit. Sample weight: 595 g

The standard deviations decrease with increasing counting time [14]. For the counting time used (1000 sec) the standard deviations are less than $\pm 5\%$, which is, of course, much less than the error which may result from sampling inhomogeneities.

The results are shown in table 1.

The results in table 1 are arranged according to the sample locations in the profile studied. As a general trend the increase of U and Th from the inner part of the massif towards its rim is evident. K remains fairly constant with the mylonite as the only exception. The rather wide horizontal extension of the massif is responsible for the considerable U-Th contrast between center and rim. Two other granitic bodies from

⁶⁾ The calculations have been carried out on an IBM 7040 machine at the Rice University, Houston, Texas (USA).

Table 1
U, Th and K concentrations, Th/U ratios and radiometric field measurements⁷⁾

Sample No.	Remarks	U ppm	Th ppm	K %	Th/U	scale div. a)
107	Mylonite	3.46 ± 0.31	13.2 ± 0.8	2.47 ± 0.10	3.8	110 b)
131	Coarse-grained granite,	3.71 ± 0.16	19.0 ± 0.4	3.34 ± 0.06	5.1	65
99	central facies	6.33 ± 0.35	24.3 ± 0.9	4.01 ± 0.11	3.8	70
104	↑	7.12 ± 0.37	34.4 ± 0.9	3.68 ± 0.12	4.8	70
9	± continuous transition	12.52 ± 0.48	33.5 ± 1.1	3.85 ± 0.15	2.7	92
133	↓	13.41 ± 0.42	31.6 ± 1.0	3.38 ± 0.12	2.4	95
134	Fine-grained rim facies	23.23 ± 0.70	42.0 ± 1.6	3.91 ± 0.19	1.8	130
135	Microgranite, intruding into the rim	25.86 ± 0.70	46.6 ± 1.6	4.15 ± 0.19	1.8	150
5	Younger granite	6.81 ± 0.40	58.0 ± 1.9	4.02 ± 0.13	8.5	105

a) 1 scale division $\approx 0.3 \mu\text{r/h}$

b) Geometry effect

the Alps have been investigated in this respect so far (Gamsboden granite-gneiss [16], Rotondo granite [17]), Rotondo shows a similar pattern. In general terms U increases most, Th noticeably, and K least in moving toward the rim and more silicic differentiates. These general trends are not uncommon [15]. Considering the close similarities in size between tetravalent Th and tetravalent U ions, one might expect much more parallel trends during differentiation. The more marked increase in U is either due to some subtle difference between tetravalent U and tetravalent Th or to varying percentages of the amount of U that is in the hexavalent state. The Th/U ratios show clearly two distinct groups: i) samples 107 to 104 (average: 4.2); ii) samples 9 to 135 (average: 2.2). To clear-up the differentiation scheme of the Mont-Blanc granite magma further study (especially extensive sampling) is necessary.

6. Acknowledgement

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⁷⁾ The field measurements were carried out with a portable scintillation counter (FS-11, Technical Associates, Burbank, USA) by one of us (J. VON RAUMER).

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