Untersuchungen über radioaktive Mineralien
und Gesteine in der Schweiz

# Nondestructive Determination of Uranium and Thorium in Accessory Minerals by Gamma Ray Spectrometry

von

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## Vorwort der Schweizerischen Geotechnischen Kommission und des Arbeitsausschusses für die Untersuchung schweizerischer Mineralien und Gesteine auf Atombrennstoffe und seltene Elemente

Die vorliegende Arbeit von L. Rybach, B. Grauert und T. P. Labhart „Nondestructive Determination of Uranium and Thorium in Accessory Minerals by Gamma Ray Spectrometry" resultiert z. T. aus Untersuchungen, die durch den Arbeitsausschuss im Rahmen seines Tätigkeitsprogrammes durchgeführt wurden, z. T. beruhen sie auf eigener Forschungstätigkeit der Autoren. Das Manuskript wurde an der Sitzung der Geotechnischen Kommission vom 17. Januar 1970 für die Serie „Kleinere Mitteilungen" angenommen.

Den Verfassern sei für ihren interessanten Beitrag zur Methodik der Bestimmung von Uran und Thorium in Mineralien der beste Dank ausgesprochen.

Für den Inhalt von Text und Figuren sind die Verfasser allein verantwortlich.

Zürich, März 1970.

Der Präsident der
Schweiz. Geotechnischen Kommission
und des Arbeitsausschusses

Prof. F. DE QUERVAIN

# Nondestructive Determination of Uranium and Thorium in Accessory Minerals by Gamma Ray Spectrometry

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## ABSTRACT

Sample preparation as well as mass-spectrometric analysis is greatly facilitated if the uranium and thorium content of the mineral concentrates to be dated is known. Standardized trays with mylar foil bottom are used to place the samples on the top surface of a 3″ × 3″ NaI crystal for measurement (sample mass requirement: 0.1–1 gm). Gamma ray spectra are obtained by gain-stabilized multi-channel equipment on punched tape output. Uranium and thorium concentrations are computed by a least squares programme using standard reference spectra. Once the standard and background spectra are established, the analysis can be performed routinely on same mineral concentrates which go subsequently to mass-spectrometry. Zircon, sphene, monazite, epidote/allanite and apatite fractions have been analyzed. Counting times ranged from 40 minutes to 20 hours to obtain a precision better than 15%.

## Introduction

Preliminary determinations of the uranium and thorium content of accessory mineral concentrates used for age determination are of considerable help in preparing the samples as well as for their subsequent mass-spectrometric analysis.

The knowledge of approximate U and Th concentrations allows a rough calculation of the radiogenic Pb for an estimated U/Pb or Th/Pb age. This in turn enables the evaluation of the minimum mineral quantity which is necessary for a given analytical procedure. In cases where hand-picking must be applied for the final purity, much time can be saved.

For the mass-spectrometric U and Th analyses, the spikes can be prepared according to the concentration ranges to be expected.

Since its introduction to geochemistry about 12 years ago (Hurley, 1956; Adams et al., 1958), gamma ray spectrometry of the natural radioisotopes became a widely used analytical tool. The determination of "whole rock" U and Th abundances is performed by measuring the gamma radiation from members of the $U^{238}$ and $Th^{232}$ series (mainly $Bi^{214}$ and, $Tl^{208}$, respectively) by standard scintillation spectrometry. In most cases the assumption of radioactive equilibrium was found to be valid.

One of the major advantages of this method is that the analysis can be performed *nondestructively*. In the case of accessory mineral concentrates the same sample is analyzed for U and Th which then is used for chemical and mass-spectrometric analysis.

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## Experimental

The radiation detector used is equipped with a standard 3″ × 3″ NaI(Tl) crystal. The mineral concentrates (for mineral separation see Appendix) were placed on the top surface of the detector. The sample tray used is shown in Fig. 1. In this sample position the geometry and self-absorption effects due to changing sample mass are negligible (KÖHLER, 1968). Sample and detector are surrounded by 5″ lead to reduce background radiation.

The gamma ray spectra were measured with a NUCLEAR DATA 128-channel pulse height analyser and were registered on punched paper tape (TALLY tape perforator). Since the data evaluation method described below is strongly influenced by gain changes, drift stabilisation is indispensable. Different spectrum stabilizers are now commercially available (e. g. Borer & Co., Solothurn, see COMUNETTI, 1965).

Generally 1 gm material was filled into the sample container. The sample weight could be reduced down to about 0.1 gm. Samples and standards (0.1 % U and 0.1 % Th from the USAEC New Brunswick Laboratory) were measured under same experimental conditions. Counting times ranged from 40 minutes to 20 hours; the effect of the counting time on the precision of the results is discussed below.

Integral alpha measurements, which give a rough estimate of the radio-isotope contents (no uranium-thorium separation is possible), have been performed with a gas flow detector (Nuclear Measurements Co., Indianapolis, USA) driven at 1000 V. The high voltage was supplied by an ELB 2.1 counter (Landis & Gyr AG, Zug, Switzerland). $3 - 10 \cdot 10^3$ counts have been accumulated per sample.



Fig. 1. Sample holder for mineral powders.

The x-ray fluorescence determination has been carried out by the ANALIX SA. (Geneva). For details see HÜGI et al. (1967). The fluorimetric determinations were based on the procedure used by the Comissariat à l'Energie Atomique (Saclay, France).

## Data reduction

For quantitative data reduction the background must be subtracted. Most data reduction methods are based on the comparison with standards. In a composite spectrum, photopeaks are characteristic of the corresponding radionuclides. In simple cases where photopeaks are superimposed on a "smooth", horizontal continuum the method of COVELL (1959) can be applied. The spectrum of an accessory mineral
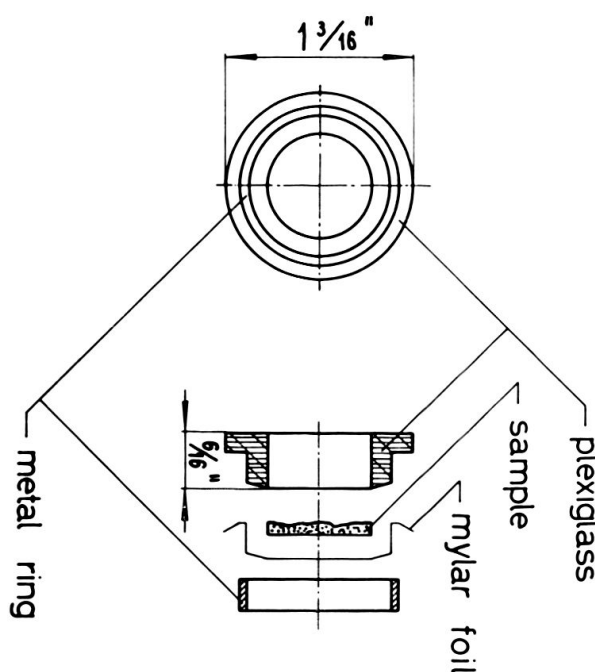
sample measured under the experimental conditions described above is, however, of complex nature (Fig. 2). Such a spectrum represents the linear sum of the contributions from the uranium and thorium series (the potassium content is negligible in minerals used for age dating by U/Pb methods).

The easiest way to take the two different contributions into consideration is the "stripping" in regions of characteristic photopeaks (2.62 Mev Tl[208] for Th, 1.76 Mev Bi[214] for U). This method gives relatively accurate results ($\pm$ 10 $-$ 30%) and does not require too much calculation[3]), i.e. solving 2 linear equations for 2 unknowns. But on the other hand it utilizes only a *fraction* (< 20%) of the information held by the recorded "multichannel" spectrum which therefore must be measured with a relatively high statistical accuracy for long counting times.

The spectra measured by multichannel analyzers and the availability of computers offer an excellent opportunity for the application of *least squares* methods. This type of analysis which is widely used in activation analysis, after its introduction by MOORE and ZEIGLER (1959), can be extended to the *whole* spectrum.

Let us define the following symbols:

$n$ = number of channels used,
$a_i$ = 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 sample in channel $i$ (cpm),
$v_i$ = a random error,
$m_U$ = U in the sample (gm),
$m_{Th}$ = Th in the sample (gm),
$M_U$ = U in the U standard (gm),
$M_{Th}$ = Th in the Th standard (gm),
$x$ = the ratio $m_U/M_U$,
$y$ = the ratio $m_{Th}/M_{Th}$,
$\sigma_x, \sigma_y$ = the corresponding standard deviations,
$W$ = sample weight (gm).

Due to the linear superposition of the U and Th contributions (Fig. 2) we can write for each channel:

$$c_i = a_i x + b_i y + v_i \tag{1}$$

Having $n$ such equations ($i = 1, 2 \ldots n$) for only two unknowns ($x$ and $y$) the application of the least squares method means the determination of the "best values" for $x$ and $y$ in the sense of

$$\sum_{i=1}^{n} v_i^2 = \sum_{i=1}^{n} [c_i - (a_i x + b_i y)]^2 = \text{minimum} , \tag{2}$$

from which the normal equations (4) can be obtained by setting

$$\frac{\partial \sum v_i^2}{\partial x} = \frac{\partial \sum v_i^2}{\partial y} = 0 \tag{3}$$

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[3]) KÖHLER (1968) used a simple graphical solution to handle data of zircon measurements obtained by single channel spectrometry.

$$x\sum_{i=1}^{n} a_i^2 + y\sum_{i=1}^{n} a_i b_i = \sum_{i=1}^{n} a_i c_i \Bigg\}$$

$$x\sum_{i=1}^{n} a_i b_i + y\sum_{i=1}^{n} b_i^2 = \sum_{i=1}^{n} b_i c_i \Bigg\}$$

$$(4)$$

The matrix solution gives the values of $x$ and $y$:

With

$$D = \sum_{i=1}^{n} a_i^2 \sum_{i=1}^{n} b_i^2 - \left( \sum_{i=1}^{n} a_i b_i \right)^2 \qquad (5)$$

$$x = (1/D) \left[ \sum_{i=1}^{n} a_i c_i \sum_{i=1}^{n} b_i^2 - \sum_{i=1}^{n} a_i b_i \sum_{i=1}^{n} b_i c_i \right] \Bigg\}$$

$$y = (1/D) \left[ \sum_{i=1}^{n} a_i^2 \sum_{i=1}^{n} b_i c_i - \sum_{i=1}^{n} a_i b_i \sum_{i=1}^{n} a_i c_i \right] \Bigg\}$$

$$(6)$$

with which the "best fit" (Fig. 3) can be computed:

$$c'_i = a_i x + b_i y \quad . \qquad (7)$$

With

$$\mu = \pm \left[ \frac{1}{n-2} \sum_{i=1}^{n} (c'_i - c_i)^2 \right]^{1/2} \qquad (8)$$

the standard deviations of the unknowns are

$$\sigma_x = \pm\mu \left( \sum_{i=1}^{n} b_i^2/D \right)^{1/2}, \ \sigma_y = \pm\mu \left( \sum_{i=1}^{n} a_i^2/D \right)^{1/2}. \qquad (9)$$

Finally we obtain the uranium and thorium concentrations in the sample:

$$\text{ppm U} = 10^6(x \pm \sigma_x) M_U/W, \quad \text{ppm Th} = 10^6(y \pm \sigma_y) M_{Th}/W. \qquad (10)$$

Experimental precautions have been undertaken to fullfil the assumptions necessary for this method: 1) the standard spectra ($a_i$ and $b_i$) are measured to high statistical accuracies; 2) there is no drift; 3) the background is constant.

## Results

The spectra on punched paper tape have been transferred to magnetic tape which serves as the input for a FORTRAN IV programme to calculate the U and Th concentrations, using channels 20 to 120. The data input deck consists of the card sets of $a_i$ and $b_i$ and of the background spectrum. For each sample spectrum a corresponding data card with sample identification, sample weight and counting time is included. The calculations have been performed on a CDC-1604 computer.

For a given sample weight the standard deviations depend on the U concentration and on the Th/U ratio. With increasing counting time the "scatter" of the spectrum
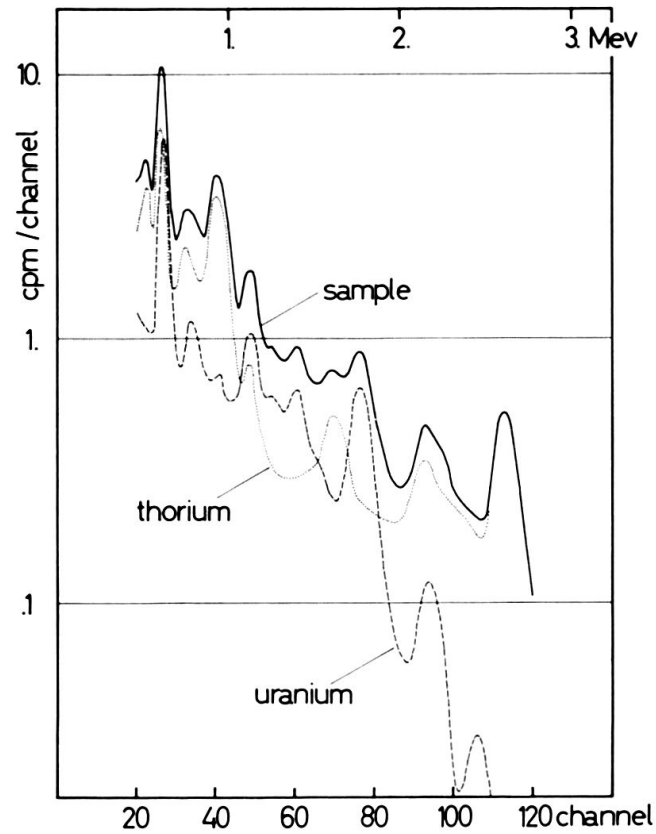
Fig. 2. Typical gamma ray spectrum of an accessory mineral concentrate (solid line) with contributions from the uranium (– – –) and thorium (.....) content.
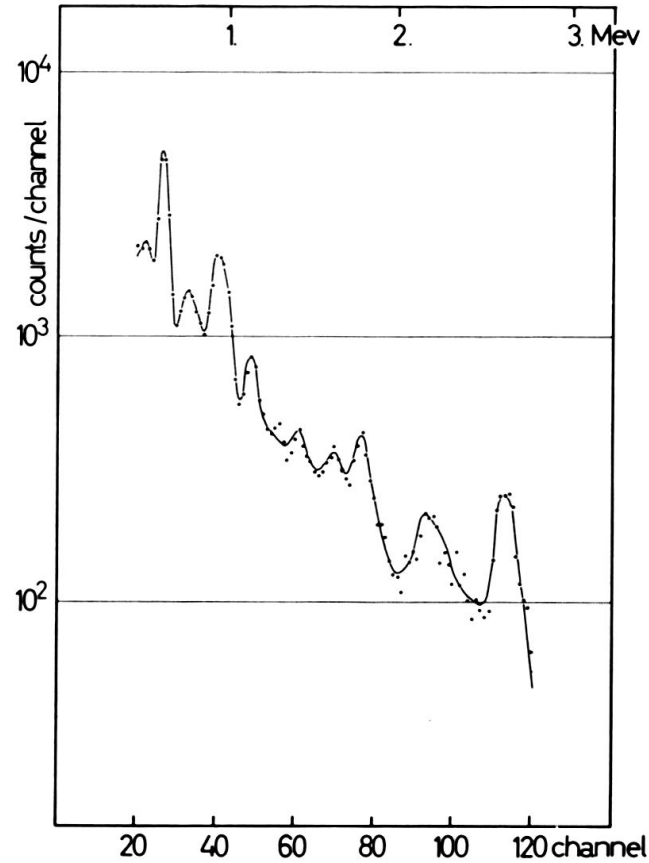


Fig. 3. Measured gamma ray spectrum of an epidote/allanite fraction (Giuv syenite, Switzerland). Dots: counts in 474 minutes (background subtracted), solid line: computed best fit. Sample weight: 1.807 gm.

points decreases (Fig. 4). The standard deviation ($\sigma_U = 100\,\sigma_x/x$, $\sigma_{Th} = 100\,\sigma_y/y$) vs. counting time ($T$) graph follow the $T^{-1/2}$ trend (Fig. 5). Counting times have been selected to obtain standard deviations around 5–15%. Detection limit with the present equipment is around 20 $\mu$g U and 60 $\mu$g Th. This sensitivity can be improved by utilising a well-type NaI crystal for better geometry.
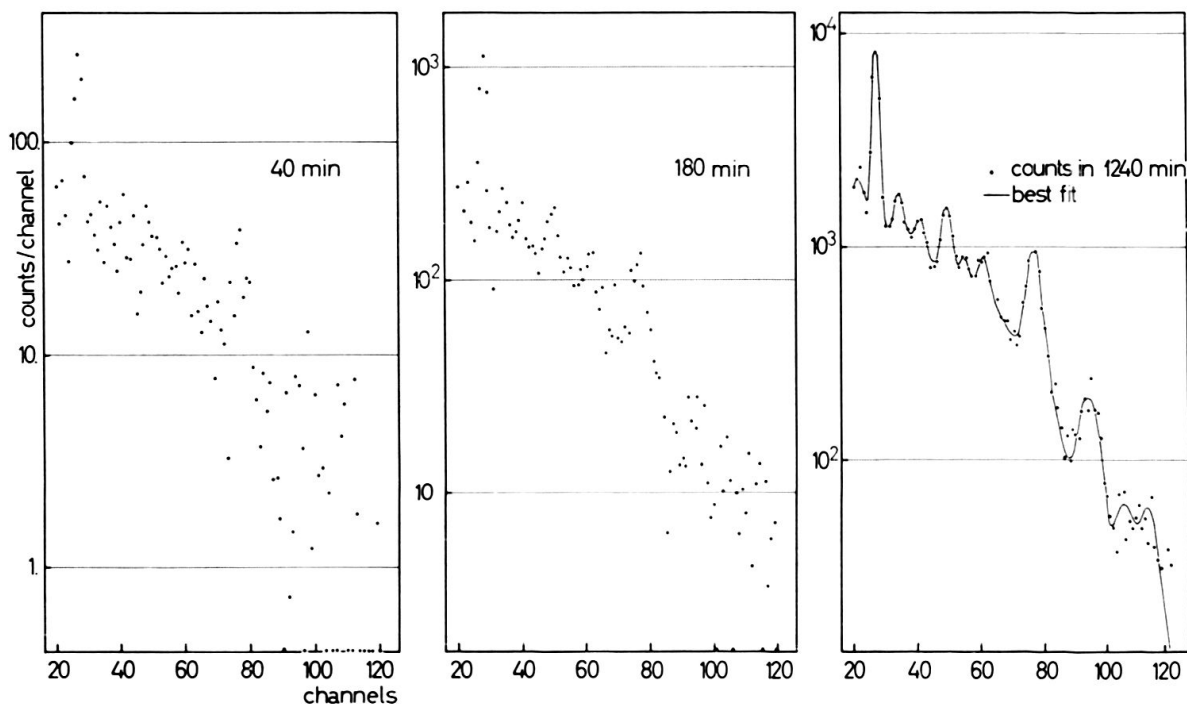


Fig.4. Measured spectrum and best fit for different counting times. 1.00 gm zircon sample (KAW 233/13) with 550 ppm U, Th/U = 0.29.

Uranium and thorium abundances have been determined in a number of accessory mineral concentrates: in sphene, epidote/allanite, apatite and zircon concentrates from the remarkably radioactive Giuv syenite (Switzerland), in zircon fractions from the Silvretta region and in monazite samples from the Moldanubian area. The results are shown in table 1, together with integral alpha measurements, x-rays fluorescence, fluorimetric and mass-spectrometric determinations. The latter methods give somewhat lower results which could be assigned to the acid treatment before the analysis.
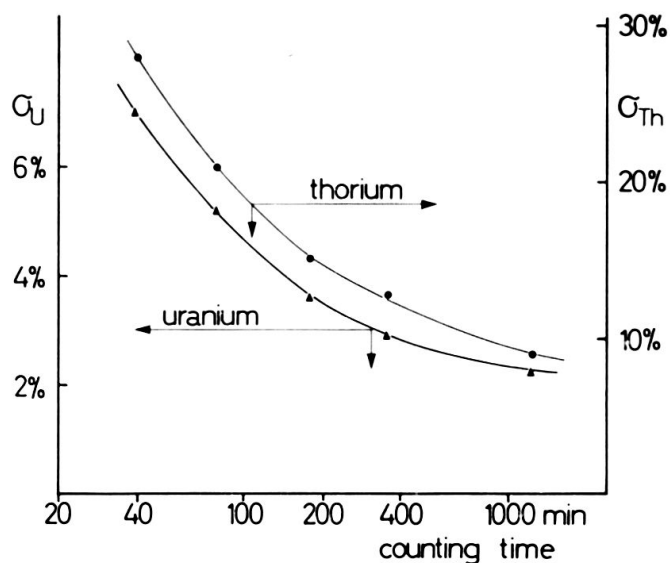
## Acknowledgment

Fig. 5. Standard deviation vs. counting time (same sample as in Fig. 4).

Table 1. Uranium and thorium concentrations, Th/U ratios in accessory mineral concentrates. The isotope dilution figures are taken from GRAUERT and ARNOLD (1968).

| Sample | $\gamma$ spectrometry | | Th/U | isotope dilution | integral $\alpha$ counting | fluorimetry | x-ray fluorescence |
|--------|--------|--------|------|------|------|------|------|
| | U (ppm) | Th (ppm) | | U (ppm) | $\alpha/cm^2/h$ | U (ppm) | U (ppm) |
| **Zircon** | | | | | | | |
| GS 1a | 2800 | 2300 | 0.82 | | | | |
| KAW 233/11 30–42 $\mu$ | 630 | 180 | 0.29 | 636 | 360 | | |
| KAW 233/12 42–53 $\mu$ | 590 | 150 | 0.25 | 571 | 345 | | |
| KAW 233/13 53–75 $\mu$ | 550 | 160 | 0.29 | 542 | 312 | | |
| **Sphene** | | | | | | | |
| GS 1b | 570 | 850 | 1.50 | | | 475 | 510 |
| **Epidote/allanite** | | | | | | | |
| GS 1c | 300 | 1100 | 3.70 | | | 92[a] | |
| **Apatite** | | | | | | | |
| GS 1d | 60 | 130 | 2.20 | | | 49 | |
| **Monazite** | | | | | | | |
| MD 20 42–75 $\mu$ | 5500 | 41000 | 7.50 | | | | |
| MD 25a 42–75 $\mu$ | 7000 | 36500 | 5.20 | | 8600 | | |
| MD 25b 75–125 $\mu$ | 7500 | 38000 | 5.10 | | | | |

[a]) from new fraction with less allanite.

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## APPENDIX
### Sample description, sample preparation

*G 1*

*rock:* Giuv syenite (fine-grained border facies), remarkable high radioactivity (ca. 70 µr/h).

*location:* 696 875/172 920 (Swiss coordinates), 50 m from the southern border of the syenite mass.

*mineral separation:* about 180 lb rock material was crushed, ground, sieved and treated on the wet vibrating table according to WÜTHRICH (1965). The heavy mineral concentrate obtained by this means was separated by the magnetic separator described in PETERS and WÜTHRICH (1963) into the following fractions:

z i r c o n : enriched in the most nonmagnetic fraction together with sphene and apatite/epidote; apatite/epidote separated by methyleniodide, sphene by its different adhesiveness on rough porcelain bowl

a p a t i t e : from the above apatite/epidote mixture at extremely high field-strength of the magnetic separator

s p h e n e : almost quantitatively from the relatively nonmagnetic zircon-free fraction by sieving out the finer-grained epidote

e p i d o t e / a l l a n i t e : from a fraction containing hornblende, biotite and sphene by magnetic separation and sieving; neither pure nor homogeneous (allanite occurs as irregular inclusions).

*KAW 233*

all details are given in GRAUERT and ARNOLD (1968).

*MD 20*

*rock:* paragneiss-metatexite

*location:* quarry "am Eck" (sheet Kötzting, Bavarian Forest) 700 m SE of the pass on the road to Arnbruck

*mineral separation:* same as for KAW 233.

m o n a z i t e : from the zircon fraction by magnetic separation and hand-picking.

*MD 25*

*rock:* perlgneiss.

*location:* quarry at the "Ruselabsatz" (sheet Lalling, Bavarian Forest) 1.5 km W of Hotel Rusel on the Bundesstrasse 11.

*mineral separation:* same as for MD 20.

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