NEUTRON ACTIVATION ANALYSIS OF SOME ZIRCON SAMPLES FROM THE APUSENI MONTAINS (ROMANIA)

Maria Sălăgean, Ana Pantelică
Institute for Physics and Nuclear Engineering
Bucharest MG-6, Romania
V. Znamirovschi, A. Moţiu
University of Cluj-Napoca, Romania

INTRODUCTION

Zircon belongs to the isolated SiO_4 tetrahedra group of silicates, its salient feature of crystal structure being the occurence of the unit cell as detached tetrahedral $(SiO_4)^{4-}$ anions. These tetrahedra stand isolated in the crystal structure, none of the oxygen ions surrounding the Si ion being shared by the adjacent silicon-oxygen tetrahedra.

From the chemical point of view the Zircon could be regarded as a salt of the hypothetical H_4SiO_4 acid. The most important cations one finds in Zircon are: Ca^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Zr^{4+}, Th^{4+}, Nb^{5+}, Ce^{3+}, Hf^{4+}, Y^{3+}, U^{6+}, Sn^{2+}, Cr^{3+} and some rare earths.

According to its formula the Zircon contains ZrO_2-67,1 % (Zr-49,5 %) and SiO-32,9 %. Practically always it has a slight admixture of Fe_2O_3 (up to 0,35 % or more) often CaO (0,05 to 4 %) and sometimes Al_2O_3. It always contains hafnium oxide sometimes up to 4 % of HfO_2, and in alvite from Kragerö (Norway) even 16 %. It may contain Y_2O_3 and rare earths, chiefly Ce_2O_3 (hagatalite) sometimes up to 16 %, with P_2O_5 content of 4 % to 5 % (amagutilite). Certain varieties may contain Nb and Ta (naegite), Th O_2 up to 7 % and even 12 % in högtveitite, and also U_3O_8, up to 1,5 % and even more. It occasionaly contains negligible Sn and Be (in alvite the content of BeO + Al_2O_3 may reach 15 %).

Varieties containing a lot of P_2O_5 are known as oxyamalite, malacons and cyrtolites rich in radioactive substances and hence metamict contains considerable amounts of H_2O (2 % to 12 %).

Usually Zircon occurs as small, rare, disseminated crystals in magmatic rocks. As a chemically inert mineral, Zircon is easily liberated from its accessories in the course of weathering and passes into placers and hence as rounded grains, into sedimentary rocks.

The X-ray investigation of the Zircon samples shows a typical radical ionic structure comprising anionic SiO_4 groups and Zr^{4+} cations surrounded by eight oxygen ions (fig.1). The SiO_4 tetrahedra alternate parallel to L^4 with the Zr^{4+} ions.

The habitus of the Zircon crystal is short-columnar, often isometric, sometimes dipyramidal. The commenest forms are: the tetragonal prisms {100} ; {110} and the tetragonal dipyramid {111} (fig.2). Twins are geniculate like those of Rutile but occur far less often.

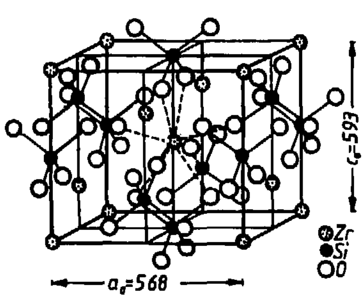

Fig.1.

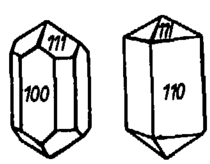

Fig.2.

The analysed samples come from the titaniferous placers of the N-NE-rn part of the Vlădeasa massif as the result of the weathering of dacites and andesites /1/. But it was pointed out that the highest concentration of $ZrSiO_4$ occur when the original rock is dacite and Zircon is almost missing when it is andesite. The spreading of titanium and zirconium minerals is closely related to the weathering extention of the dacites. The frequency of Zircon crystals is raising with the content of magnetite and ilmenite in the placers originated exclusively from dacites.

Considering the extention of the dacites as well as old dacite quarries and the frequency of the placers along the torents and rivers of the Apuseni Mts. this area could represent a highly interesting zone for the industrial extraction of the Zircon. This mineral being the only source for metallic zirconium, which has a wide use in technology, a more advanced study of this raw material absolutely necessary is considered.

EXPERIMENTAL

Using INAA the concentrations of 23 elements in a Zircon sample have been determined. The sample and SL-1, Soil-5 standards were irradiated for 50 hours in a thermal flux of $1.1x10^{11}n/cm^2.s.$ for the long lived isotopes determination. For Zr determination a ZrO_2 standard was used. The measurements were carried out by a Ge(Li) detector with 2 keV resolution after 8 - 30 days coo-

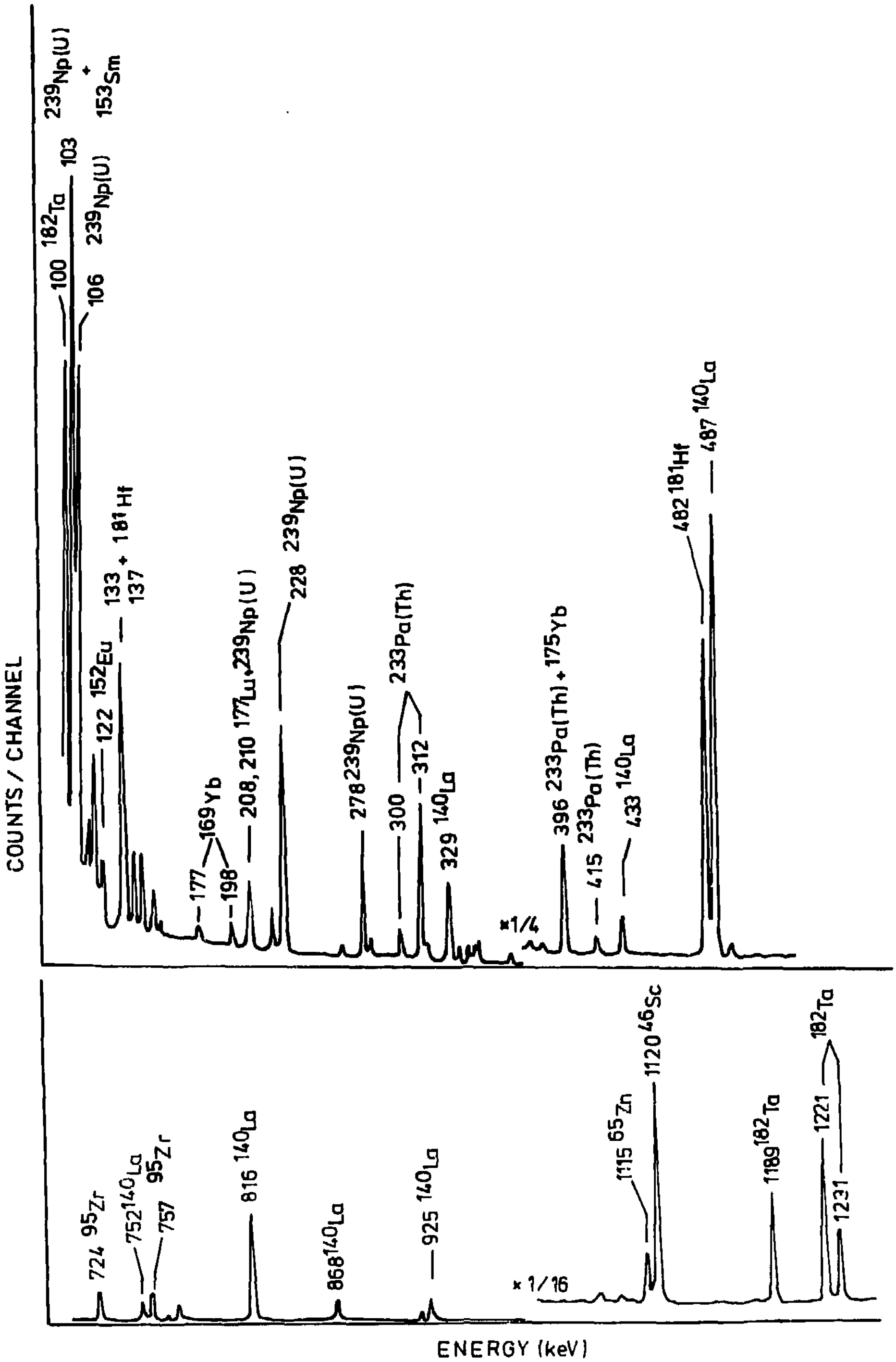

Figure 3.

ling time. In fig.3 a spectrum of the Zircon sample is presented. After an irradiation for 1 min. in a $2x10^{12}n/cm^2.s.$ flux, short lived isotopes Al, Dy, Mn, Ti, V have been determined. W-1 standard was used in this case.

RESULTS AND DISCUSSION

The results of major and trace elements concentrations are shown in table 1. The elemental content of Zircon concentrates proves to be extremely interesting for geochemists and petrologists /2/.

TABLE 1

Element	Concentration (ppm)
Al(%)	0.72 ± 0.04
Au	0.06 ± 0.02
Ce	1694 ± 115
Co	2.0 ± 0.3
Cr	127 ± 32
Dy	172 ± 2
Eu	26 ± 2
Fe(%)	0.88 ± 0.13
Hf(%)	0.67 ± 0.03
La	1037 ± 31
Lu	59 ± 6
Mn	206 ± 20
Nd	732 ± 130
Sc	63 ± 5
Sm	105 ± 7
Ta	9 ± 2
Tb	18 ± 3
Th	514 ± 26
Ti(%)	3.7 ± 0.2
U	206 ± 31
V	46 ± 5
Zr(%)	35.0 ± 2.5
Yb	402 ± 52

The Zr/Hf ratio emphasizes the origin and affiliation of the Zircon to a certain rock type. The value of this ratio (48.9) given in /3/ proves as Zircon bearing rock a granite that is an acidic rock. The Hf content is lowering in Zircons from alkaline rocks. From our results a ratio of 52.2 ± 4.5 was obtained.

According to /4/ where the Th/U ratio for different rock types is calculated, this ratio for acidic rocks varies from 3 to 4. Uranium content increases according to the acidity of the rock. For the examined sample this ratio is 2.5 ± 0.4.

It can be observed either a selective concentration of the uranium inside the Zircon lattice, or a rather complicated process by which these placers were formed.

A high enough concentration of some rare-earths Ce, La, Nd, Yb, Dy, Sm, Lu, Eu, Tb was found.

The presence of certain minor elements, as well as their content and respective ratios can provide a very peculiar key to put into evidence what one calls "geochemical signature" allowing the geologist to identify those specific rocks and areas the Zircon came from.

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