Study of the optical phenomena in zircon with a Scanning Electron Microscope (SEM), using cathodoluminescence method and secondary electrons

Luís Sérgio Brasiliense Cairo[1], Alan Freitas Machado[2], Luiz Pinheiro Cordovil da Silva[3], Claudio Elias da Silva[4], Armando Dias Tavares Junior[5]

[1]Faculdade de Oceanografia, Universidade do Estado do Rio de Janeiro – UERJ, Rio de Janeiro (RJ), Brasil. – luisbcairo@gmail.com

[2]Prof. Associado - Instituto de Física – Departamento de Física Teórica, Universidade do Estado do Rio de Janeiro – UERJ. Rio de Janeiro (RJ), Brasil. – alanfmac@gmail.com

[3]Prof. Associado - Associado - Instituto de Física – Departamento de Eletrônica Quântica, Universidade do Estado do Rio de Janeiro – UERJ. Rio de Janeiro (RJ), Brasil. – luiz.pinheiro@gmail.com

[4] Prof. Associado - Instituto de Física – Departamento de Física Teórica, Universidade do Estado do Rio de Janeiro – UERJ. Rio de Janeiro (RJ), Brasil. – claudio.elias13@gmail.com

[5] Prof. Associado - Associado - Instituto de Física – Departamento de Eletrônica Quântica, Universidade do Estado do Rio de Janeiro – UERJ. Rio de Janeiro (RJ), Brasil. –tavares.armandodias@gmail.com

This paper was prepared for presentation during the 15th International Congress of the Brazilian Geophysical Society held in Rio de Janeiro, Brazil, 31 July to 3 August, 2017.

Abstract

The objective of this study is to analyze, describe and characterize images in SEM (Scanning Electron Microscopy) and how a zircon sample ZR 008 (CRL05) behaves, in order to determine the possible locations where the laser ablation will be made (Ar/F). This procedure will be done to assist in the geological dating process, using the method by ICP / MS.
Cathodluminescence and secondary electrons method were used in the process.
Homogeneous fringes will be used for laser ablation, for in it there is a large difference in thickness, which gives it uniformity in the image. What happens with other fringes have different intensities, it is that in them are thickness differences (either error fracture, recrystallization different times, different crystal forms ...) and, when irradiated by the electron beam gives a different areas thicknesses. As expected (S, R, Rosana, 2011), for analysis by laser, it is seen that the zircon crystals with homogeneous fringes (ideally) are the best possible candidates for laser ablation for the next stages of work dating geological.

Introduction

A sand sample is used (several minerals), the zircon grains are collected, and then with the zircon crystals we will have a unique sample. For mapping we will use a computer, a scanning electron microscope (SEM). To analyze the type of zircon and its crystallization, hexagonal shape, we will consult a table form.

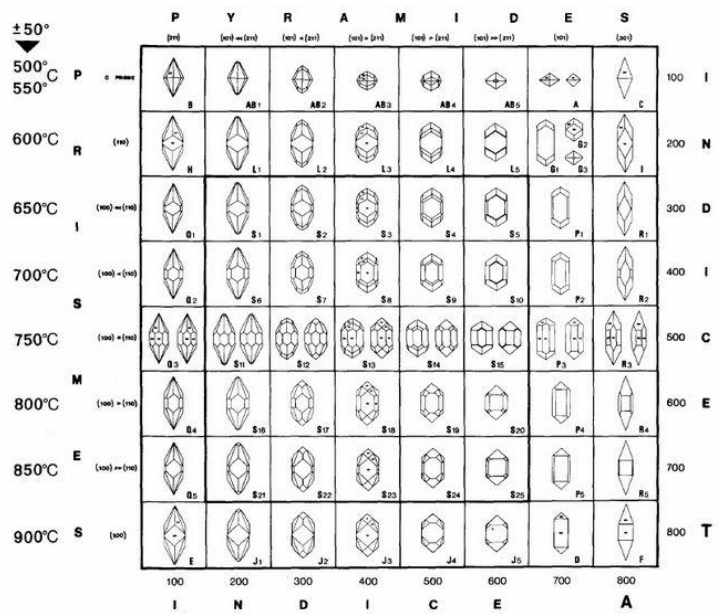

Table 1 - Table showing that zircon forms due to interaction of Temperature x Chemistry, wherein the crystals change form according they become more alkaline, and in relation to temperature increases.

Zircon is a mineral which belongs to the group of chemical formula silicate and $ZrSiO_4$ occurs differently in different rocks: in igneous rocks as a primary crystallization product; in metamorphic rocks as recrystallized grains; and in sedimentary rocks as detrital grains.
It has a resinous to adamantine brightness and its composition is 67.22% of ZrO_2 and 32.78% of SiO_2, and it has a hexagonal crystallography of the tetragonal bipyramidal class. Because it contains considerable amounts of uranium and thorium, it is also widely used for radiometric dating. They are also widely used as a proteolytic indicator, due to their ability to survive geological processes such as erosion, transportation, high temperatures and metamorphism.
The geochronological study zircon can be made in five (5) directions: 1) Estimation of the crystallization age of igneous rocks; 2) Determination of maximum age of deposition of clastic sediments; 3) Estimation of ages inherited in meta-igneous and metasedimentary

rocks, in provenance studies and paleogeographic studies; 4) dating of metamorphism and associated hydrothermal systems; 5) estimation age of deformation.

Method

The SEM is one of the most versatile tools available for observation and analysis of micro structural characteristics of solid objects. The main reason for its widespread use is the high resolution obtained in the study of samples; with values of the order of 2 to 5nm in commercial instruments, while advanced research tools are capable of achieving resolutions better than 0.8 to 0,2nm (Nakatani et al., 2002). Another important feature of SEM is the three-dimensional appearance image of the samples, a direct result of the fields' large depth. It also allows the examination in small increments and with great depth of focus, which is extremely useful because the electronic image complements the information given by the optical image.

The operating principle of a scanning electron microscope (SEM) is to use a beam of electrons, small diameter (1-10 nm) to explore the sample surface, point by point, in successive lines and pass the detector signal to a cathode screen scanning which is perfectly synchronized with that of the incident beam (Figure 1). The beam can be guided to scan the sample surface according to a rectangular mesh. The image signal results from the interaction of the incident beam with the sample surface. And then the signal collected by the detector is used to modulate the monitor brightness, allowing the observation.

Figure 1 - Scanning electron microscope equipment (SEM)

-Cathodoluminescence:

When insulating materials or semiconductors are bombarded by the electron beam, great length of photon, such as ultraviolet and visible wave (200V to 30.000kV), are issued. The spectrum obtained depends on the studied material and its purity. Some materials fluoresce in the visible light range under electron bombardment. The radiation is in many cases a function of impurity levels within the material and it is widely used in semiconductor research and in many mineralogical investigations.

-Elétrons Secondary ("secondary electron" - SE):

The secondary electrons in SEM result from the interaction of the electron beam with the sample material. These electrons that were generated are low energy electrons, and they will form images with high resolution (3-5 nm). The physical configuration of the SEM works in a way that only the secondary electrons generated near the surface can be detected. The image contrast is given, especially, by the sample's relief which is the main formation imaging mode in SEM. Secondary electrons generated from the sample electron-atom interactions have a mean free path of 2 to 20 nm, so only those generated near the surface can be reissued, and even these are very vulnerable to absorption by the topography surface.

- Image resolution:

The parameters that influence more in the resolution of the image in a SEM are:
a) the electron acceleration voltage;
b) Probe current: the higher the current, the larger the beam diameter;
c) The working distance - which is the distance between the sample and the objective's lens.

For the image resolution, the diameter of the incident beam interaction region with the sample, to generate the backscattered electrons depends on the electron penetration depth which essentially depends on three factors:
a) accelerating voltage;
b) atomic number of the sample;
c) angle of incidence of the beam with the surface.

In relation to the electron acceleration voltage and the sample's atomic number, the depth of penetration of the electrons is higher as the acceleration voltage is stronger. The penetration depth of the electrons may vary from a few dozen to several tens of micrometers. The atomic number also influences on the depth of penetration of the electrons, since the higher the atomic number, the lower the electrons penetrating power. Likewise, the penetration will be greater when the surface is perpendicular to the incident beam. In conclusion, the best resolution is obtained at high atomic weight materials.

Zircon and factors that influence sample preparation

1 Inlay:

When the sample presents a very small size, they should be mounted, recessed, in suitable devices. In this case, the epoxy resin is the most recommended to be used in electron microscopy, being well accepted in most SEM equipment.

2 Sanding:

The sanding step is important to remove mechanical damage introduced by sectioning. The sanding is done by successive use of sandpaper. It also acts in order to remove debris and abrasive, minimizing the tendency to introduce particles in the sample matrix. The types of sandpapers are first in 1000, then in 800/2400 and finally in 1200/4000.

3 Polishing:
After planning the surface with the sanding, the sample must be polished to obtain a smooth surface, with low roughness. The abrasive used is a diamond paste, grass.

Zircon
It is a mineral of the neosilicates or orthosilicates Group ($ZrSiO_4$). Usually it has a tetragonal crystallographic system consisting of SiO_4 tetrahedrons and $Zr2O_8$ octahedrons, with its standard stoichiometric composition and 67.2% of ZrO_2 and 32.8% of SiO_2 (HOSKIN; Schaltegger, 2003, p. 32). According to Dana (1969), the zircon is an accessory mineral, widely distributed in igneous rocks, especially granite, granodiorites, syenites and commonly in monzonites and pegmatite, shales, gneiss and quartzite. Because of its resistance to mechanical and chemical disintegration, it is also commonly found as heavy mineral in sandstones (WAGNER; HAUTE, 1992, p 185.).

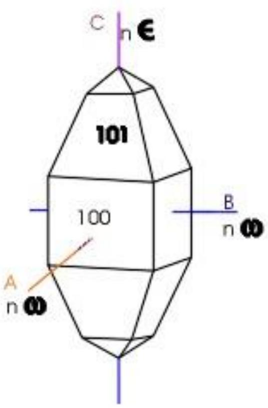

Figure 2 - Representation of tetragonal zircon crystal in three dimensions

Its grain can be rounded, ovoid and prismatic, sometimes finished or unfinished pyramids and rounded edges, clear or small inclusions (GASPARETTO; SANTOS, 2005). It has an adamantine, usually translucent and in some cases transparent brightness. It presents brown, gray, green, red and colorless coloring (DANA 1969). The birefringence is very high, ranging from 0.060 to 0.062. Its occurrence as an accessory mineral in plutonic rocks occurs mostly in salt-rich rocks, such as in granites and pegmatites, and in sedimentary rocks such as sandstones. The zircon's use in commercial applications would be buds, production of ceramic opacifiers, obtaining zirconium oxide for use in the chemical industry, among others.

Results

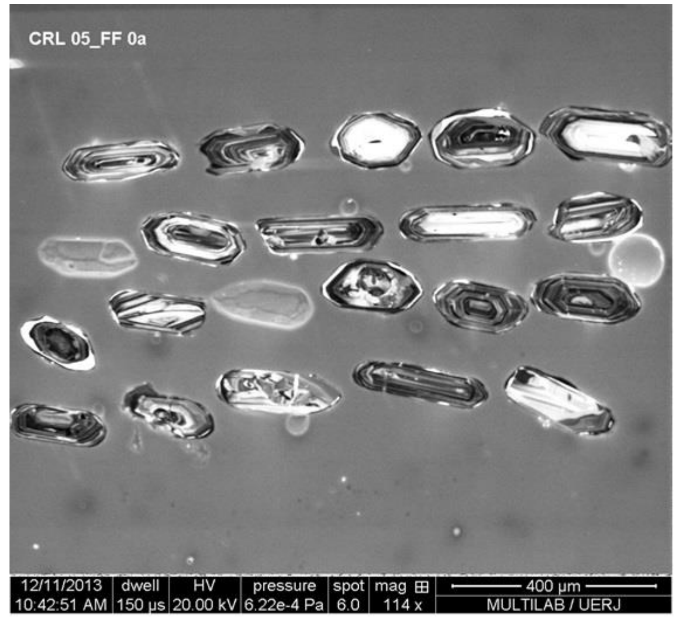

Figure 3 - zircon crystals mounted on a sample observed using SEM on a detector Cathodoluminescence

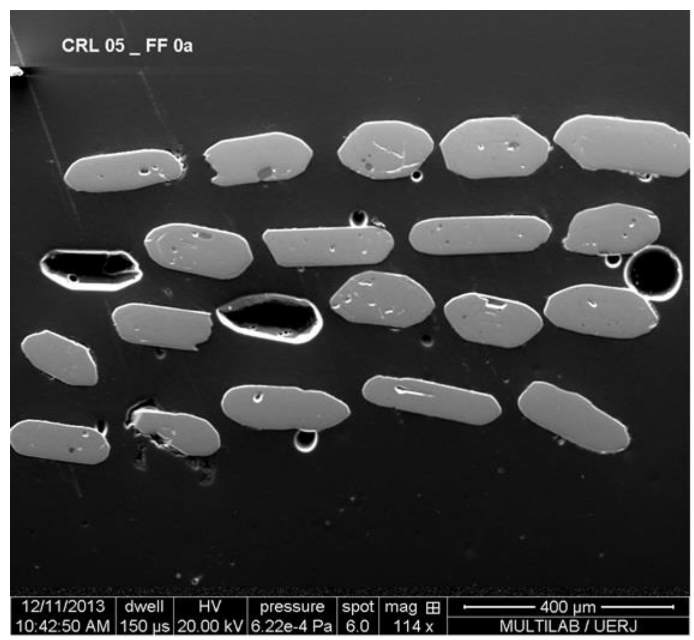

Figure 4 - zircon crystals mounted on a sample observed by using a SEM secondary electron

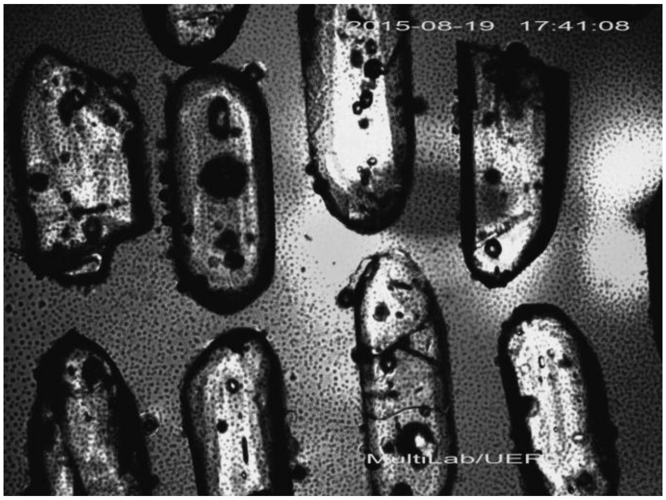

Figure 5 - Optical polarizing microscope, showing the differences in the layers of zircon crystal breaks, which can be noticed by the color difference.

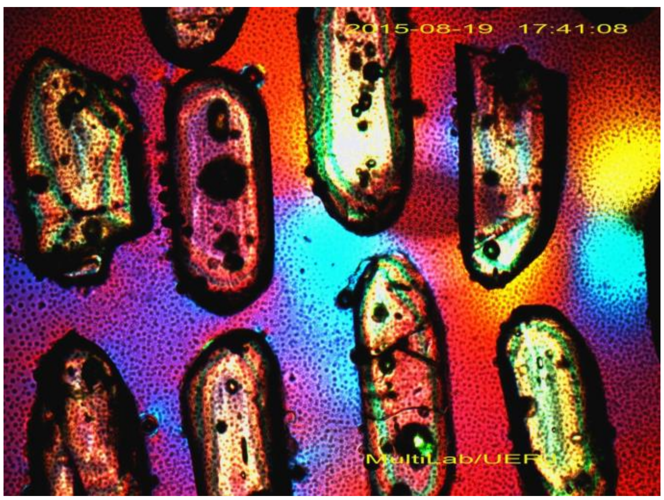

Figure 6 - Optical polarizing microscope, showing the differences in the layers of zircon crystal breaks, which can be noticed by the color difference.

Some fractures represent the thickness difference, as seen in figures 3 and 5. The Cathodoluminescence and polarization methods were then applied, respectively, in detectors which make possible to visualize different bangs. Uniform bangs with unique coloring were identified with these methods, as seen in figure 4. Homogeneous fringes will be used for laser ablation, since there is not a large difference in thickness which gives it a uniform image in the SEM. What happens to the other fringes, that present different intensities, it is that they present differences of thickness (which can be fracture's error; different times of recrystallization of the crystals; different forms of crystals and etc) and when irradiated by the electron beam assigns zones of different thicknesses.
In order to perform the analysis by laser, we must have (ideally) clearly uniform regions. Therefore, the bangs chosen for analysis were homogeneous since they had no different thicknesses, and thereby, can have a better mapping.
The photochemical processes are based on the absorption of electromagnetic radiation by matter leading a molecule to and excited state by taking an electron from its ground state for a higher energy electronic level. The physical processes of excitation by radiation absorption and deactivation of the excited state are represented by the Jablonski diagram shown below (Lakowicz, 2006; Michl, 2006).

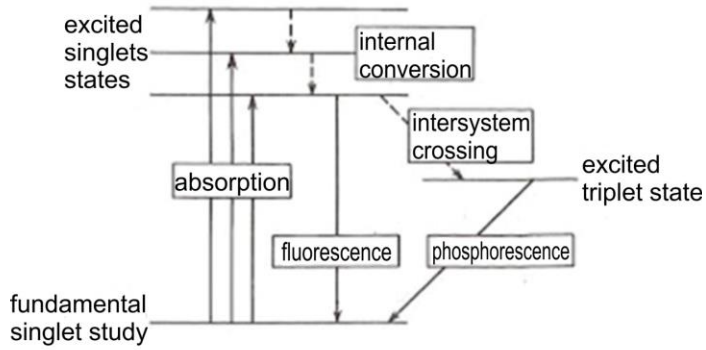

Figure 7 - Scheme Jablonski diagram

In electronic excitation, an electron from one connection per pair of electrons is excited to a higher energy state. If the excited electron has an antiparallel spin to his companion, the excited state will be a singlet, but if the spin of the excited electron is parallel to his companion, the state will be a triplet. Interpreting the figure above, we have the photochemical activation processes in terms of this state model. After the primary quantum leap, a series of events occur extremely fast before any photochemical reaction or emission of luminescent radiation can occur.

Conclusions

As expected (S, R, Rosana, 2011), we see that the zircon crystals with homogeneous bangs are the best possible candidates for laser ablation for the next stages of the geological dating work.

References

Berenice Anina Dedavid, Carmem Isse Gomes, Giovanna Machado. – Porto Alegre: EDIPUCRS, 2007. Microscopia eletrônica de varredura: aplicações e preparação de amostras: materiais poliméricos, metálicos e semicondutores [recurso eletrônico]

Costa e Castro,Cassiano.- 2007.Metais raros associados ao Plúton Desemborque: estudo mineralógico e químico utilizando MEV-EDS[i]

Gasparetto, N.V.L. e Santos, M.L. 2005. O emprego de minerais pesados como indicador da proveniência da cobertura pedológica do Arenito Caiuá na região Noroeste do Paraná

Hoskin, P.W.O., and Schaltegger, U., 2003, the Composition of Zircon and Igneous and Metamorphic Petrogenesis: Reviews in Mineralogy and Geochemistry, v. 53, no. 1, p. 27-62.

lakowiczjr (2006) principles of fluorescence spectroscopy 3rd ed. springer berlin

NAGATANI, T. et al. Development of an ultra high resolution scanning electron microscope by means of a field emission source and inlens system. Scanning Microsc., v.11, p.901-909, 1987

WAGNER, Günther A.; HAUTE, Peter Van den. Fission-track datingDordrecht: Kluwer Academic Publishers, v. 6, 1992. 292 p.