

# Investigation of zircon by CL (Cathodoluminescence) and Raman Spectroscopy

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**Abstract.** Pütürge metamorphites consists of schist, gneisse, metagranite gneisse, amphibolite, kyanite quartzite and marble type rocks. Mineralogical studies, geochemical analysis (LA-ICPMS), Raman spectroscopy and cathodoluminescence (CL) imaging that it representing amphibolite facies and greenschist facies. Zircon imaging called as a metamict from the cathodoluminescence images of zircon minerals. The partially radiated zircon particles is higher radiogenetic mineral ratio in comparison with other zircon particles. The ratio of the radiogenetic elements (U, Pb and Th) arises from chemical difference between the core and rims of zircons. The solubility of zircon effects environmental conditions such as high pH, Zr with hydroxyl ions. Especially alkaline fluids in environment can dissolve zircon. The results show that radiogenetic elements loss in zircons can be generated from metamict zircon through volume diffusion at low temperatures or by an external fluid (H<sub>2</sub>O). The loss of lead in zircon signifies that the fluids inserting the crystal lattice causes radiation damage processes.

## 1. Introduction

Zircon (ZrSiO<sub>4</sub>) is mineral wide range of metamorphic degree, magmatic and sediment rocks. It is the most important mineral for U-Pb dating of metamorphic or igneous and can form by mechanism of recrystallization and growth (solid-state transformation, replacement alteration, dissolution reprecipitation or chemical precipitation from aqueous fluid/hydrous melt) under nearly all geological conditions [1]. Given these circumstances, radiation damage in zircon caused by radioactive decay of trace amounts of U and Th substituting for Zr. This damage is generally metamictization and considered to be the result of recoiling nuclei produced in the emission process [2]. Specifics of the transitional and crystal structures of zircon undergoing metamictization are important to the understanding of the process. The structure of crystalline zircon consists of isolated [SiO<sub>4</sub>]<sup>4-</sup> tetrahedra with strong internal Si-O bonds. The tetrahedra are joined by weaker M-O bonds involving Zr cations (and any species substituting for Zr) in eightfold coordination. Metamict state in zircons has been detected from Pütürge metamorphites in pelrites during cathodoluminescence analyses and electro-microprobe analyses performed to chemically characterize and internal structure. The zircons form euhedral or subhedral crystals varying from a few millimetres to one centimetre of length and in cathodoluminescence (CL) images zircons show a grey or sometimes dark brown spongy texture and oscillatory zonations can be seen which is indicative of the magmatic origin. The spongy texture can occur by supercritical fluid and its high concentration of trace elements. The common phenomenon of structural metamict in minerals is predominantly due to atomic displacements that are caused by alpha decays of radio-nuclides (i.e., uranium and thorium, and their instable daughter nuclei). The beta-decay events in the same decay



chains, and gamma radiation, are in general considered insignificant for the creation of permanent structural damage though the displacement of lattice atoms [3]. The structural damage is known to suppress in general the emission performance of crystals [3,4]. On the other hand, damage may enhance the emission, as observed from the strongly luminescent radio-haloes in naturally non or weakly luminescent minerals [5]. The effects of radiation damage on the inner structure of zircon can be seen as systematic changes of physical properties: an increase in cell parameters and broadening of x-ray diffraction patterns [4] a decrease in IR and Raman intensities and dramatic band broadening [6], decreases in refractive index and birefringence, absorption of hydrous species [7], an increase in fracture toughness; a decrease in density, a variation of HRTEM diffraction patterns a variation of  $^{29}\text{Si}$ NMR features, decreases in hardness and bulk modulus, a variation of diffuse x-ray scattering from single crystals and the appearance of Huang type diffuse x-ray diffraction [6] indicated that the Si–O bonding in heavily damaged zircon was not too different from that in glassy  $\text{SiO}_2$ , as infrared spectra of Si–O vibrations in heavily damaged zircon were similar to that of vitreous  $\text{SiO}_2$ . The presence of crystalline  $\text{ZrO}_2$  was observed in heavily damaged zircon annealed at high temperatures [7]. Zhang et al., 2000[6] determined an observation of decomposition of synthetic zircon under high-temperature heavy-ion irradiation and proposed the formation of a ‘liquid-like’ state in displacement cascades and that a low cooling rate could allow the nucleation of crystalline  $\text{ZrO}_2$  in displacement cascade regions. Salje et al (1999) [8] and [9] showed recently that metamictization in zircon could not be a phase transition driven by a critical defect concentration, but rather was a heterogeneous process of cascade formation and overlap. Instead of a ‘driven phase transition’, two percolation points are expected, one for the crystalline material and one for the amorphous material [6]. The focus was to identify which processes contribute to results of Raman and CL analyses of zircon in metamorphites and to investigate the structural characterization of zircon and effects in the structural changes of fluids.

## **2. Geological setting and samples**

Pütürge metamorphite located within the Southeastern Anatolia thrust belt on the Eastern Taurus Orogenic Belt and Arap platform is a metamorphic massive that had developed as a result of the closure and collision of the Eurasia and Arab plates starting from the upper Cretaceous [10]. Generally, the rocks that belong to Pütürge metamorphite consist of metagranite gneisse, gneisse, schiste, amphibolite, marble and kyanite quartzite. The suite of zircon samples from granitic gneisse study was chosen from the Pütürge metamorphite. In this rock, primary minerals were quartz, feldspar, mica minerals and apatite, sphene. U–Pb age of  $84.2 \pm 1.1$  Ma of the zircons was obtained from the metagranitic gneiss of massis suggests that the magmatism occurred during the Upper Cretaceous-Santonian time [10,11].

## **3. Analytical Methods**

Thin sections of examples selected for petrographical and geochemical examination have been prepared in the geology lab of Firat University. ICP-MS (Inductively Paired Plasma Mass Spectrometry) analyses of rocks made in ACTLAB (Canada). EMPA analyses were prepared in the Hacettepe University (Turkey). A Cathodoluminescence (CL) analyser was used for CL-images of zircons. Zircons separated from granitic-gneisse via heavy fluids that their size varies from a few millimetres to centimetre with colours of gray or sometimes dark brown. Cathodoluminescence images of the zircons (108 grain) were taken before in-situ LA-ICPMS ITU Eurasia Institute of Earth Sciences (Turkey) to characterize zircons to be dated by [10]. The CL images were produced by a Zeiss Evo-50 SEM equipped with cathode-luminescence and EDS detectors. Raman spectra were analysed in physics laboratories in METU. Raman spectra were recorded with aDILORZ24 spectrometer triple monochromator in a single channel mode, coupled to a Coherent 90-3 argon ion laser.

## **4. Results and Discussion**

### *4.1. Cathodoluminescans views and chemical compositions of zircon*

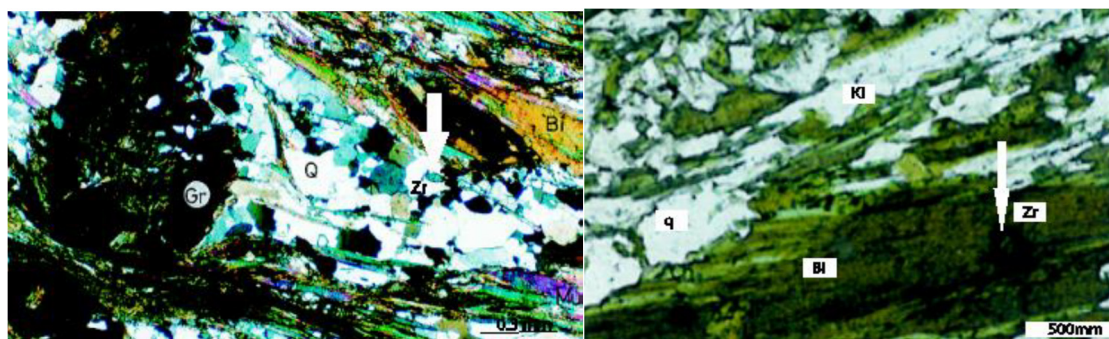
The zircons in Pütürge metamorphites shows in two locations as a particles or inside porphyroblasts with inclusions (Figure 1). Metamict zircons indicated high temperature conditions are located inside

biotite mineral. In microscopic investigated, the transformation to chlorite and biotite minerals of the garnet mineral indicate kyanite-almandine-muscovite and staurolite-almandine sub-facies of the amphibolite facies. As well transformation to muscovite mineral of the kyanite mineral show that the massive has undergone two retrograde metamorphisms on the greenschist facies [10]. The CL images are shown in Figure 2. The Raman and chemical composition profiles for nine zircon grains are shown in Figure 3 and Table 1.

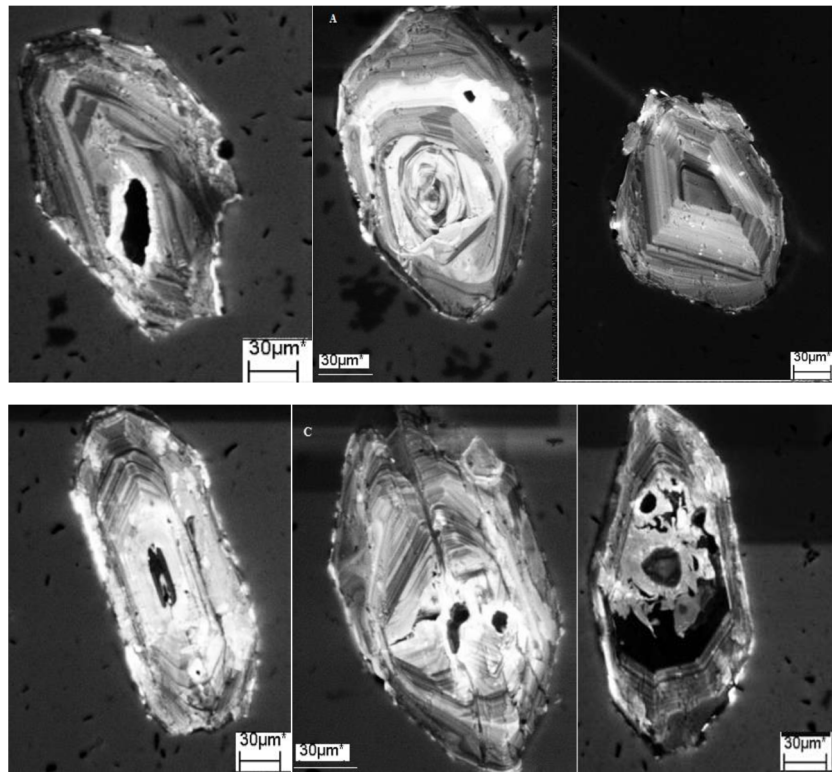
**Table 1.** Electron microprobe analyses results (oxide wt%) of kyanites

Grain	Sample	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	MnO	K <sub>2</sub> O	CaO	Na <sub>2</sub> O	Total
1	KY-1	37.00	0.00	61.98	0.09	0.26	0.03	0.03	0.01	0.00	0.02	99.42
2	KY-1	36.41	0.12	62.51	0.06	0.23	0.04	0.03	0.00	0.00	0.00	99.38
3	KY-1	37.26	0.06	61.42	0.08	0.43	0.05	0.00	0.00	0.00	0.01	99.32
4	KY-1	37.48	0.01	62.37	0.04	0.17	0.00	0.00	0.00	0.00	0.01	100.08
5	KY-1	36.40	0.02	63.15	0.06	0.15	0.01	0.01	0.00	0.00	0.03	99.82
6	KY-1	36.56	0.03	62.73	0.03	0.30	0.07	0.08	0.01	0.00	0.00	99.80
7	KY-1	36.69	0.00	63.74	0.11	0.16	0.02	0.00	0.00	0.00	0.03	100.74
8	KY-1	36.79	0.06	63.12	0.05	0.27	0.01	0.00	0.00	0.00	0.00	100.30
9	KY-1	36.47	0.02	62.25	0.03	0.75	0.14	0.00	0.00	0.00	0.00	99.64
10	KY-1	36.60	0.00	62.37	0.02	0.20	0.01	0.00	0.00	0.00	0.00	99.20

The zircons are shown as dark (unzone inner core) and bright (oscillatory zoning rim) in CL images. Cracks are mostly vertical in zircon rim that can be identified on the CL images (Figure 2) and are believed to be the result of radiation from contained Th-U [13]. In CL images, patchy zoning texture showed in core or weak luminescent core is the product of prograde dehydration reactions during regional metamorphism and factors such as temperature, fluid or melts that help recrystallization may be cause the extent of the damage [10]. The formation of zircons with different textural properties from the same root rock at the same temperature conditions was interpreted as the diversity of the variables that causes radiation. The visible by Cathodoluminescence (CL) views irregularly curved rose like in core of zircon (Figure 2), homogeneously luminescent or inclusion rich sources from radiation and PH. Generally, zircons in granitic-gneiss are round to slightly subhedral and grains ranging from 100 to 300  $\mu\text{m}$ . Most grains are colorless-brown and they are composed of CL weak. These results show that the light or high luminescent regions of CL images is higher in U, Th, and Y, so the core of zircon is generally higher in Th, U, Ca, Na, Mg, K and Y. Dark region on CL image represents low contents of U, Th and Y [12].



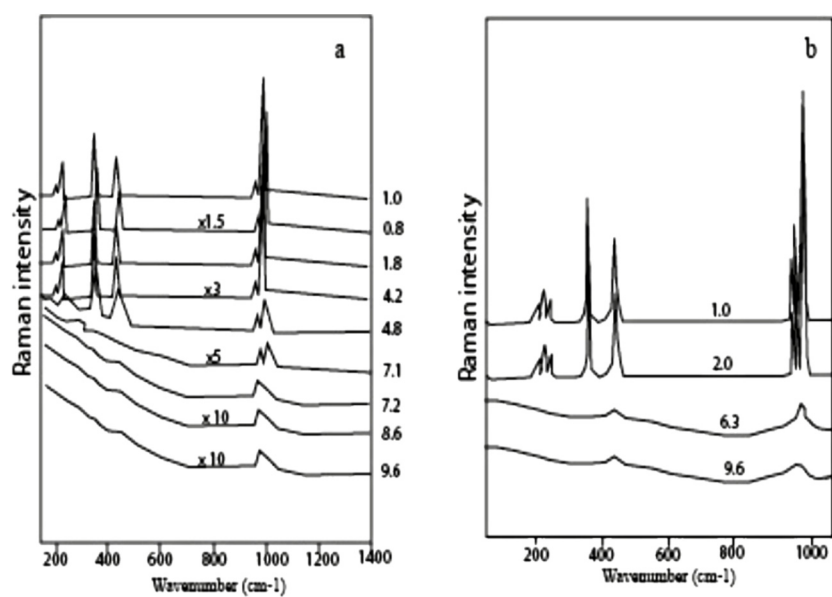
**Figure 1.** Prismatic zircon crystal (left) and metamict zircon inclusion in biotite [15], (right)



**Figure 2.** CL-images zircons. Zircon with dark core, rose image zircon, oscillatory zone zircon, vertical cracks in zircon and metamict zircon.

#### 4.2. Destruction of the crystal structure by Raman

Raman spectra of zircons show systematic changes with increasing degree of radiation damage (Figure 2). The raman modes were observed in the all crystalline zircon 108 (Figure 3a) and spectra images of analysed zircon grains shows that the peak values are 290.429, 386.671, 541.554, 988.413 and 1300.078  $\text{cm}^{-1}$ .



**Figure 3.** Raman spectra images of zircon

The effects of  $\alpha$ -decay radiation damage on the structure of zircon are typical by a decrease in Raman intensity, a decrease in phonon frequencies and line-broadening of Raman modes [14]. Well crystallized zircon samples show sharp and well resolved Raman modes (Figure 3a, 3b). With increasing  $\alpha$ -decay radiation dose, the two Si–O stretching modes between 988 and 1300  $\text{cm}^{-1}$  become weaker and broader while the lower-frequency modes become gradually weak and could not be analysed for a high dose. Non broad features can clearly represent impurity luminescence of zircons [14]. More and more radiation damage in zircon changes the frequencies of the Si–O strain mode near 1300  $\text{cm}^{-1}$  and the external vibration near 290  $\text{cm}^{-1}$  decrease. The frequency decrease is  $\sim 1.8\%$  for the Si–O stretching mode at 988  $\text{cm}^{-1}$ , 1.0% for the Si–O stretching at 541  $\text{cm}^{-1}$ , 0.8% for the Si–O bending near 290  $\text{cm}^{-1}$  which is related to the motion of  $\text{SiO}_4$  as a unit against Zr [6]. The frequency changes for the external bands below from 290  $\text{cm}^{-1}$  is difficult to determine as their intensities [6]. In analysed samples, Raman peaks from the crystalline part of the sample exhibit a continuous decrease of the wave frequencies and an increase of line widths with increasing radiation dose. The correlation between width and frequency of Raman Si–O strain and degree of radiation in zircon may be used for the determination of the degree of damage from Raman peak parameters [6]. The high Hf, U, Th content of zircon shows impurities. These elements comprise always less than 3 mol%. Hf content from radiogenetic elements in samples effects Raman frequency in the spectrum of zircon one would expect to see, because of the difference of the ionic radius between Zr and Hf and complex host lattice silicate interactions a weak increase in frequency for the Si–O strain instead of the observed decrease [6]. In metamict zircon loses Zr, Hf, Si, U, Th, REE to fluid, so cations in zircon can soluble from its structure. The element difference due to the approaching of the fluid to the crystal lattice or due to enclosure minerals affects luminescence properties. Porous and patch core types are seen in both rock samples [10]. The porous structure and cracks of zircon represent the first stage of radiation damage. Thus, Hf content in samples causes a significant frequency shift in the spectrum of zircon.

## 5. Conclusions

Püttürge metamorphic rocks compose of metagranite gneiss, schist, amphibolite, marble and kyanite quartzite. This study shows that two Raman analyses in signal from the crystalline phase shows spectral variations due to a softening of the crystal structure of zircon with increasing damage. Cathodoluminescence (CL) view of the zircons in pelites consist of core and rim zones; the core is rich in uranium and that the emission from the core causes volumetric expansion in zircon particles along with radial cracks [8]. The first stage of metamictisation comprise porous structure and cracks that it is partial oxidation state. Loss of Pb, Hf, Y in zircon arise from fluids inserted to crystal lattice and in this grains change Th/U ratio and U-Pb ageing. Th/U high ratio is characteristic radiation effect. Structural differences in the core and rim of zircons arise from chemical difference, mineral reactions and radiation damage in both the enclosure and the prismatic zircon crystals. In the impurities, zircon is high in Hf, U, Th contents. The Raman peaks from the crystalline part of the sample show a continuous decrease of the wave frequencies and an increase of line widths with increasing radiation dose. High temperatures result in a recovery of the damaged structure of zircon as indicated by a band sharpening and an increase of phonon frequencies up to those of well crystallized samples [4]. These zircons in CL images are homogenized.

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